



International conference

# ANALYTICAL CHEMISTRY AND CHEMICAL ANALYSIS

(AC&CA-05)

*devoted to 100 anniversary of Anatoly BABKO*

**Kyiv, Ukraine**

**September 12-18, 2005**

## Organized by

Scientific Council of Analytical Chemistry  
at Academy of Sciences of Ukraine,

Ukrainian Chemical Society,

Kyiv Taras Shevchenko National University;

*under collaboration with*

European Association for Chemical and Molecular Sciences (EuCheMS)

and

International Union of Pure and Applied Chemistry (IUPAC)



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*Original author's style including interpretation, formulas and names of chemical compounds, schemes, pictures and explanations, is preserved in the abstracts published in this book.*



*This conference has been held with the financial assistance of INTAS*

## PREFACE

The organizing committee extends a cordial invitation to participate in International conference on Analytical Chemistry and Chemical Analysis (AC&CA-05) which is hold in scenic city of Kyiv, Ukraine, from September 12 to 18, 2005. This conference belongs to the series of Ukrainian conferences in analytical chemistry established in 1970<sup>th</sup> by Ukrainian chemical society and chemical division of Ukrainian Academy of Sciences. AC&CA-05 is a 7<sup>th</sup> conference in analytical chemistry in Ukraine and it is dedicated to the centenary of the birth of the outstanding Ukrainian scientist, Anatoly K. Babko for his expertise in analytical chemistry and in the chemistry of complex compounds. The current conference is organised by Analytical Scientific Council at Academy of Sciences of Ukraine under collaboration with European Association for Chemical and Molecular Sciences (EuChemS) and sponsored by International Union of Pure and Applied Chemistry (IUPAC) and by the International Association for the Promotion of Co-operation with Scientists from the New Independent States of the Former Soviet Union (INTAS).

Main goals of the conference are to survey a status of modern analytical science in Ukraine against the global one, to renew international collaboration of Ukrainian analytical chemists and educators, and to approach positions of scientists and analytical engineers.

The idea of the conference is to demonstrate renaissance of science and analytical practice in Ukraine after it gained independence. Organizing committee meets great help and gets support for realisation of this idea from many international bodies, such as chemical societies of Russia, Japan, Austria, Germany and Great Britain, as well as from scientific web portals: SpectroscopyNOW, ChemWeb.com, etc. As a result of such support AC&CA-05 have about 450 participants from 31 countries. This provided an excellent opportunity for young Ukrainian researchers, teachers and students, and for scientists from neighbouring countries, to meet the representatives of international scientific community and to re-establish links with their European colleagues and thus initiate new collaborative work.

All main aspects of analytical and bioanalytical sciences is covered by the conference program. AC&CA-05 consists of 12 invited lectures and seven symposia: General Aspects of Analytical Chemistry, Analytical Methods, Objects of the Analysis, Sensors and Tests, Separation and Pre-concentration, Pharmaceutical and Biomedical Analysis, History and Methodology of Analytical Chemistry. Conference program includes two special symposia: Memorial one, dedicated to Anatoly Babko and Analytical Russian-Germany-Ukrainian symposium (ARGUS-9).

It is great that AC&CA-05 took place in 2005. This year Ukraine demonstrates Eurointegration policy and we are in the vanguard of this process. In 2004 Analytical Chemistry Council NAS of Ukraine becomes a member of European Association for Chemical and Molecular Sciences. AC&CA-05 is the next step towards Eurointegration of Ukrainian analytical science. The first steps are always hard to make. We tried to do our best ... Thanks all participants for coming to AC&CA-05.

*The Chairman of organizing committee,  
Chair of Analytical Chemistry Scientific Council of NASU*

*Prof. Vladimir N. Zaitsev*

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# Anatoly Kirillovich BABKO

(15.10.1905 - 7.01.1968)

## *A Short Biography*



In October, 2005 the Ukrainian scientific community will celebrate the centenary of the birth of the outstanding Ukrainian scientist, **Anatoly K. Babko** for his expertise in analytical chemistry and in the chemistry of complex compounds.

The scientific work of Anatoly K. Babko was conducted mainly at the Kyiv State University where he chaired the Department of Analytical Chemistry as from 1944 to 1960, after when during 1960 to 1968 he retained the title of Professor. His scientific duties were performed primarily at the Institute of General and Inorganic Chemistry of the Ukrainian Academy of Sciences, where he headed the Department of Analytical Chemistry from 1941 to 1968.

The scientific interests of Anatoly K. Babko ranged widely, especially in regard to fundamental aspects of analytical chemistry, applications of organic reagents in inorganic analysis, chemistry of complex compounds (including heteropolyacids), analytical applications of complex compounds in photometry, luminescence and chemiluminescence, ion chromatography, and liquid-liquid extraction.

A significant achievement of Anatoly K. Babko was in the area of systematic physicochemical research of complex compounds in solution based on their photometric properties. Anatoly K. Babko showed the stability constants of complexes to be highly important, and demonstrated the relevance of the step-wise character of the dissociation of complex compounds.

In developing theoretical problems he always thought about practical uses of results in the national economy. His theoretical and experimental results were applied to developing numerous methods of analytical determination of elements in complex natural and technical situations, and also he also used the principles for improving the university curriculum and to generate new special courses.

Anatoly K. Babko published more than 450 scientific works and 9 books that were translated into several languages. It is noted that his scientific heritage continues to this day – as testified by data of the Institute of Scientific Information (ISI). Within the website (<http://isiwebofknowledge.com>) for 2000 to 2004 (35 years from Anatoly K. Babko's death) there were citations to more than 100 of his articles. His monograph of *Physical and Chemical Analysis of*

*Complex Compounds in Solution* was quoted 250 times in the same period.

A talented teacher, tutor and lecturer he delivered lectures on general and special courses for university students, and trained his students to expertise of high rank. He supervised 50 PhD and 9 DSc theses, and founded the Kyiv School of Analytical Chemists.

As seen by his numerous scientific seminars, meetings and conferences Anatoly K. Babko was a good organizer. He was a member of the editorial board of the Analytical Chemistry Journal, *Ukrainski Khmicheski Zhurnal*, being its editor-in-chief from 1958 to 1968. His highly professional annual reviews in the development of analytical chemistry during 1957-1967 were published in *Zavodskaya Laboratoria* – a time of important developments in analytical science not only in Ukraine but also in the USSR. He also contributed much to the organization of analytical services in Ukraine.

Anatoly K. Babko was born on October 15, 1905 in the province of Tomsk (Russia) to a railwayman's family. In 1908 the family moved to the Ukraine, where he graduated from secondary school in 1921. In 1922 he was admitted to the Chemistry Department of the Kyiv Polytechnic Institute, and in 1928 he was accepted there for PhD study under the supervision of Professor N.A. Tananaev. In 1930 he became a lecturer at the Kyiv Institute of Food-processing Industry, and in 1934 he was appointed senior lecturer in the Department of Analytical Chemistry at Kyiv State University where he worked for the rest of his life, working also from 1937 in the Institute of General and Inorganic Chemistry of the Ukrainian Academy of Sciences.

Anatoly K. Babko obtained his PhD degree in 1937 and the degree of DSc in 1940. In 1943 he was promoted to full professor at Kyiv State University. In 1963 Anatoly K. Babko was elected a member of the Analytical Chemistry Commission of the International Union of Pure and Applied Chemistry (IUPAC).

During the Second World War Anatoly K. Babko and his students were evacuated to Ufa (Russia) to work for the defensive industry.

1948 saw Anatoly K. Babko elected as Corresponding Member to the Ukrainian Academy of Sciences, and in 1957, he became a full member (Academician) of the Academy of Sciences of Ukraine. In 1966, he awarded the title of "Honoured Scientist of Ukraine". He also held the awards of "The Order of Lenin" and "The Order of Honour".

In celebrating the centenary of the birth of Anatoly K. Babko we appreciatively recall his diligence, scientific, pedagogical and organizing talents. His active and purposeful character will always feature in our strikingly kind memory of Anatoly K. Babko – who through all his life maintained a love and loyalty to science.

*Vladimir N. Zaitsev, Miroslava M. Tananaiko\**

*\* Authors appreciate essential help in preparation of the biography they received from Professor JDR. Thomas*

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# ***PLENARY LECTURES***

# PHYSICOCHEMICAL ASPECTS OF NEUROTRANSMISSION: RELEASE BY SINGLE CHROMAFFIN CELLS

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Living cells exchange information through the emission of several chemical messengers including hormones and neurotransmitters. The importance of such messengers has been widely recognized by biologists. However what is less understood is how these chemical messengers are released by the cell in its outer-cytoplasmic fluids. This difficulty is easily understood when one becomes aware that most of these releases occur in the zepto- to femtomole ranges which prevents the use of classical analytical methods. We wish to show here that using the concept of artificial synapse with ultramicroelectrodes is extremely useful for monitoring such events with sufficient accuracy and precision so that the delicate physicochemical and biological mechanisms which sustain them may be revealed.

In this lecture we will be concerned by exocytosis of neurotransmitters by chromaffin cells. These cells, located above kidneys, produce the adrenaline burst which induces fast body reactions; they are used in neurosciences as standard models for the study of exocytosis by catecholaminergic neurons. Prior to exocytosis, adrenaline is contained at highly concentrated solutions into a polyelectrolyte gel matrix packed into small vesicles present in the cell cytoplasm and brought by the cytoskeleton near the cell outer membrane. Stimulation of the cell by divalent ions induces the fusion of the vesicles membrane with that of the cell and hence the release of the intravesicular content into the outer-cytoplasmic region.

Precise kinetic electroanalytical data permit to describe quantitatively the kinetics of the whole process with a precision that has never been achieved before by patch-clamp techniques or spectroscopic near-field methods. This enables to investigate finely these events and to identify the exact physicochemical nature of all the individual physicochemical and biological factors which concur to produce vesicular release.

# ON-LINE COUPLING OF SPE-HPLC-MS/MS FOR FAST TRACE ANALYSIS OF PESTICIDES IN DRINKING AND SURFACE WATER

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The intense use of pesticides has given rise to concern about their effects on the environment. As a consequence, implementation of drinking water guidelines is in process in many EU countries. A high number of organic micropollutants being of especially high risk are listed in a recently scheduled EU-Priority List [1]. Thus, it is necessary to develop an effective method for multicomponent analysis.

Commonly used methods for the measurement of pesticides in water samples involve Solid Phase Extraction (SPE) followed by Gas Chromatography or High Performance Liquid Chromatography (HPLC) analysis. SPE is a multiple step procedure and, thus, time consuming.

This paper describes a rapid and versatile on-line-SPE LC-MS/MS method developed for the determination of various pesticides and their metabolites in water. 28 pesticides, including various triazines, phenylureas, organophosphorous compounds and other species, were selected for systematic investigations.

The methodical concept is based on the combination of the following instrumental parts:

- I) Rapid on-line enrichment of pesticides from water, using Turbulent-flow Chromatography (TFC) columns as SPE cartridges
- II) On-line coupling of SPE to LC-MS/MS with mixing of the organic SPE effluent with aqueous eluent for optimum band focussing on the LC column
- III) Fast LC-APCI-MS/MS analysis using a short monolithic separation column coupled to a triple-quadrupole mass spectrometer operating in multiple reaction monitoring (MRM) detection mode.

TFC column geometry (50mm x 1mm, 30-50  $\mu\text{m}$  particle size) allows high flow rate during sample enrichment and low desorption volume, which are important points to minimise the analysis time, and to increase the sensitivity. This paper provides the result for testing of various TFC columns (modified silica, porous polymers and porous graphitized carbon) for trace enrichment of selected pesticides.

Fast LC separation of the enriched pesticides was performed on a short monolithic column. Selective tandem-MS detection allowed to reduce chromatographic separation resulting in further gain of time.

The method developed enables efficient matrix management. Application to natural and drinking water samples appeared very promising for future pesticides monitoring.

# **$^{195}\text{Pt}$ , $^1\text{H}$ AND $^{129}\text{Xe}$ NMR STUDIES OF SUPPORTED METAL CATALYSTS (Pt, Pd)**

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Oxide-supported metals constitute one of the most important classes of heterogeneous catalysts, and for this reason they have been investigated by many techniques: adsorption isotherms, IR of chemisorbed molecules, electron microscopy, EXAFS, etc. However, the fact that they have been studied by so many methods proves that no one technique is totally satisfactory.

The physical and chemical properties of sufficiently small particles, in particular their magnetism, must depend on their size, whence the idea of using NMR to study them. Because of the theoretical and technical difficulties associated with the NMR detection of metals, and specially since only a few can be detected, NMR work has been mainly devoted to the indirect study of metallic properties, by the intermediary of easily detected chemisorbed phases ( $^1\text{H}$ ,  $^{13}\text{C}$ ) or of physically adsorbed probes ( $^{129}\text{Xe}$ ). We will develop the cases of Pt and Pd.

However, when the metal can be detected directly (mainly Pt), it is possible to relate the form of the NMR spectrum to the dispersion of the metal and to calculate the electron density of states at the Fermi level.

$^1\text{H}$  NMR of chemisorbed hydrogen can also be used for the study of alloys. For example, in mixed Pt-Pd nanoparticles in NaY zeolite comparison of the results of hydrogen chemisorption and  $^1\text{H}$  NMR with the formation energy of the alloy indicates that the alloy with platinum concentration of 40% has the most stable metal-metal bonds. The highest stability of the particles and a lowest reactivity of the metal surface are due to a strong alloying effect.

# QUALITY MANAGEMENT IN THE INDUSTRIAL ANALYTICAL LABORATORY - DO WE GET OUR MONEY'S WORTH?

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The significance of quality management (QM) in the analytical laboratories of the chemical industry has increased dramatically over the past years. Registration of new chemical substances, toxicological and ecological studies of novel pharmaceutically active ingredients (AI) and agrochemicals are impossible without the appropriate GLP (good laboratory practice) certification. Likewise, quality control and product release analysis of food and feed additives or cosmetics must adhere to GMP standards (good manufacturing practice). On the other hand, environmental analysis requires accreditation according to ISO 17025 - a hallmark of superior analytical expertise.

Due to their wide range of analytical challenges centralized analytical laboratories are required to adopt a series of QM systems simultaneously. For example, the Competence Center Analytics of BASF AG in Ludwigshafen is certified and accredited to operate under four different QM systems. Undoubtedly, QM systems play a vital role in a modern industrial analytical laboratory. The sale of many products of the chemical industry is not possible without a GLP-certified analytical laboratory. However, in practical terms the different QM systems can potentially reduce the efficiency of the analytical process and lead to increased costs.

The presentation will focus on the differences and similarities of these systems as well as problems encountered in their practical use. By looking at the analytical process chain characteristics, such as the reliability and traceability of data, documentation standards and total costs of QM are discussed and evaluated. Suggestions for harmonization of QM-Systems and reduction of bureaucracy will be made, resulting in an improvement of the overall practical applicability and cost reduction of QM.

# SOME NEW ADVANCES IN DEVELOPING MICROWAVE PLASMA TORCH SPECTROMETRY

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In pursuing the “ideal” excitation source for analytical atomic spectrometry, a novel device, QJ torch, for sustaining atmospheric pressure microwave plasmas was developed in our laboratory in 1985 [1]. The structure of the QJ torch is very similar to ICP torch. It consists also of three concentric tubes but not made of quartz but of copper or brass. The torch was modified by Jin and Hieftje in 1991 and the microwave plasmas sustained with it, named microwave plasma torches (MPTs), have been studied extensively since then. It was shown that the QJ torch could easily sustain MPTs at low microwave forward power (<100 W) and low flow-rate of plasma supporting gas (<1000 mL/min) with a variety of gases including argon, helium or even air at atmospheric pressure. The MPTs were shown to be ionizing plasmas and in non-LTE. When MPT is used as an excitation source with a desolvation system for AES, the figures of merit are mostly comparable with ICP-AES except it has relative serious matrix effect. Since it can work with helium at atmospheric pressure, the determination of halogens is also possible. It can be easily coupled to GC and SFC as a detector because its good tolerance to the introduction of water and molecular species. He-MPT has been shown to be a good ionization source for mass spectrometry and the coupling of a He-MPT with TOFMS was considered a system “ideally suited for GC detection” by some authors [2]. In this presentation, the following new advances will be highlighted:

- 1) an oxygen-sheathed argon MPT (OS-ArMPT) and its improvement in figures of merit as an excitation source for AES;
- 2) a commercialized atomic emission spectrometer using OS-ArMPT as the source for aqueous solution analysis;
- 3) the real-time on-site, continuous air particulate monitoring by using air-MPT-AES;
- 4) a miniaturized simultaneous MPT spectrometer for on-site use;
- 5) a GC-HeMPT-TOFMS for metallic and nonmetallic elemental determination;
- 6) an MPT-cavity ring down spectrometry(MPT-CRDS) for elemental & isotopic analysis.

[1] Q. Jin, G. Yang, A. Yu, J. Liu, H. Zhang, Y. Ben, *Acta Sci. Nat. Univ. Jilin.*, 1985(1): 90

[2] B.W. Pack, J.A. C.Broekaert, J.P. Guzowski, J. Poehlman, G.M. Hieftje, *Anal. Chem.*, 1998, **70**(18): 3957

# ENVIRONMENTAL AND FOOD APPLICATIONS WITH DNA ELECTROCHEMICAL BIOSENSORS

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A Biosensor is a device where a coupling has been realized between a biological element responsible for the molecular recognition and the element responsible for the transduction of the signal.

As DNA Biosensor we refer as a coupling between an oligonucleotide formed with known sequence of bases or a complex structure of DNA (like a DNA from calf thymus) and a transduction device, which could be electrochemical, optical or piezoelectric sensor. In the last years great interest has raised for such coupling and in the laboratory of the applicant several procedures and applications have been worked out to exploit for analytical purposes such coupling. The most important points are related to the possibility to obtain a device rapid, cheap, simple and reliable. This is necessary to solve the increasing analytical problems linked to pollution, to the detection of genetic disorders, to the detection of polymorphism, to the detection of GMO (genetic modified organisms) and again to the detection of pathogen microorganisms by the evaluation of the hybridization reaction.

Results on DNA-based biosensors will be presented; they have been used mainly for two kind of applications 1) for the determination of low-molecular weight compounds with affinity for nucleic acids and 2) for the detection of hybridization reaction.

The first application is related to the molecular interaction between surface-linked DNA and pollutants or drugs, in order to develop a simple device for rapid screening of toxic compounds or better to try to quantify the genotoxicity of a specific sample.

The determination of such compounds was measured by their effect on the oxidation signal of the guanine peak of calf thymus DNA immobilised on the electrode surface and investigated by chronopotentiometric or voltammetric analysis. Applicability to river and wastewater samples is demonstrated.

Moreover, disposable electrochemical sensors for the detection of a specific sequence of DNA were realised by immobilising synthetic single-stranded oligonucleotides onto a graphite or a gold screen-printed electrode. The probes became hybridised with different concentrations of complementary sequences present in the sample.

Recently a biosensor as new analytical tool for GMO (genetic modified organism) detection has been reported.

Screen-printed gold electrodes were, firstly, modified with a mixed monolayer of a 25-mer thiol-tethered DNA probe and a spacer thiol, 6-mercapto-1-hexanol (MCH). The DNA probe sequence was internal to the sequence of the 35S promoter, which sequence is inserted in the genome of GMOs regulating the transgene expression.

An enzyme-amplified detection scheme, based on the coupling of a streptavidin-alkaline phosphatase conjugate and biotinylated target sequences was then applied. The enzyme catalysed the hydrolysis of the electroinactive *o*-naphthyl phosphate to *o*-naphthol; this product is electroactive and has been detected by means of differential

pulse voltammetry.

In other recent papers we exploit a piezoelectric device by immobilizing a specific sequence of bases of the pathogen microorganism *Aeromonas* belonging to the gene codifying for the formation of the toxin Aerolysin.

*Aeromonas* can be present in water, milk, cheese, in ice cream, in sausages etc.

Therefore it seems quite important establish its presence and its eventual pathogenicity.

In such occasion the oligonucleotide has been immobilized with a procedure more complex exploiting the affinity avidin-biotin and by reacting on the gold surface, (the reactive and sensitive surface of the piezoelectric crystal), a thiol to which avidin can be immobilized and then the oligonucleotide biotinilated can be easily fixed. This allows obtaining the final probe, which is able to detect in various real samples, the presence of the pathogen microorganism.

## **TEMPERATURE - THE FORGOTTEN VARIABLE IN HPLC**

Roger M. Smith

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Temperature is often a forgotten variable in HPLC but can influence the robustness and selectivity of many separations or if exploited can provide novel high temperature separation conditions with either high efficiency, a unique selectivity or enable new detection methods to be applied.

If uncontrolled, temperature can have a significant effect on reproducibility and the robustness of separations. This can cause major problems in method transferability between laboratories and at its worst can require a method to be reoptimised or revalidated. Most separations therefore require a thermostated environment. However, the important factor is the temperature within the column bed, not just the surrounding enclosure. Circulating air ovens, static air ovens, metal block heaters and circulating water baths can all generate different effective temperatures even if set to the same nominal values.

The temperature of the incoming mobile phase will also alter the environment within the column. Some laboratories have advocated that equilibration of the incoming mobile phase with the column temperature is essential for good peak shapes and optimum efficiency. However, a number of studies have now demonstrated that if the mobile phase is cooler than the column the efficiency is improved, in some cases quite markedly.

In recent years, the use of elevated temperatures has been recognised as a potential variable in method development. With increased temperature, aqueous-organic mobile phases separations can improve, viscosity decreases and diffusion increases so back pressures are reduced. At higher temperatures (usually with superheated water > 100 °C under modest pressures) water alone can be used as the mobile phase and can provide unique separation opportunities. The absence of an organic solvent enables the use in HPLC of alternative detectors such as FID or on-line LC-NMR using deuterium oxide as the eluent.



# RECENT ADVANCES IN POLYMER ANALYSIS BY MODERN PYROLYSIS-GAS CHROMATOGRAPHY/MASS SPECTROMTERY (Py-GC/MS)

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Analytical pyrolysis has been performed by humans probably since prehistoric time, typically smelling smoke and fume yielded from burning and/or degrading materials to identify them. Although analytical pyrolysis often provide unique compositional and structural information not only for synthetic but also natural polymers, it has been regarded for a long time as a relatively crude technique mainly because of its poor reproducibility between interlaboratories. However, owing to recent developments in highly specific pyrolysis devices, highly efficient separation columns for GC, and specific identification of the peaks in the resulting pyrograms by GC/MS equipped with a library search system, modern Py-GC/MS has made a great stride toward being one of the practically powerful techniques for polymer characterization.

Modern analytical pyrolysis has conventionally been carried out only by thermal energy to break some covalent bonds in the sample molecules at elevated temperatures to produce smaller and/or volatile fragments (pyrolyzates). On the other hand, the reactive pyrolysis in the presence of organic alkaline, such as tetramethylammonium hydroxide  $[(\text{CH}_3)_4\text{NOH}]$  (TMAH) has recently received much attention especially in the field of characterizing condensation polymers.

After brief discussion of the state-of-the-art of modern Py-GC/MS, some most recent applications for structural and compositional characterization of polymeric materials are described in detail. These include microstructural studies on sequence distributions of copolymers, stereoregularity and end group characterization for various vinyl-type polymers such as polystyrene and polymethyl methacrylate by use of conventional analytical pyrolysis.

Furthermore, newly developed reactive pyrolysis in the presence of organic alkalines applied for characterization of various condensation polymers is also discussed by demonstrating recent applications such as precise compositional analysis of liquid aromatic polyesters, branching and end group analysis of polycarbonates, network structure characterization of UV-cured resins, and highly sensitive determination of trace additives such as hindered amine light stabilizers (HALS) in polyolefins. Finally, the reactive pyrolysis applied to fatty acid characterization of zooplankton individuals will also be discussed.

# RECEPTORS AND SAMPLING SYSTEMS FOR NANODIAGNOSTICS

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Early concepts of nanotechnology as an engineering discipline principally concerned with building structures in the nm range have given way to a broader concept encompassing biotechnology, supramolecular technology and colloid chemistry. Nowhere is this more applicable than in modern designs for nanobiosensors and biomimetic sensors. Over 1,500 papers are published each year describing the various permutations of sensing element and transducer. The most significant impact of biosensors to date has been in the field of diabetes, where mediated amperometric biosensors account for over US\$ 5 billion in sales. Until now, however, no device has come close to delivering a truly one-step procedure. This presentation will describe how new technology has been developed to deliver this objective comprising an electromechanical lancing engine, microfluidics and a nanolitre sensor array. The development of suitably robust biosensors for many situations outside of glucose monitoring, has been hindered by several problems associated with the properties of biological material. The search for possible solutions to these problems has led to the development of biomimetic systems such as Molecularly Imprinted Polymers (MIPs). A key element here is the need for rational design and we have undertaken a series of studies to elucidate the effect of the various physical and chemical conditions required to achieve optimum performance. In addition, we have introduced a computational approach to the selection of appropriate monomers using a virtual library of functional monomers and screening them for their ability to form a molecular complex with the template. Work at Cranfield has shown the utility of this approach for high throughput screening of pharmaceuticals, medical and environmental diagnostics and for the production of sensor arrays for detection of, for example, drugs of abuse. The ability to construct highly stable sensing structures which are either small enough to be implanted in the body, distributed widely in the environment, configured as high density arrays or coupled to modern information systems, offers exciting new horizons in analytical chemistry.

# MULTISENSOR SYSTEMS “ELECTRONIC TONGUE” BASED ON LOW-SELECTIVE SENSORS AND MULTIWAY METHODS OF RECEIVED DATA TREATMENT

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A great advantage in sensor R&D at the end of last century is the development such devices as “electronic nose” and “electronic tongue”, which consist of multisensor arrays. The history of chemical sensors belongs to the last century. It started from pH-glass electrode (1906). Later on many different conventional ion-selective electrodes (1961-1969) and microelectronic sensors like ISFETs (starting from 1970) have been developed. The first papers on “electronic nose” and “electronic tongue” were published in 1982 and 1995, correspondingly.

The design of these devices is based on biological principles of organization of human olfactory and tasting abilities.

The “electronic nose” and “electronic tongue” can be considered as a specific branch of the development of artificial intelligence and application of the electronic brain.

Definition: “the “electronic tongue” is an analytical instrument including an array of low-selective chemical sensors and appropriate pattern recognition tool, capable to recognize quantitative and qualitative compositions of simple and complex solutions”.

The principle things of “electronic tongue” are:

- application of low-selective, cross-sensitive sensors;
- application of modern mathematical methods of signal processing based on pattern recognition (artificial neural network, principal component analysis, partial least squares, etc.);
- possibility to recognize the quality of the food and concentration of solution components for which no selective sensors exist.

The paper describes the different chemical sensors and mathematical methods applied and presents the review of “electronic tongue” application for quantitative analysis (heavy metals and other impurities in river water, uranium in former mines, metal impurities in exhaust gases, etc) and for classification and taste determination of some beverages (coffee, bear, juice, wines), vegetable oil, milk, etc. [1].

1. Vlasov Y., Legin A., Rudnitskaya A. Electronic tongues and their analytical application. *Anal.Bioanal.Chem.*, 2002, v.373, p.136-146.

# ANALYTICAL CHEMISTRY IN THE FORMER SOVIET UNION: LEADING SCIENTISTS AND THEIR CONTRIBUTION

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The review covers the studies in analytical chemistry carried out in XVIII-XX centuries on the space of the former USSR.

Serious science started in Russian empire in the middle of the XVIII century. The first known Russian scientist M.V. Lomonosov obtained (in the 1750s) experimental data on the preservation of the mass of substances in chemical reactions. T.E. Lovits discovered adsorption from solutions; he used wood carbon as an adsorbent. Among other scientists, Lovits detected compounds using characteristic forms of their crystals. V.M. Severgin published a book on analysis of mineral raw materials.

In the XIX century K.K. Klaus discovered ruthenium and developed methods of its detection and determination; he used compounds of platinum-group metals as analytical reagents ( $H_2PtCl_6$  for potassium and so on). G.V. Struve and Svandberg found and applied the known reaction of phosphorus with ammonium molybdate; Struve proposed also the analogous reaction for arsenic. Yu.F. Fritshe proposed (1863)  $\beta$ -dinitroanthraquinone as a reagent for aromatic hydrocarbons ("Fritshe reaction"). P.N. Akhmatov was probably the first, who used xanthogenates as analytical reagents; he published a monograph on these compounds (1874). N.A. Bunge, a professor of Kiev University, found out (1892) an effect of electric current and anode surface area on the rate and completeness of electrolytic metal separation; in joint work with A.P. Lidov, he proposed (1875) an application of solid sorbents in gas analysis. F.F. Beilstein, a well-known author of the famous handbook, made some remarkable works in analytical chemistry. He proposed a reaction for halides in organic compounds: a green colour of a flame while heating with a pure copper oxide ("Beilstein test"). Beilstein and L.Yu. Yavein wrote "Testbook of Qualitative Chemical Analysis" which was published in main European languages. I.I. Klobukov used a rotating anode in electrolysis (1888). M.A. Il'insky and G. Knorre proposed 1-nitroso-2-naphthol as a reagent for cobalt and Zh.I. Iotsich – magnesium diiodine acetylene as a reagent for carbonyl group. F.M. Flavitsky developed a method for qualitative analysis based on solid substances as well as a portable laboratory for qualitative analysis. G.V. Khlopin proposed a method for determining oxygen dissolved in water.

In the XX century, many important discoveries were done and thorough studies were carried out. At the beginning of the century (1903) M.S. Tsvet invented chromatography and L.A. Chugaev (1905 and others) developed the basis of organic complex-forming reagents action (and proposed dimethylglyoxime as a reagent for nickel).

The first paper in TLC was published by N.A. Izmailov and M.S. Shraiber (1938). A.A. Zhuchovitsky, A.V. Kiselev and others made significant contributions in GC. As to analytical spectroscopy, some important achievements can be mentioned: developing ETAAS by B.V. L'vov, "cold vapour" method for mercury by N.S. Poluektov. "Shpol'sky effect" (appearance of linear luminescence spectra at low temperature used, i.g. for determining PAH) is well known. A lot of important works in photometry with coordination compounds were done, especially in Ukraine (A.K. Babko, N.P. Komar', V.A. Nazarenko and others). A XRS school in 1950-1960s was maybe the most powerful in the world (M.A. Blokhin, N.F. Losev). As early as in 1920-1930s N.A. Tananaev, simultaneously with F. Feigl, developed the spot analysis. Known "Tseremitinov method" for determining labile hydrogen atoms in organic compounds (1902-1907 should be noted (the method was later improved by A.P. Terent'ev). In the USSR, there were powerful schools in liquid-liquid extraction and inverse voltammetry.

# **GENERAL ASPECTS**

*Keynote lectures*

# ROBUST AND UNBIASED ESTIMATIONS IN CHEMICAL DATA TREATMENT

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As usually the statistical properties of the experimental data are poorly known, nobody can guarantee that the standard statistical procedures give the trustworthy results. The history of chemical data treatment exemplifies impressively the persistent struggle for obtaining more and more reliable meaningful information from the experimental data.

The report is concentrated at a few procedures of data treatment that allow overcoming some drawbacks of standard statistical procedures. The main attention is paid to the problems of the regression analysis, especially to the Quantitative Structure-Activity Relationships (QSAR).

The first task considered is the robust estimation of fitting parameters. Following to Peter Huber, the consideration is built at the assumption that the density function of the experimental random errors ( $\epsilon$ ) can be presented in the following form:

$$p(\epsilon) = [(100 - \delta) \cdot \varphi(\epsilon) + \delta \cdot h(\epsilon)] / 100,$$

where  $\varphi(\epsilon)$  is the Gaussian density function with zero mean,  $h(\epsilon)$  is the density of “outliers” (the density function with long tails) and  $\delta$  is the intensity of outliers (%). Varying the hypothesis on the  $\delta$  value, one obtains different criterions to find the maximum likelihood estimations of fitting parameters.

The properties of the least squares (LS) method ( $\delta = 0$ , the non-robust procedure) and the least modules (LM) one ( $\delta = 100\%$ , the robust procedure) are comprehensively compared with the use of several examples of data treatment in the QSAR problems.

The second task discussed is the validation of the regression models with the aid of the cross-validation (CV) procedures. The leave-one-out (LOO) as well as the leave-many-out CV methods are used to evaluate the prognostic possibilities of QSAR. In the case of noisy and/or heterogeneous data the LM method is shown to exceed sufficiently the LS one with respect to the suitability of the regression models built. The especially noticeable distinctions between the LS and LM methods are demonstrated with the use of the LOO CV criterion.

Also, the excellent properties of the robust procedures are demonstrated at constructing the nonlinear regression models for the two-atomic system potential energy curves.

# STRATEGY AND PROGRAM TOWARD DEVELOPING CUTTING-EDGE ANALYTICAL INSTRUMENTS AND DEVICES: A NEW INITIATIVE BY JAPANESE GOVERNMENT

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Analytical instruments play an increasingly important role in modern analytical chemistry. The trend is not limited in chemistry but in all phases of natural science and technology, as one easily can watch in rapid progresses in molecular biology, nano-materials technology, and the related bio-medical research. Instrumental developments can now even be a determining factor in the advancement of science itself.

Under this situation, a government-supported special program was launched in Japan from 2004 (Analytical instrument-developing program). This is aimed at developing cutting-edge analytical techniques and instrumental devices for supporting creative research in selected areas of strategic importance in science and technology. Some of the areas overlap those of analytical chemist's traditional interest, and it is hoped that a presentation of the picture of the program could serve people of AC&CA-05 through offering ideas around the techniques or apparatus they may be involved in their laboratory.

Developmental proposals were called for grant application in five major fields as defined by the following keywords. Proposals not covered by the listing were also considered when persuasive enough.

1. High-resolution observation of dynamics of bio-macromolecules in cells and bio-organisms: atomic or molecular level, regional or focused observation, three-dimensional analysis;
2. Non-invasive visualization and analysis of metabolism in laboratory animals: individual body level;
3. Nano-level, three-dimensional observation and visualization of matters;
4. Multi- or simultaneous measurement of nano-level properties and nano-level functions of materials;
5. Direct multi-element or multi-component simultaneous determination of ultra-trace matter in samples of environmental concern.

In 2005 call, the major areas were for the following two fields.

6. Exhaustive and quantitative determination of bio-macromolecules, genes or metals etc. in a single cell;
7. Nano-characterization of materials: trace metals, point defects, chemical states, and their distribution

Features will be given including application statistics and adoption.

# METROLOGICAL UNCERTAINTY ESTIMATIONS IN QUALITATIVE ANALYSIS

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Qualitative analysis methods should have well-grounded and generally adopted quantitative reliability estimations. At first the problem was formulated by N.P. Komar in 1955. Its actuality increased when test methods and identification software systems (ISS) entered the market. Metrological aspects evolution for qualitative analysis is possible only within the scope of the uncertainty theory. To estimate the result reliability while detecting a substance X it is necessary to calculate both constituents of uncertainty: the probability of misidentifications and the probability of unrevealing for an actual X. There are two mutual complementary approaches to evaluate uncertainties in qualitative analysis, just as in quantitative analysis:

- 1) *statistic evaluations*, calculated from controlled tests results for a big set of reference materials (RM) with known composition;
- 2) *a priori evaluations*, calculated by summation of elementary uncertainties for initial measurements.

The principles, advantages, limitations and applications for both approaches are discussed in the actual report. The statistic evaluations are necessary for any qualitative method certification, especially for test methods. These evaluations are developed better (S.Ellison, M.Valcarse, W.Bremser, B.Milman, L.Konopelko, E.Reshetniak). As the statistical evaluations demand to analyze hundreds of RM's for one test method, quite often such approach is impossible. Now statistic evaluations are widely applied only in the clinical medicine and toxicology. The new methodology of *a priori* evaluations is being discussed in more detail. *A priori* evaluations show their preferences during the instrumental method optimization. Such evaluations don't demand a plenty of RM's. Their adaptability in any instrumental method is possible only within the limits of the certain model which determines the factors resulting in the above mentioned errors. Calculation algorithms for both uncertainty constituents are specific for every analytical method; they should take into account the initial measurement accuracy, the expected sample's composition, the number and selectivity of the identification features and so on. The final result depends on the analysis conditions and on the concentration of X. In this way it is possible beforehand to choose the right criteria, which assure the desirable reliability level for identification. The report is showing that *a priori* estimations application leads to significant results of computerized chromatographic analysis and spectral analysis of mixtures as well.



*Oral presentations*

# PECULIARITIES OF THE “HOST-GUEST” PHENOMENA APPEARANCE IN THE SURFACTANT BASED ORGANIZED MEDIA

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The character of the organized media, which are widely used in analysis, is the appearance of the “host-guest” phenomena. These phenomena are studied for organized media with the molecules of receptors (crowns, calyxarenes, cyclodextrines etc.) in details. Nevertheless such effects for surfactants based organized media (micellar solutions, emulsions, microemulsions etc.), which are also referred to organized systems, are mostly declared but not yet studied or even described. On the basis of own experimental and literature data some demonstrations of the “host-guest” phenomena in the surfactant-based organized systems are presented. The effects appear for both two- and multicomponent systems in the premicellar and micellar surfactant systems:

- the increase of the stability of two-component “ionic reagent - counter ionic surfactant” associates at ions size correspondence in premicellar solutions. The effect was observed and studied in the “triphenylmethane basic dye - alkylsulphate anion” systems;
- the increase of the stability of “anionic reagent - cationic surfactant - nonionic surfactant” ternary associates for cations with medium hydrocarbon radical length. The phenomenon was examined for “methyl orange - alkylpyridinium cation - polyoxyethylated alkylphenol” systems;
- the increase of the stability and absorbance of four-component “metal ion - organic reagent - cationic surfactant - nonionic surfactant” complexes for cations of medium hydrophobicity;
- the increase of the solubilization capacity of micellar solutions when sizes of the substrate molecules and micelles corresponds;
- certain specific features of the cloud-point extraction of substrates by the phases of nonionic surfactants.

These effects appearance is explained by the nature of hydrophobic interactions and the structural organization of micellar solutions. The “host-guest” phenomena determine the increase of the selectivity of analytical reactions in the surfactant-based organized systems.

# METAL SPECIES IN THE AQUATIC ECOSYSTEMS AND THEIR EFFECT ON THE WATER QUALITY

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Among diverse toxic components in the hydrosphere, the some trace metals (i.e.  $\text{Hg}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Cr(VI)}$ ,  $\text{Al}^{3+}$  etc.) present a serious danger to plants and animals and finally to man, because many of them have mutagenic and carcinogenic effects. However, the mobility, bioavailability and toxicity of trace elements in natural aquatic systems are to a large extent determined by the physical and chemical forms in which the metals occur. Free (hydrated) metal ions as well as organometallic species of some metals are regarded as the most toxic form. Speciation of metals in surface waters is dominated by interactions with dissolved organic matter and adsorption on the suspended particles and bottom sediments. These important processes more often than not decrease or completely suppress the metal toxicity.

The methods of investigation of metal species in natural waters must possess by well dividing ability and high sensitivity and selectivity to determination of several metal forms. The catalytic including chemiluminescent (CL) techniques and anodic stripping voltammetry (ASV) are the most useful to determination of trace metals and their forms. The methods considered are characterized by a low detection limits. Moreover, they allow detection of the most toxic form of metals, that is, metal free ions and labile complexes.

The use of membrane filtration, ion-exchange and gel-permeation chromatography coupled with CL and ASV methods has allowed to receive the data on a physicochemical state of a number of metals (Fe, Mn, Zn, Cu, Pb, Cd, Cr, Al) in the water objects of Ukraine (Dnieper water bodies, Danube and Dniester rivers etc.). Complexation with participation of the dissolved organic matter (DOM) of a various chemical nature and molecular weight, first of all humic substances (HS), plays an essential role in migration of metals in water objects studied. The binding degree of metals investigated in complexes with DOM reaches 70–98%, the share of metal complexes with fulvic acids makes up 50–65%. Molecular weight of the most part of metal complex compounds does not exceed 5 kDa.

It is established by biotesting that complexation and adsorption are the most important processes promoting transformation of metal compounds in biologically and the chemically inactive forms and essential decrease their toxicity. The kinetics data have shown the maximal decrease in toxicity was observed in natural water where the complexation occurred with participation of both DOM and added HS.

# COMPUTER SIMULATION OF DYNAMIC PROCESSES IN COMPLEX ELECTROLYTIC MEDIA

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The holistic thermodynamic approach based on material (charge, concentration and electron) balances is a firm and valuable tool for a choice of the best a priori conditions of chemical analyses performed in electrolytic systems. Such an approach has been already presented in a series of papers issued in recent years, see [1–4] and references cited therein. In this communication, the approach will be exemplified with electrolytic systems, with special emphasis put on the complex systems where all particular types (acid–base, redox, complexation and precipitation) of chemical equilibria occur in parallel and/or sequentially. All attainable physicochemical knowledge can be involved in calculations and none simplifying assumptions are needed. All analytical prescriptions can be followed. The approach enables all possible (from thermodynamic viewpoint) reactions to be included and all effects resulting from activation barrier(s) and incomplete set of equilibrium data presumed can be tested. The problems involved are presented on some examples of analytical systems considered lately, concerning potentiometric titrations in complex titrand + titrant systems. All calculations were done with use of iterative computer programs MATLAB and DELPHI.

1. T. Michałowski, M. Toporek, M. Rymanowski, *Talanta*, **65** (2005) 1241
2. T. Michałowski, M. Rymanowski, A. Pietrzyk, *J.Chem.Educ.*, **82** (2005) 470
3. T. Michałowski, *Calculations in analytical chemistry with elements of computer programming*, PK, Cracow, 2001
4. T. Michałowski, M. Rymanowski, M. Toporek, *Czas.Tech.*, **191** (2004) 85

**THE ENVIRONMENTAL MULTIELEMENT REFERENCE  
MATERIAL COLLECTION OF THE INSTITUTE  
OF GEOCHEMISTRY, SIBERIAN BRANCH,  
RUSSIAN ACADEMY OF SCIENCES**

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It is known that the reliability of analytical information obtained depends particularly on the range of reference materials (RM) used. The most of RMs developed by the Institute of Geochemistry, SB RAS are included in the State Register of certified types of National Certified Reference Materials of Russian Federation. The reference materials are routinely analyzed for the stability and their life durations are timely prolonged. Developed RMs (27 samples) characterize mainly mineral substances.

The subcollection of magmatic rocks (9 samples) involves the most widespread varieties of dunite (SDU-1) through traps (ST-1a and ST-2) and essexite gabbro (SGD-1a and SGD-2) to quartz diorite (SKD-1) and sviatonossite (SSv-1) and to granites (SG-1a and SG-3). RMs were certified for different number of elements ranging from 20 for RM SDU-1 to 58 for RM SGD-1a. The subcollection of metamorphic rocks comprises five RMs as Certified RMs and five RMs as Standard RMs. Certified RMs include alumina silicate metamorphic shale SS1-1 (30 certified values) and dolomitized limestone SI-2 (24 certified values) and SI-3 (23 certified values). Unique black shale RM, SCHS-1 and SLg-1, created from the ore of the Sukhoy Log gold deposit were certified for 51 and 43 elements, respectively. The subcollection of recent sedimentary rocks consisting of 9 Certified RMs includes bottom sediment BIL-1 and BIL-2, river sediments SGH-1, 3, 5 and terrestrial loose sediment SGHM-1÷4. This subcollection is unique as some RMs correspond with alumina silica matrix while others have carbonate silica composition that allows covering the composition field of such rocks. The subcollection of man-caused substances includes 6 RMs: two RMs of coal ash ZUK-1 (45 certified values) and ZUA-1 (31 certified values) and four RMs of products obtained from processing of gold-bearing ores (certified for Au, Ag, S, As and Sb).

RMs being under development are divided into two groups: traditional geological RMs – garnet-biotite plagiogneiss GBPg-1, granite SG-4, synnyrite SG-5, spinel lherzolite LSHZ-1 and minerals – quartz Qu-1, microcline Mi-1, amphibole Amf-1; and biological RMs - birch leaf LB-1, mixture of meadow herbs Tr-1, Canadian pondweed EK-1, perch tissue Bok-2 and dry residue of Baikal water SOVB-1.

# PHENOMENOLOGICAL MODELING OF SERIES OF ANALYTICAL SIGNALS IN CASE OF COMPLEX CHARACTER OF THEIR FORM CHANGE

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Modelling analytical signal series is especially important for studying a mathematical processing of analytical signals. For example for studying a resolution of analytical chemical method, also for studying systematic error of analytical signal mathematical treatment (a base line approximation, smoothing and/or differentiation analytical signals) and next for estimating of efficiency and correctness of the overlapped analytical signals numerical resolution procedures.

In this case results don't depend on random errors. The shape and size of analytical signal can vary smoothly. Physicochemical simulation is difficult because of irreproducibility many experimental factors.

In previous researches it was shown that new phenomenological models are available to approximation any analytical peaks. These models can be used for modelling analytical experiments.

For this purpose, first of all, this model must be universal enough for the exact approximation the whole series of analytical signals and description of analytical signals in the research range of determined component concentration.

The procedure has the following stages:

1. Plotting diagrams showing dependence of peak parameters (such as peakedness, tailing, semi-half-width of peak, peak asymmetric *etc.*) on peak height;
2. Selecting the most suitable model of classification;
3. Processing all peaks for the model by nonlinear least square procedure;
4. Plotting diagrams showing dependence of model parameters on peak height;
5. Approximating the dependences by polynomial and making finally function system;
6. Calculating the function system for the whole peaks series.
7. Adding the real experimental base line to the result date to get "experimental" series.

The mathematical modelling of series of analytical signals in case of complex character of their form change can be applied for studying mathematical processing of analytical signals more effectively, for searching the ways to decrease a minimal determined concentration and increasing resolution *etc.*

*Poster presentations*

# SPEKTROPHOTOMETRIC DETERMINATION OF INDIUM BIS(2,3,4-TRIHIDROXYFENILAZO)BENZIDINE IN PRESENCE PAPAVERINE, DIBAZOL, UROTROPIN

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Reactions of complexes formation of In(III) with bis-(2,3,4-trioxy-phenylazo)benzidine (R) in presence of papaverine (Pap), dibazole (Dib), urotropine (Ur) has been studied by the spektrophotometric method. It has been established that the optimal conditions of complex formation for complexes of In(III) R-Pap, In(III) R-Dib and In(III) R-Ur are pH=2.

The maximal light absorbtion of complexes In(III) R-Pap, In(III) R-Dib and In(III) R-Ur is observed at 442, 449, 457 nm, but the reagent itself under this condition absorbs at 354 nm.

Complexes immediately form the optical density and its stablefill heading 70°C and aday. By the izomolar series method and Starik Barbanel method has been established that the relation of components in structure complexes is 1:1:1. Molar coefficients of light absorbtion of complexes In(III) R-Pap, In(III) R-Dib and In(III) R-Ur are 28500, 29000 and 30000 respectively. The Beerçs law is obeyed in the region 0,23-4,6 mg/ml for In(III) R-Pap, In(III) R-Dib and In(III) R-Ur. Stability constant for InR-Pap is  $8,55\pm 0,06$ , for InR-Dib is  $8,74\pm 0,15$  and for InR-Ur is  $8,36\pm 0,24$ . Also the affection margin ions and screening ions have been determined. The determination of In(III) is not interfered by Cu(II), Cd(II), Pb(II), Zn(II), Al(III), Co(II), Mn(II), Ga(III), Ba(II), Sr(II), SCN<sup>-</sup>, sulfates, etc. This methods is highly sensitive and selective. It is a veri rapid and a simple technique.



# CRITERIA TO SELECT LABORATORIES TO BE PARTICIPATED IN INTERLABORATORY INVESTIGATION BASED ON RANK ASSESSMENTS

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For further interlaboratory investigation scheduling it is advisable to determine the range of laboratories proving their reliability from previous interlaboratory experiment results. To describe the rank situation the criterion  $R$  suggested by Abbey [1] (formula (1)) was applied for analytical results obtained for the reference material of garnet-biotite plagiogneiss, GBPg-1, and national certified reference materials of black shale, SCHS-1 and SLg-1, developed by the Institute of Geochemistry SB RAS.

$$R = \frac{N_x - N_n}{N_x + N_y + N_n}, \quad (1)$$

where  $N_x$  – the number of element content determinations falling into the interval  $(C_{cert} \pm \Delta)$  ( $C_{cert}$  – certified value,  $\Delta$  – certification uncertainty),  $N_y$  – the number of element content determinations falling into the intervals  $(C_{cert} - \Delta) \div (C_{cert} - 2\Delta)$  and  $(C_{cert} + \Delta) \div (C_{cert} + 2\Delta)$ ,  $N_n$  – the number of element content determinations falling outside of these intervals.

In addition to  $R$ , the informational capability of a laboratory,  $I$ , was assessed as the entropy of complex system [2], using the information about analytical resources of the laboratory.

$$I_{lab} = \sum_{ij}^{N_1, N_2} \log_2 n_{i,j}, \text{ bit}, \quad (2)$$

where  $n = C_{max} / C_{min}$  and  $C_{max}$  and  $C_{min}$  – higher and lower limits of the analytical interval,  $N_1$  – the number of elements determined by the laboratory using  $N_2$  methods.

The comparison of approaches applied was carried out.

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2. Ventzel' E.S. Theory of probability. Akademiya, Moscow, 2003. P. 468-476. (in Russian)

# HPLC INVESTIGATION OF pH DEPENDENCY OF THE LIPOPHILICITY PARAMETER OF PARABENS

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Parabens exhibit a broad spectrum of antimicrobial activity and are widely used preservatives for drugs and foods. As a first step of their antimicrobial action, the penetration through the cellular membrane is considered. An important indication of this process is the lipophilicity parameter of the antimicrobial compounds. As method for determination of the lipophilicity parameter in last years, high performance liquid chromatography (HPLC) is suggested in the literature [1]. This technique has been used mostly due to the identity of the lipophilicity parameter to the capacity factor  $K$  [2]. The capacity factor is easily determined using the method of reversed phase HPLC applying the following equation:

$$K = \frac{(R_t - R_0)}{R_0},$$

where  $K$  is the capacity factor,

$R_t$  is the retention time of the compound investigated,

$R_0$  is the retention time of the non-retained compound [3].

Very often, the pH is a key factor for the value of  $R_t$  (respectively  $K$ ). Investigating the pH dependency of the capacity factor of parabens, and drawing the curves of this dependency, important information about the strength of the processes of protonation and deprotonation for the parabens investigated can be obtained. The HPLC method is susceptible enough to determine the strength of protonation at the oxygen atom in C=O group which depends on the chain length of the substituent in the ester group and its induction effect. The conclusion in this situation is that the pH dependency decreases with the ester chain getting shorter.

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# ANALYTICAL POSSIBILITIES OF IONIC ASSOCIATES OF THE METALS Pd, Zn AND Hg WITH CATIONIC DYES IN IONOMETRY

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Ionoselective electrodes are widely utilized in analytical check, and the most easily in use are plasticized membrane electrodes. However, for many substances the efficient membranes are still not designed. We have shown the possibility to use the ionic pairs formed by anionic thiocyanate complexes of the metals and by cationic cyanine dyes as electrode-active substances of the plasticized ionoselective electrodes.

The compounds obtained in solid state have the general formula  $[\text{Me}(\text{SCN})_4]\text{R}_2$  (R-cations of cyanine dyes) and could be embedded into polyvinylchloride matrix. Using the matrix as work element of electrodes shows the anionic function concerning the anionic thiocyanate complexes of Pd, Hg, Zn and the response to separately present thiocyanate and metallic ions is not exhibited.

The way to obtain the membranes as well their composition has been optimized. The main operational criterion for the membranes is the solubility of applicable ionic pairs. The solubility should be quite low – else the substance will be outwashed from the membrane. At the same time, the ionic pairs which have very low solubility are not suitable too because of the complicated obtaining homogeneous membranes.

The main chemico-analytical properties of the designed ionoselective electrodes have been determined. The work pH range of the electrodes is 1 to 5. The steepness of the electrode function is close to the idealized one calculated for two-charged ions (26-29 mV/pC). The electrode function have been established in the concentration range from 0.1 to 0.00001 mole/l. The principal advantage of such electrodes is the fact that thiocyanate ions are simultaneously both complexing ligands and the ionic power. The sensitivity (the discovery limits), selectivity (coefficient of selectivity) and the influence of the main temporal factors (drift of a potential, time of the response, lifetime of the membranes) were determined for these electrodes.

The obtained results exhibit the efficacy of using the mentioned ionic pairs as electrode-active substances for plasticized ionoselective electrodes.

# DETECTION LIMIT AND IDENTIFICATION SUBSTANTIATION AND EVALUATION OF WORLD ANTI-DOPING AGENCY PROHIBITED LIST COMPOUNDS

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Standard analysis methods couldn't be applied in doping-control in sports. The laboratory should work out, validate and document methods for The Prohibited list substances. Therefore, it is important to differentiate term meaning of "detection limit" and "determination limit" by processing quantitative chemical analysis. In detection limits determination n measuring quantity is low and it is unclear beforehand, if we can consider the distribution to be normal. In the opinion of many authors, near the results of detection limit the distribution and inaccuracy of analysis don't obey the law of normal distribution. That is why, because of information lack concerning distribution character by the estimation of detection limit, it is possible to use Chebyshev's inequality. Accordingly, in every distribution the basic deviation serves as dispersion measure of chance variable. Chebyshev's estimation leads to understated reliability value in comparison with normal distribution. Because normalized indexes of many prohibited compounds are absent, an analyst should aim at maximum absolute system sensitivity which is used in analysis processing. So statistic estimation of detection limit is a complicated task. IUPAC recommends the usage of  $k = 3$  ( $k$  – the sigma quantity), International commission of microchemical technique and trace analyses recommends the usage of  $k=10$ . In actual practice the lower detection limit should be statistically based. In this article the method of detection limit ascertainment was used. But we haven't taken the law of error distribution into account. In further investigations the approaches of steady signals discovery on the background of noise will be worked out. It will be carried out considering the law of error distribution.

## INDICATIVE OXIDATION OF AROMATIC AMINES IN PLATINUM METALS' CATALIMETRY

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The ability of platinum metals to catalyze some redox processes, in particular oxidation reactions of aromatic amines, allows to develop high-sensitivity techniques of platinum metals determination. Sulphoderivative aromatic amines containing volumetric substitutes in N-position (N-methyldiphenylamine-4-sulfonic acid (MDASA) and triphenylamine-4-sulfonic acid (TPASA)) are represented interest as redox indicators. The features of an electronic and geometrical structure of amines' molecules predetermine the specificity of these reagents to positively charged complexes of the small size with high redox potential, especially cations of platinum metals of rare group.

Kinetic rules of oxidation of MDASA and TPASA by periodate ions in the weak-acidic medium at the presence of ruthenium (VI), iridium (IV), rhodium (III) and their mixtures are investigated by spectrophotometric method. The influence of high temperature treatment with mineral acids of catalysts, concentration of reactants, interfering ions, temperature and ionic strength of solutions on the rate of reactions was investigated. Optimal conditions of indicator reactions, rate constants and energy of activation for arylamine oxidation reactions at the presence of individual catalysts are determined.

Significant distinction in rate constants of MDASA and TPASA oxidation reactions by periodate ions at the presence of individual catalysts allow to use them for differential determination of platinum metals in complex mixtures. The range of concentration ratios iridium (IV): rhodium (III) is determined where sinergetic effect of concentration of one catalyst on the rate of oxidation MDASA and TPASA by periodate ions at the presence of another is not observed. Optimal conditions of iridium (IV) and rhodium (III) determination are established at theirs simultaneous presence. Indicative oxidation reactions of MDASA and TPASA are applied to differential determination of iridium (IV) and rhodium (III) in artificial mixtures and a complex industrial sample by the method of the proportional equations.

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# HEXAMETHYLENETETRAMINE AS AN ORGANIC REAGENT FOR TITROMETRIC ANALYSIS

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Aqueous solutions of hexamethylenetetramine (HMTA) can be used as titrant for acids concentration determination [1]. Aqueous solutions HMTA are extensively used in complexometry as a buffer.

One of the requirements to initial standards is their stability is at keeping. HMTA in aqueous solutions is declined to hydrolysis. In the present work the stability of aqueous solutions of HMTA towards hydrolysis was investigated as a function of time in a range of temperatures 1-21 °C.

It is stated that in time the acidity (up to 2,5 units) of 0,1-1,0 M HMTA aqueous solutions changes maximally at 1°C, in comparatively to other temperatures (11, 16, 21°C). When the temperature arises the change of HMTA aqueous solutions pH values decreases in time. Formaldehyde and ammonium ions (end products of HMTA hydrolysis) have been fixed only in more diluted solutions (0,10 and 0,25M). The concentration of  $\text{NH}_4^+$  in them in some times is higher than  $\text{H}_2\text{C}=\text{O}$  concentration that is caused by oxidation of the last one to a formic acid, being accompanied by the change of the system platinum electrode potential. It is stated that concentration  $\text{NH}_4^+$  in solutions does not exceed 5% from HMTA general content. The conclusion the mechanism of HMTA destruction in  $\text{H}_2\text{O}$  to depend essentially on its concentration and temperature has been made.

The higher concentration (0,5, 1,0 M) HMTA solutions are recommended to use as initial standards for determination of acids concentrations. It is recommended to keep them at room temperature because they are more stable under these conditions.

The method of preparation of buffer solutions with the certain acidity value from HMTA and HCl aqueous solutions is offered. It is recommended to use the equations:

$$V_{\text{HMTA}} = 584,43 - 331,98\text{pH} + 61,284\text{pH}^2 - 3,5428\text{pH}^3 \quad (R^2 = 0,997),$$

$$V_{\text{HCl}} = 50 - V_{\text{HMTA}},$$

( $V_{\text{HMTA}}$  and  $V_{\text{HCl}}$  - volumes of 1,0 M HMTA and 0,1 M HCl, respectively) to prepare the buffer solutions with certain pH value in the range 4,30-7,40.

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# COMBINED APPLICATION OF COMPOSITION AND STRUCTURE ANALYSIS METHODS TO THE DETERMINATION OF MAGNESIUM CONCENTRATION AND LOCATION IN BONE BIOAPATITE

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Magnesium ( $Mg^{2+}$ ) is one of the more important minor cations in mineral of skeletal tissues: bioapatite. It can markedly affect behavior of bioapatite, particularly its solubility. In bone Mg is found at around 0,6 wt. %. The results of the different approaches indicate that the degree of Mg substitution for Ca in apatites structure can be at most ~ 10 % of atoms. The excess is probably located in the amorphous phase and/or on the crystallite surface. The manner of incorporation and the role of Mg in biapatite require further clarification. Mg promotes the thermal conversion of hydroxyapatite (HA) into  $\beta$ -tricalcium-magnesium phosphate ( $\beta$ -TCMP), where it partially replaces Ca. The extent of apatite conversion into  $\beta$ -TCMP appears strongly related to Mg content of the apatitic solid phase. The amount of Mg substituted for Ca in the structure of  $\beta$ -TCMP is almost the same for the different samples and accounts for about 8 atom %. In the present work, X-ray diffraction, electrothermal atomic absorption spectrometry and scanning electron microscopy with X-ray electron probe microanalysis were used to study phase decomposition of bioapatite and synthetic Mg-containing HA heated at 900°C to produce  $\beta$ -TCMP. With a simplified model, the expression was derived to relate the initial Mg content to the amount of apatite converted into  $\beta$ -TCMP. It is shown that for the  $\beta$ -TCMP contents measured in the bioapatite samples after the thermal decomposition and for the 8 % Ca amount replaced by Mg the calculated Mg concentrations in the bioapatite agree with literary data (0.2-0.6 wt. %). From the structure and composition analyses of thermally decomposed bioapatite and synthetic Mg-containing HA it was found that the formation of  $\beta$ -TCMP is limited by both the insufficient Mg concentration, and small crystal size. Investigations performed by the authors combined with experimental data available show that the Mg distribution in the bulk of bioapatite and HA crystals is highly nonuniform with primary Mg localization in the crystal subsurface.

**THERMODYNAMIC STUDIES ON THE PROTONATION  
EQUILIBRIA OF SOME HYDROXAMIC ACIDS IN NaNO<sub>3</sub>  
SOLUTIONS IN WATER AND IN MIXTURES  
OF WATER AND DIOXANE**

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The protonation equilibria for nine hydroxamic acids in solutions have been studied pH-potentiometrically via a modified Irving and Rossotti technique. The dissociation constants ( $pK_a$  values) of hydroxamic acids and the thermodynamic functions ( $\Delta G^\circ$ ,  $\Delta H^\circ$ ,  $\Delta S^\circ$ , and  $\delta$ ) for the successive and overall protonation processes of hydroxamic acids have been derived at different temperatures in water and in three different mixtures of water and dioxane (the mole fractions of dioxane were 0.083, 0.174, and 0.33). Titrations were also carried out in water ionic strengths of (0.15, 0.20, and 0.25) mol dm<sup>-3</sup> NaNO<sub>3</sub>, and the resulting dissociation constants are reported. A detailed thermodynamic analysis of the effects of organic solvent (dioxane), temperature, and ionic strength on the protonation processes of hydroxamic acids is presented and discussed to determine the factors which control these processes.



# SYNTHESIS AND PROTOLYTIC PROPERTIES OF THE PERIODICALLY ORDERED MESOPOROUS ORGANOSILICAS WITH MCM-41-TYPE ARCHITECTURES FUNCTIONALISED BY ALKYLAMINES

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The mesoporous ordered silicas of different type represent the new generation of materials with unique properties. The discovery of these materials became basis for creation of new catalysts, adsorbents, sensors and supporter for other molecules. The most important way of the modifying physical and chemical properties of mesoporous silicas consist in organic components incorporation on the silica surface as part of the silicate walls or their insertion within channels of the mesopores. This ensured that interest in synthesis and study of functionalized mesoporous materials sharply grew. In spite of it, these materials are studied insufficiently.

In the present work, periodically ordered mesoporous organosilicas (POMO) with MCM-41-type architectures and different contents of alkylamine functional groups on the inner surface of mesopores with fine ordering have been obtained by means of sol-gel method with cetyltrimethylammonium bromide as surfactant. Methods of the pH-potentiometric and conductometric titration were used for determination of propylamine groups concentration in synthesized POMO and study their protolytic properties. It is found, that samples contain from 0,54 to 0,85 mmol/g functional alkylamine groups and have hexagonal structure, the large volume of pores and high area of surface.

Calculated constants of the protolytic equilibrium ( $pK_1$  and  $pK_2$ ) are indicating about various basicity of functional groups on a surface of mesopores,  $pK$  these groups have considerably smaller values than their analogues in solution. In addition, the increasing of concentration of functional groups and consequently their density on the inner surface of mesopores result in the decreasing of constant of protonation ( $pK_2$ ), that allows to suggest screen character of location of the propylamine groups. Comparative analysis of the obtained POMO with analogues CMS revealed significant influence silica matrix structure on their protolytic properties.

# SYNTHESIS AND INVESTIGATION OF COMPLEX COMPOUNDS OF IRON (II) AND HYDROXYLAMINE

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Until now complex compounds of iron and hydroxylamine haven't been received. It is connected with liability of complex compounds of iron with monodentant amines and complication of interaction in the system of  $\text{Fe}^{2+}/\text{Fe}^{3+} - \text{NH}_2\text{OH}$ . Usual methods that are used to synthesis hydroxylamine complexes in this case turned out to be non-effective. For depression of oxidation-reduction processes and hydrolisation we used the method of synthesis in anaerobic conditions – in atmosphere of argon. Outlet  $\text{FeCl}_2$  was received using the method of high-temperature synthesis.  $\text{NH}_2\text{OH}\cdot\text{HCl}$  passed vacuum drying process. Absolute low alcohols were used as solutions. We have received two kinetic unstable complex of iron (II) and hydroxylamine in solution dark-green (pH 3,0 -6,0) (I) and brown-red (pH 6,5 – 7,5) (II). Absorption spectrums of complexes were made, spectral lines were assigned. For the (I) parameter  $10 \text{ Dg} - 9756 \text{ cm}^{-1}$  was found. The character of spectrums shows that I high spin complex of Fe (II) and II is low-spin complex. Using the method A.K. Babko  $\beta$ -constants of compounds was counted.

Two complexes of  $\text{FeCl}_2$  with  $\text{NH}_2\text{OH}$  were received in crystalline state-one-brown by precipitation from the solution (III) and pink-brown compound was received by lyophilic drying of the solution (IV).

The individuality of received complexes was proved by X-ray phase analysis (DRON-3.0). Preparative investigation of complexes was made. Infrared spectrums of complexes were made (Uh-20, KBr). It was proved that in the III complex hydroxylamine is coordinated with Fe (II) by oxygen in the form of n-oxyde-o- $\text{NH}_3$ - and in IV - by nitrogen in the form of  $\text{NH}_4\text{OH}$ . The composition of IV hasn't been proved in dry ruminant because of surplus age of reagent. The composition of III responds to formula of  $[\text{Fe}(\text{NH}_2\text{OH})_4\text{Cl}_2]$ .

## MONITORING WATER CONCENTRATION IN ORGANIC SOLVENT WITH FLUORESCENT DYES IN A SOL-GEL MEMBRANE

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An optical chemical, highly sensitive sensor for determining water concentration in organic solvents has been prepared by incorporating the indicator dye, 10-allylacridine orange in to sol-gel layers, prepared from tetramethoxysilane and methyltrimethoxysilane. Sensor layers based on TMOS and MTMS doped with 10-allylacridine were found to be most appropriate for purpose of sensing water concentration in organic solvents. The membrane processes relatively long lifetime (>9 months) and short response (<5 s) and recovering time. The reversibility and reproducibility of the sensor are adequate for practical measurements.

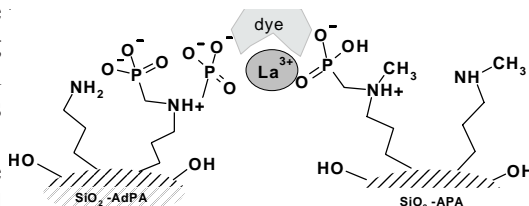
# MIXED-LIGAND COMPLEXES (MLC) OF La WITH AMINOPHOSPHONIC ACID GRAFTED ON SILICA AND ARSENAZO I, III AND XYLENOLE ORANGE

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The complexes on surface of chelate-functionalized silica often include ligands available in solution in the coordination sphere. Use of a chromophore reagent as a ligand leads to the formation of colored mixed ligand complexes (MLC). The phenomena can be used as a basis for developing test-systems for visual determination of microquantities of inorganic cations in water.

With the use of UV-Vis we studied the potential and conditions of formation of MLC on the surface of silica grafted with aminophosphonic (APA) and aminodiphosphonic (AdPA) acid using La(III) as central atom and aqueous solution of arsenazo (Ars-I, Ars-III) and xylenole orange (XO) as organic dyes. The choice of dyes was based on their sensitivity for spectrophotometric determination of Ln.



In the absence of dyes, APA- and AdPA-grafted silica bind La(III) with, respectively, 0.20 and 0.27 mmol/g sorption capacity, resulting in formation of 1:2 (La:L) complexes. 50% of introduced cation is bonded at pH=5 (APA), pH=6.1 (AdPA) and complete adsorption occurs at pH=6 (APA), pH=6.5 (AdPA). The grafted support in absence of La adsorbs the chosen dyes at pH<4 due to the electrostatic interaction with the -NH<sub>2</sub> groups on the surface, present as a result of grafting procedure. The adsorption of dyes at pH>4 is insignificant.

In the complex system containing APA (AdPA), La(III), and dye (either Ars-I or XO), strong adsorption of dye and La occurs at pH 6-8. Analysis of UV-Vis of prepared solids shows formation of MLC. Their composition, UV-Vis adsorption maxima ( $\lambda$ , nm) and the shifts relatively to the monoligand La-dye complexes in solution ( $\Delta\lambda$ , nm) are shown in the table below. Ars-III was unsuitable for MLC, as it strongly complexes with La at pH=2-5 and desorbs it from surface of AdPA- and APA-silica.

MLC SiO <sub>2</sub> -L	(SiO <sub>2</sub> -L <sub>2</sub> -La <sup>3+</sup> ) <sub>1</sub> Ars-I		(SiO <sub>2</sub> -L <sub>2</sub> -La <sup>3+</sup> ) <sub>2</sub> XO	
	$\lambda$ , nm	$\Delta\lambda$ , nm	$\lambda$ , nm	$\Delta\lambda$ , nm
APA	565	0	620	45
AdPA	560	-5	620	45

When the MLC preparation involves either adsorption of dye on the SiO<sub>2</sub>-L<sub>2</sub>-La<sup>3+</sup> complex, or adsorption of La<sup>3+</sup>-dye complex on SiO<sub>2</sub>-L it proceeds via coordination of dye to pre-formed grafted complex SiO<sub>2</sub>-L<sub>2</sub>-La<sup>3+</sup> without its decomposition. However, in case of pre-adsorbing dye on the surface, it blocks off the chelating groups. This results in formation of monoligand La-dye complexes and eventually prevents formation of MLC.

# ANALYSIS OF OVERLAPPING PEAK-SHAPED ANALYTICAL SIGNALS BY THE TRIANGLE HEIGHT

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The height of the peak and area of the peak are traditionally used for calibration techniques in analytical chemistry. Peak maximum can also be evaluated by the height of a triangle formed by the tangents at the inflection points and the asymptotes to the peak branches. We propose to apply the tangent method for the maximum estimation of the overlapped peaks.

The systematic errors arising from determination of the triangle height, peak height and peak area were evaluated by modeling of overlapped peaks. We use the symmetrical and the asymmetrical peak shape models. These are the Gaussian peak and the derivatives of logistic with logarithmic modification of the abscissa. The systematic errors for different values of the resolution criteria, the ratio of peaks heights and peak asymmetry were investigated.

Our calculations show that the systematic errors for the evaluation of the triangle height are lower than for the peak height and peak area. It is to be noted that tangent method allows estimating of the latent peak in the overlapped signals when peak area and peak maximum determination is impossible.

The tangent approach was valid on example of voltametric overlapping peaks of the Cd and Tl at their different concentration in a mixture. When plotting calibration curve the results correctness is validated. It was founded that systematic error is not significant for the triangle height of Tl peak. In case of Cd peak the significant systematic error arising from tailing of the ascending part of Tl peak is observed. Hence corrections are necessary. The systematic error is estimated by modelling of the overlapped analytical signals of the Tl and Cd with the empirical functions for the real range of concentration, value of resolution and asymmetry factor. The calculated systematic errors are obtained and the experimental results are corrected. It is shown, that after correction of the experimental results the essential approach of result value to the entered concentration is obtained.

To sum up, in some instances the proposed tangent method and procedure of systematic error correction allows excluding the necessity of mathematical or chemical resolution of overlapped peak-shaped analytical signals.

## ESTIMATION OF RETENTION MODELS ADEQUACY IN MICELLAR LIQUID CHROMATOGRAPHY

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The development of micellar liquid chromatography and accumulation of numerous experimental data have given rise to the theory of chromatographic retention and optimization methods of mobile phase composition. This task has had some problems because the presence of micelles in mobile phase and its modification by organic solvent provides a great variety of solutes interactions.

The known models for describing retention factor in whole variable space are based on three-phase model and containing from three to six parameters and variety combinations of two independent factors (micelle concentration, volume fraction of organic modifier). When the retention models are comparing or the accuracy of fitting establishing, the closeness of correlation coefficient to 1 and the sum of the squared residuals or the sum of absolute deviations and their relative values is taken into account. A number of problems are appear in this case:

- 1) value of correlation coefficient always tends to 1 when the degrees of freedom decrease;
- 2) the magnitudes of the remaining sums are independent from the degrees of freedom;
- 3) in the different models the different functions of retention factor ( $k$ ,  $1/k$ ,  $\log k$ ) with unknown probability distribution are used;
- 4) adequacy – goodness of fit is not the same as prediction.

Usually goodness of fit is provided by adding new parameters in the model, but it decreases the prediction capability of the retention model and influences on the optimization results of mobile phase composition.

Different tests for estimation the accuracy of fit and prediction capability of the retention models were investigated in this work. Distribution of the residuals with taking into account their statistical weights characterizes the goodness of fit. For the application of statistical weights the scedastic functions of retention factor were constructed. Was established that random errors of the retention factor  $k$  are distributed normally that permits to use the statistical criteria for prediction capability and goodness of fit correctly.

The criteria characterizing the robustness of parameters of retention model for the changing of experimental data number were proposed to estimate the prediction capability of the models.

# COMPLEXATION OF BORON WITH THE REAGENTS OF BERYLLON III GROUP

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The complexation of boron with hydroxyazo-compounds was investigated. The constitution characteristics of such compounds follows from the fact that when the boron-nitrogen bond is formed total number of electrons corresponds to their number in carbon-carbon combination and the sum of boron and nitrogen radii (0.158 nm) approximates the sum of two covalent carbon radii (0.152 nm). This gives rise to the near resemblance in properties and chemical behaviour of some boron-nitrogen compounds and corresponding organic derivatives which comprise C-C bonds.

The combination of acid (-OH) and basic (-NH<sub>2</sub>, -N(CH<sub>3</sub>)<sub>2</sub>, -N=N-) groups is also responsible for the properties of generated boron complexes. As a rule, such compounds comprise N→B coordination bond formed due to boron atom striving to compensate the lack of electrons, and to the fact that nitrogen has a lone-electron pair on the other.

The unambiguous solution of the problem regarding constitution of boron complex compounds with the reagents of azo- and azomethine substituted H-acid (H-resorcin, H-aminophenol, beryllon III, azomethine-H) is hardly possible following the complexity of ligand molecule. We used the complex of indirect data obtained from the analysis of reactions conditions, protolytic properties of reagents and the count of the number of protons escaped during the complexation and NMR method.

The mole ratio of components in complexes equals 1:1 protons. During the complexation escaped one proton, determined the conditional equilibrium constants of complexes forming.

The following linear correlations are ascertained and described: pK<sub>ion</sub> of *o*-hydroxy group of reagents benzene ring - pH<sub>max</sub> of complexation, pK<sub>ion</sub> of *o*-hydroxy group of reagents benzene ring - pK<sub>inst</sub> of forming complexes. It shows that ionization process of *o*-hydroxy group of benzene ring is determinative for the complexation of reagents with boron.

Following <sup>11</sup>B NMR-spectroscopy results the tetrahedral coordination of boron in the complex is determined. There boron is bound with O-atoms of *peri*- and *ortho*-hydroxy groups of reagents by two covalent bonds and with "naphthyl" N-atom by coordination bond forming two hexagons with the reagent. One of the boric acid OH-groups remains in the complex. Using <sup>1</sup>H, <sup>15</sup>N NMR-spec-troscopy is shown the azo-hydrazone tautomerism for the complexes with azo-reagents. In case of beryllon III and H-aminophenol the equilibrium shifts to the hydrazone form, in case of H-resorcin it is azo form that dominates in the complex.

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# PROPERTIES AND USE IN ANALYSIS OF WATER-SOLUBLE POLYMER – POLYVINYLPIRROLIDONE

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The use of polymers in various areas of chemistry allows to improve the characteristics of known methods of separation, concentration, and identification of many inorganic and organic substances. One of the areas of interesting applications is the modification of properties and reactivity of various reagents. The reason for these modifications is the formation of neutral particles of adducts, which are stabilized by electrostatic and hydrophobic interactions.

Polyvinylpyrrolidone (PVP) is water-soluble polymer, which is widely used in various industries and agriculture because of high inclination to the complex formation and capacity to stabilization of different systems.

The interaction of PVP for various molecular masses ( $8 \cdot 10^3$  -  $360 \cdot 10^3$ ) with 3 groups of organic reagents such as triphenylmethane, trioxyfluorone and azodyes is established with the methods of UV-, VIS- and IR- spectroscopy. The changes of spectroscopic properties of dyes at addition of polymer are shown in shift of maximum of absorption bands, displacement of reagent dissociation. The influence of molecular masses of polymer on properties of azodye-PVP adducts is studied.

Membrane electrodes with obtained PVP-dye adducts in polymeric matrixes are developed to measure free concentrations of polymer in solution. Membrane film electrodes are prepared using polyvinyl chloride as a matrix. We investigated properties of electrodes containing triphenylmethane - PVP and azodye - PVP adducts in water solution of polymer in presence of different electrolytes.

Investigation of PVP influence on processes of organic reagents complexing with ions of metals let us quantitatively estimate the modifying capacity of polymer. The influence of PVP and polymer in presence of electrolytes on complex formation of dyes with ions of metals is shown in increase of contrast, sensitivity and selectivity of analytical reactions.

The techniques of spectrophotometry determination of ion metals, electrochemistry determination of PVP content in medicine, bioobjects, waste water and spectrophotometry and chromatography techniques of determination of PVP molecular masses in substation and medicine are developed with the help of polymer-dye adducts.

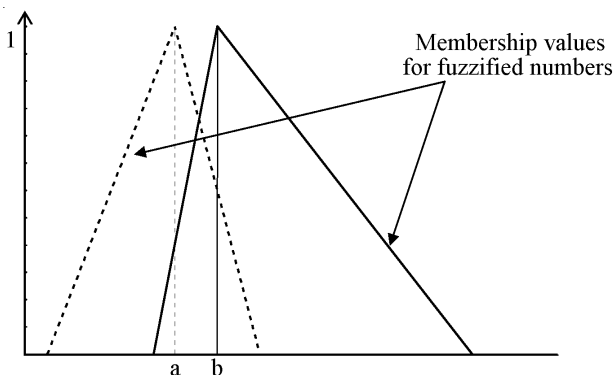
# APPLICATION OF FUZZY SETS THEORY TO SOLVING TASKS OF MULTICOMPONENT QUALITATIVE ANALYSIS

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Data collected by modern analytical instruments are usually presented by the multidimensional arrays. To perform the detection/identification of the supposed component or to verify the authenticity of a product, it is necessary to estimate the “similarity” of the analyte to the reference. The similarity is commonly estimated with the use of the distance between the multidimensional arrays corresponding to the compared objects. To exclude within the limits of the possible the influence of the random errors and the nonreproductivity of the experimental conditions and to make the comparison of samples more robust, it is possible to handle the arrays with the use of the fuzzy set theory apparatus.

In this work, the crisp numerical data for the analyte and reference samples were transformed into the fuzzy form with the application of the *LR*-representation. The procedure of fuzzyfication is illustrated roughly by the figure, where *a* and *b* are the nominal (crisp) measured values:



The distance  $D$  between the analyte and the reference was found as the normed sum of intersections of the corresponding membership values, and the similarity was estimated as  $S = 1 - D/D_{\max}$ .

The described procedure, applied to the comparison of UV spectra, was proved to be stable in respect of the variation of the conditions of measurements and other disturbing factors.



## REFERENCE SAMPLE OF LAKE BAIKAL WATER DRY RESIDUE. THE STATUS OF ITS DEVELOPMENT

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Obtaining of data concerning the chemical composition of water is critical significance for monitoring water reservoirs and forecasting the quality of drinking water from different water supply sources. A dry residue is commonly used with the methods AAS, ICP-AES, ICP-MS (analysis of liquid) widely applied for determination of water composition. So it is vital to create a standard sample of the composition of dry residue of ultra-fresh Lake Baikal water, its development launched since 1992 at the Institute of Geochemistry SB RAS.

The initial materials for a standard sample were collected from saline deposit tailings in the boiler facilities located on the southern coast of Baikal, which are operating with Baikal water without any preliminary chemical treatment. A complete cycle of selected material processing e.g. washing, magnet separation, crushing, grinding and its homogenization  $\approx 150$  kg, has been performed. The mineral composition of the initial sample and homogeneity of the material have been identified in study.

The inter-laboratory experiment on attestation of the standard sample was commenced in 1995. Analyses were performed by laboratories of Russia, FSU, England, Belgium, Netherlands, etc. By the present time, the data for 69 elements (components) were obtained by methods AES, XRF, FM, FAES, INNA, TM and LM. However, only for 14 elements (components)  $\text{SiO}_2$ ,  $\text{Fe}_2\text{O}_{3\text{tot}}$ ,  $\text{MgO}$ ,  $\text{MnO}$ ,  $\text{CaO}$ ,  $\text{Na}_2\text{O}_3$ ,  $\text{P}_2\text{O}_5$ ,  $\text{LOI}$ ,  $\text{Co}$ ,  $\text{Cr}$ ,  $\text{Cu}$ ,  $\text{Sr}$ ,  $\text{Ni}$  and  $\text{Zn}$  sufficient amount of results on quality and quantity were acquired to have them attested as the State Standard Sample. As regards 14 elements  $\text{TiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{FeO}$ ,  $\text{K}_2\text{O}$ ,  $\text{CO}_2$ ,  $\text{Ba}$ ,  $\text{Pb}$ ,  $\text{Li}$ ,  $\text{Mo}$ ,  $\text{U}$ ,  $\text{Rb}$ ,  $\text{V}$ ,  $\text{U}$ ,  $\text{Zr}$  the resultant data were referred to the rank "tentatively defined values". For the remaining 41 elements  $\text{Ag}$ ,  $\text{As}$ ,  $\text{Au}$ ,  $\text{B}$ ,  $\text{Be}$ ,  $\text{Bi}$ ,  $\text{Br}$ ,  $\text{Cd}$ ,  $\text{Ce}$ ,  $\text{Cs}$ ,  $\text{Dy}$ ,  $\text{Er}$ ,  $\text{Eu}$ ,  $\text{F}$ ,  $\text{Ga}$ ,  $\text{Ge}$ ,  $\text{Hf}$ ,  $\text{Hg}$ ,  $\text{Ho}$ ,  $\text{H}_2\text{O}^-$ ,  $\text{H}_2\text{O}^+$ ,  $\text{La}$ ,  $\text{Lu}$ ,  $\text{Nb}$ ,  $\text{Nd}$ ,  $\text{Pr}$ ,  $\text{S}_{\text{tot}}$ ,  $\text{SO}_{3\text{tot}}$ ,  $\text{Sb}$ ,  $\text{Sc}$ ,  $\text{Se}$ ,  $\text{Sm}$ ,  $\text{Sn}$ ,  $\text{Ta}$ ,  $\text{Tb}$ ,  $\text{Th}$ ,  $\text{Tl}$ ,  $\text{Tm}$ ,  $\text{W}$ ,  $\text{Y}$ ,  $\text{Yb}$  the results are considered to be merely "informational". For a complete certification of the dry residue sample there is a necessity to invite new laboratories possessing up-to-date analytical equipment to assess low concentrations of wide range of elements.

# LIOPHILIC PROPERTIES OF THE SURFACTANT-RICH PHASES OF POLYETHOXYLATED ALKYLPHENOLS OP-7 AND OP-10

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Recent publications indicate the cloud-point extraction by phases of non-ionic surfactant as an effective procedure for preconcentrating and separation of metal ions, organic pollutants and biologically active compounds. The effectiveness of the cloud-point extraction is due to its high selectivity and the possibility to obtain high coefficients of absolute preconcentrating while analyzing small volumes of the sample. Besides, the cloud-point extraction with non-ionic surfactants insures the low-cost, simple and accurate analytic procedures.

In this study we examined the influence of concentration conditions, acidity of solutions, and electrolytes inclusions on the liophilic properties of the surfactant-rich phases of polyethoxylated alkylphenols OP-7 and OP-10 at the cloud point temperature. The liophilic properties of micellar phases formed under different conditions were determined by the estimation of effective hydration values and solvation free energy of methylene and carboxyl groups at cloud-point extraction of aliphatic acids. It was demonstrated that micellar phases formed from the low concentrated aqueous solutions of the surfactant have more hydrophobic properties than the phases resulting from highly concentrated solutions. The influence of media acidity on the liophilic properties of the surfactant phases was also exposed.

Possibility of changing the properties of micellar phases by electrolyte inclusions was shown. Under this condition, in the systems with manifestation of complexes formation between the cationic compound of the electrolyte and the polyoxyethylene chain of the surfactant, increase of the hydrophilic properties of micellar phases was observed. The electrolytes that do not have affinity to the surfactant's molecule practically do not influence the liophily of the nonionic surfactant-rich phases.

Based on the calculation of the solvation free energy of methylene fragment with carboxyl at the aliphatic carboxylic acids extraction, the uniqueness of cloud-point phases was demonstrated, manifested in their ability to energetically profitably extract both hydrophilic and hydrophobic molecules of substrates. The conclusion is made about the universality of this phenomenon and its applicability to other kinds of organized media on the surfactant base.

# DETERMINATION OF TRACE AMOUNTS OF Cu(II) IONS IN AQUEOUS SOLUTION BY USING A NEW BIDENTATE SCHIFF BASE COMPOUND

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Recently, SPE cartridges and disks have been widely and successfully used in preconcentration processes [1-3]. They reduce solvent usage, disposal costs, and extraction time for sample preparation and obtain large enrichment factors.

I have carried out widespread studies on the application of a sensitive and selective preconcentration method for the determination of trace amounts of nickel by atomic absorption spectrometry. The method is based on sorption of Cu(II) ions on natural Analcime Zeolit column modified with a new Schiff base 5-((4-hexaoxyphenylazo)-N-(n-hexyl-aminophenyl)) Salicylaldimine and then eluted with 0.1M EDTA and determination by FAAS. Various parameters such as the effect of pH, flow rate, type and minimum amount of stripping and the effects of various cationic interferences on the recovery of ions were studied in the present work.

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# DFT STUDY OF 8-MERCAPTOQUINOLINE: INTRAMOLECULAR HYDROGEN BOND, SINGLE PROTON TRANSFER AND WATER-ASSISTED TAUTOMERIZATION

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A DFT study of the intramolecular hydrogen bond (IHB) in 8-mercaptoquinoline has been carried out at the B3LYP/6-311++G(d,p), B3LYP/6-31+G(2d,2p), MPW1K/6-311++G(d,p), MPW1K/6-31+G(2d,2p), BH&HLYP/6-311++G(d,p), G96LYP/6-311++G(d,p) theory levels [1]. The most successful result of the IHB enthalpy evaluation ( $DH_{\text{theor}} = -2.3$  kcal/mol,  $DH_{\text{exper}} = -2.8$  kcal/mol [2]) has been achieved on the MPW1K/6-311++G(d,p) consideration. The Onsager and PCM reaction field methods have been applied to study solvent (benzene, 1,2-dichloroethane, ethanol, nitromethane, water) effects on the IHB energies, conformational equilibria, rotational (around the S-H bond) barriers and tautomerism. The proton transfer on zwitterization is featured by a gaseous-phase barrier about 10.5 kcal/mol, and the reverse proton transfer nearly has no barrier. Concerted and synchronous double proton transfer in the prototropic tautomerization of 8-mercaptoquinoline complex with one water molecule in the gaseous phase and in solution has been studied. The NBO results indicate that the hydrogen bonds with the water molecule are stronger in the case of zwitterion than for the non-ionized 8-mercaptoquinoline molecule, especially in the aqueous medium. The water-assisted tautomerization is kinetically less and thermodynamically more favourable than the single proton transfer. The tautomerization energy and barrier height are decreased as the dielectric constant is increased both for single proton transfer and water-assisted reaction. Contrary to 8-hydroxyquinoline, the polar medium plays a decisive role for governing the relative stability of tautomers.

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2. Bankovskii Yu.A. *Chemistry of Internal Complex Compounds of 8-Mercaptoquinoline and Its Derivatives (in Russian)*. Riga: Zinatne, 1978. 488 p.

# INVESTIGATION OF POLYMETHYNE DYES OF DERIVATES INDOLIUM AND BENSTHIAZOLIUM AS A NEW HIGHLY SENSITIVE REAGENTS FOR THE SPECTROPHOTOMETRIC DETERMINATION OF NITROPHENOLS

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The nitrophenols are widely used in industry. For the determination of nitrophenols (NP) classic chemical methods such as titration, as well as potentiometry, voltametry, spectrophotometry and chromatography are used. Existing methods are poorly selective and don't allow to determinat of nitrophenols in solution without their preliminary separation.

A new, simple, rapid, and sensitive spectrophotometric method has been developed for the determination of nitrophenols wastewater samples. The method is based on the reaction of nitrophenols with polymethyne dyes of derivates indolium and benstthiazolium reagent to form a colored ion associates which are extracted by organic solvents. One-time extraction removed 97% of the trinitrophenols and 90% of the dinitrophenols (DNP). The absorbances of the colored extracts are stable for a minimum of 3 h. The molar absorptivity of the investigated ion associates of picric acid (PA) with investigated reagents ranges from  $6.6 \cdot 10^4$  to  $14.3 \cdot 10^4$  depending on the extractant. The practical interest has the determination of the impurity of PA in phenol, and the determination of nitrophenols in their mixtures. In view that from the acidic medium only PA is extracted in the form of ion associates with polymethyne dye 1,3,3-trimethyl-2-[(1*E*,3*E*,5*E*)-6-(1*H*-1-piroyl)-1,3,5-hexatrienyl]-3*H*-indolium chloride, and that from the alkali medium at pH 8.5–10.0 the DNP are also extracted, it is possible to determine PA and DNP in their mixtures. The determination of PA is not hindered even by 4000 fold of  $\text{SO}_4^{2-}$ , 500 fold of  $\text{Cl}^-$  and  $\text{Br}^-$ , 50 fold of  $\text{NO}_3^-$ , 1250 fold of  $\text{HPO}_4^{2-}$ , 1000 fold of  $\text{CH}_3\text{COO}^-$ , 6000 fold of phenol, 300 fold of DNP, 600 fold of NP. The determination of DNP is not hindered even by 400-600 fold of  $\text{SO}_4^{2-}$ ,  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{CH}_3\text{COO}^-$ , 500 fold of phenol, 100 fold of NP. The absorbance of the colored extracts obeys Beer's law in the range of 0,04-6,87 mg/L PA, 0.6-18.4 mg/L 2,4-DNP and 0.7-17.4 mg/L 2,6-DNP, respectively. The limit of detections calculated from a blank test ( $n=10$ ;  $P=0,95$ ), are 0,04 mg/L PA, 0.6 mg/L (2,4-DNP) and 0.7 mg/L (2,6-DNP), respectively.

# INVESTIGATION OF PEROXID OXIDATION PROCESSES OF BIOMACROMOLECULES LEADING TO CHEMILUMINESCENCE

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Peroxide oxidation processes in human organism are one of based phenomena that is responsible for homeostasis. For this reason development and investigation of interaction mechanism between different biomacromolecules and lipids peroxide are important for forming complete picture of functioning of human being as biological system.

The task of adequate mathematical model creation that reflects chemical processes of creation and interaction of radicals during hydrogen peroxide decomposition in the organism (*in vivo*) is very important for doctors and biologists. The difficulty of this phenomenon investigation is concerned with the complexity of the processes, their multistage, multifactor and probabilistic nature. Thus to make modeling possible one should reduce the range of accounted chemical interactions that leads to simplification of chemico-physical model of process. The mathematical description of simplified model allows prediction of system's behavior under different external actions. In this aspect the reaction of organism to cyclic influence of oxidant stress that occurs during ozone therapy, radiation influence etc. is very interesting.

In this work the development of mathematical model is done assuming simplifications of physico-chemical model of peroxide oxidation of the model system with the chemiluminescence intensity as the analytical signal. The mathematical model allows to describe basic stages of chemiluminescence process *in vitro*, namely spontaneous luminescence, slow and fast flashes due to initiating by chemical substances e.g.  $Fe^{2+}$  ions, chemiluminescent reaction at different stages of chain reactions evolution.

The verification of theoretical data obtained by simulation of peroxide oxidation kinetics of macromolecules with experimental data, obtained from chemiluminescent analysis of blood using automated complex ChLC-1. This automated complex was developed by the authors and laboratory colleagues.

## **SOME ASPECTS OF THE OF CRIMINAL LAW STUDY OF THE GELL INK HANDLE**

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Need of the study material letter enough often appears when undertaking technician-of criminal law expert operation document.

The analysis investigation and expert practical persons shows that in recently aside from the most wide-spread and known material letter such as ink for fountain-pen and soft-tip pen, pastes for ball-point pens and other, object technician-of criminal law study document all more often become the more modern material a letter, in particular gell ink handle, which are worked out, basically, foreign company (Japan, USA, Germany, Korea, China).

The problem difference and identifications given type material letter gains all greater urgency. In this connection purpose persisting work was a study of the possibility difference gell ink handle of one colour, made different company.

The sated results of the of criminal law study stalemate gell ink handle black, blue, green and red colour, made family different company countries China, Korea, Russia, Germany. The results of the study morphological sign stroke solubilize in different solvent, abilities strokes to copying were show. Besides, studied luminescent characteristic of strokes, is organized their study in reflected by IR-ray.

It is shown possibility difference some gell ink handle by method TLC, are brought the most optimum systems of the solvents, is brought importances  $R_f$ . It is attention to typical problems diagnostic and identification nature, which can be solved when undertaking the of criminal law study of the gell ink handle.

# FTIR SPECTROSCOPIC EVIDENCE FOR THE BASICITY INDUCED BY ADSORPTION

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Effect of adsorbed molecules upon the acidic and basic properties of surface sites has been studied for weak acids and bases coadsorbed on silica by means of FTIR spectroscopy at low temperatures. Addition of acidic molecules results in the increase of proton-donating properties of silanol groups, and could lead even to protonation of strong bases, such as ammonia or pyridine [1]. On the other hand, presence of bases increases the strength of acid interaction with the oxygen atom of silanol group, making adsorption of SO<sub>2</sub> or NO<sub>2</sub> irreversible at 300K. This effect should manifest itself in the increased basicity of silanol oxygen atom that can be revealed by adsorption of test molecules sensitive for electron-donating properties of surface sites.

In the present work low temperature adsorption of fluoroform and CO<sub>2</sub> were used to characterize surface basicity of silica, both pure and exposed to bases. It was found that adsorption of deuterated ammonia results in appearance of a new CH stretching vibration band of adsorbed CHF<sub>3</sub>, with the position typical of strong basic sites, absent on the surface of pure silica. Low-frequency shift of  $\nu_{\text{as}}$  mode of adsorbed CO<sub>2</sub> supports the conclusion about such basicity induced by the presence of H-bonded bases.

The same effect of mutual enhancement of adsorption was observed in the spectra of amorphous ice for ethylene and CHF<sub>3</sub> coadsorbed at 77K.

Possible role of the induced acidity and basicity in catalysis and environmental chemistry is discussed. The suggested mechanism explains the earlier reported promotive effect of some gases in the reactions catalyzed by Bronsted acid sites. Interaction between the weakly adsorbed air pollutants could lead to the enhancement of their uptake by aerosol particles as compared with separate adsorption, thus favoring air purification.

*The work was partially supported by the INTAS grant 03-51-5698.*

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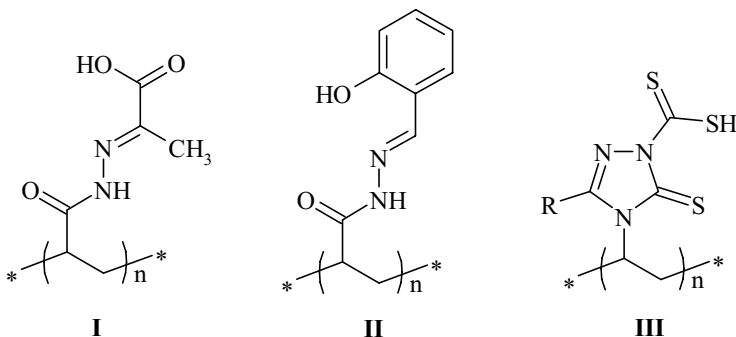
# POLYMERIZATION OF ORGANIC DERIVATIVES OF HYDRAZINE AS A WAY OF OPTIMIZATION OF THESE REAGENTS

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The organic reagents are used extensively for determinations series of elements by different methods of analysis. We carry out the systematical investigation of organic derivatives of hydrazine as a reagent for determinations ion of metals by photometric and extractive-photometric methods or analysis, as well as methods of atomic absorption spectrometry. Series procedure determinations ion of metals in technical and environmental objects have been developed.

The polymerization of organic derivatives of hydrazine allowed finding reagents with knowingly adjusted properties by reactions of complexformatiionic with ion of metals and in a new fashion to examine potential organic compounds of this class. We have found a new polymeric compounds, derivatives of hydrazones of pyruvic acid (**I**), hydrazones of salicylaldehydes (**II**) and thioderivatives 1,2,4-thiazoles (**III**). The general formula of new organic reagents are given below:



These organic reagents were found effective for selective and group concentrate ion of metals, for sorption-photometry determinations ion of metals and for separation of metals. The high selectivity by concentrations ion of metals reach regulation pH solutions and selections replaces (R-) in the reagents type **III**.

On the basis of these reagents a procedure of determinations of Al(III), Cr(III), Hg(II), Cd(II), Pb(II) in deferent objects was develop and showed prospect in a subsequent investigation of these compounds.

# THE CONSTANTS OF REPLACEMENT AND THE CONSTANT OF STABILITE MIXED BROMID-THIOUREA COMPLEXES OF GOLD (III)

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Bases on the data of curve of the potentiometric titrations of  $[\text{AuBr}_4]^-$  ions by thiourea (*Thio*), it consistently replaces bromide ions in  $[\text{AuBr}_4]^-$  ion. They are formed mixed bromide-thiourea complexes of Au(III):  $\text{AuBr}_3\text{Thio}$ ,  $\text{AuBr}_2\text{Thio}_2^+$ ,  $\text{AuBrThio}_3^{2+}$ ,  $\text{AuBrThio}_4^{3+}$ .

Process of the consecutive replacement  $\text{Br}^-$ -ions on *Thio* in  $[\text{AuBr}_4]^-$  ions can be characterized constants of replacement:  $K_3^I$ ;  $K_3^{II}$ ;  $K_3^{III}$ ;  $K_3^{IV}$ . They can be determined on the points of the curve of potentiometric titrations in which equilibrium concentration of the initial form of a complex, for example,  $[\text{AuBr}_4]^-$  ions and the subsequent  $[\text{AuBr}_3\text{Thio}]$ , will be equal. Correlation of quantity connected ligands and initial complex will be forms: 0,5; 1,5; 2,5; 3,5. Definition of these points carried spent on the function of formation in coordinates: the number mol *Thio*, which has replaced (has superseded) mol  $\text{Br}^-$  ions in one mol of from  $-\lg[\text{Thio}]_p$ . On a curve of formation 8,15; 6,50; 4,90 and 4,40 have been. They for:  $7,08 \cdot 10^{-9}$ ;  $3,16 \cdot 10^{-7}$ ;  $1,26 \cdot 10^{-5}$ ;  $3,98 \cdot 10^{-5}$ . The constants of replacement at  $[\text{Br}^-] = 0,1$  mol/l have been consider, on the following equations:

$$K_3^I = \frac{[\text{AuBr}_3\text{Thio}] \cdot [\text{Br}^-]}{[\text{AuBr}_4^-] \cdot [\text{Thio}]_{0,5}} = \frac{[\text{Br}^-]}{[\text{Thio}]_{0,5}} = \frac{0,1}{7,08 \cdot 10^{-9}} = 1,41 \cdot 10^7$$

$$\lg K_3^I = 7,15$$

Values the constants of replacement received form:  $K_3^I$ ;  $K_3^{II}$ ;  $K_3^{III}$ ;  $K_3^{IV}$  -  $1,41 \cdot 10^7$ ;  $3,16 \cdot 10^5$ ;  $7,94 \cdot 10^3$ ;  $2,51 \cdot 10^3$  accordingly.

The equations connecting constants of stability of initial and subsequent complexes with constants of replacement can be considered:

$$K_3^I = \frac{[\text{AuBr}_3\text{Thio}] \cdot [\text{Br}^-]}{[\text{AuBr}_4^-] \cdot [\text{Thio}]} = \frac{\beta[\text{AuBr}_3\text{Thio}] \cdot [\text{Au}^{3+}] \cdot [\text{Br}^-]^3 \cdot [\text{Thio}] \cdot [\text{Br}^-]}{\beta[\text{AuBr}_4^-] \cdot [\text{Au}^{3+}] \cdot [\text{Br}^-]^4 \cdot [\text{Thio}]} = \frac{\beta[\text{AuBr}_3\text{Thio}]}{\beta[\text{AuBr}_4^-]}$$

$$\text{From here: } \beta_1[\text{AuBr}_3\text{Thio}] = K_3^I \cdot \beta_1[\text{AuBr}_4^-] = 8,90 \cdot 10^{43}$$

The values of constants of stability of complexes  $\text{AuBr}_3\text{Thio}$ ,  $\text{AuBr}_2\text{Thio}_2^+$ ,  $\text{AuBrThio}_3^{2+}$ ,  $\text{AuBrThio}_4^{3+}$  have been calculate. They equal:  $8,90 \cdot 10^{43}$ ;  $2,81 \cdot 10^{49}$ ;  $2,23 \cdot 10^{53}$ ;  $5,60 \cdot 10^{56}$ .

# THE USE OF PROTONIC EQUILIBRIUM OF DIMERIC RHODAMINE 6G ON EXTRACTION OF IONIC ASSOCIATIONS

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Aggregation equilibrium of rhodamines (including rhodamine 6G) are researched by many scientists. The dimerization constants and spectral luminescent properties of dimeric forms are well known.

During the research of equilibrium of the anion surfactants associates with rhodamine 6G extraction we are found anomalous behavior of associates with the anions of higher carbonic acids. The extraction of such ionic associates appears in narrow pH range 8-10. As in this narrow pH range carbonic acids are completely dissociated, it was obvious, that the extraction is determined by the condition of the particles of rhodamine 6G.

The solubility of rhodamine 6G was measured in wide pH range. This model presumes predominating influence of dimeric forms on the solubility.

Dependence of the solubility from pH value was described in balances:



where ROH, R<sup>+</sup> - carbinolic and cationic forms of rhodamine 6G.

The data of rhodamine 6G solubility in aqueous-salt solutions at different pH value are given.

The protonization constants of dimeric form at different ionic strength were also measured. We received valuations of thermodynamic constants of protonization for dimeric forms of rhodamine 6G:



Out of the received data we made a conclusion about the predominance of mixed cation-carbinolic dimeric form of rhodamine 6G in pH range of 8-10, that creates extractable ionic associates with anions of higher carbonic acids.

There were received valuations of dimerization constants at different pH values: 3,12 (s = 0,19) for pH=7 and 3,40 (s = 0,08) for pH=9.

The dependence of the extraction of anions of higher carbonic acids from the concentration of rhodamine 6G in the solution at pH=8.6 was measured.

# THE SOLID-PHASE REAGENTS FOR THE DETERMINATION OF PHOSPHORUS AND ORGANIC REDUCTANTS

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Heteropolyacids (HPA) are the unique class of inorganic complexes. They are widely used in different areas of science: in biochemistry for the precipitation of albumens and alkaloids, in medicine as anticarcinogenic agents, in industry as catalysts. HPA are well known analytical reagents for determination of phosphorus, silica and arsenic, nitrogen-containing organic compounds, oxidants and reductants in solution etc.

The immobilization of reagents onto sorbents often results in increase of their sensitivity and, in some cases, selectivity, allows to simplify the analysis and to avoid necessity of use of toxic organic solvents. At the same time silicas are characterized by absence of swelling, thermal and chemical stability, rapid achievement of heterogeneous equilibrium.

Unloaded silica does not recover HPA from aqueous solution. The surface of silica gel modified with quarternary ammonium salts (QAS) gets anion-exchange properties. The aim of the work is the elaboration of solid-phase reagents on the base of ion associate of HPA with QAS immobilized onto silica surface for the determination of phosphorus and organic reductants. Heterocyclic (safranin and lucigenin) and aliphatic (trinonyloctadecyl ammonium iodide and tetradecyl ammonium nitrate) compounds have been examined as QAS.

Reduced molibdophosphoric HPA was found to be well recovered by silica modified with tetradecyl ammonium nitrate. It was assumed as a basis of phosphorus determination in the range of 0.5–5  $\mu\text{mole l}^{-1}$  using solid-phase spectrometry.

Two techniques for sorption-spectroscopic determination of ascorbic acid have been proposed. The first one is the recovery by silica modified with tetradecyl ammonium nitrate of “blue” form of molibdophosphoric HPA in the presence of vitamin C. And the second one is the interaction between the ascorbic acid in solution and immobilized on silica ion associate of molibdophosphoric acid with lucigenin. The detection limits of vitamin C are 0.07 and 2.6  $\text{mg l}^{-1}$  respectively. The techniques were successfully applied to the determination of ascorbic acid in fruit juices.

# THE REACTION OF THE OXIDATION OF FERROIN WITH PEROXYMONOSULPHURIC ACID AND ITS UTILIZATION IN ANALYSIS

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Peroxymonosulphuric acid (PMSA,  $\text{H}_2\text{SO}_5$ ) proved to be a promising oxidizer in reactions with chemiluminescent substances (luminol) with participation of such ions as: Mn(II), Cu(II), Ni(II), Cr(IV), V(V). The literature data show the possibility of utilization PMSA in indicating reaction with ferriin ( $[\text{Fe}(1,10\text{-phenanthrolyne})_3]^{2+}$ ) which is accelerated by Mn(II) compounds.

PMSA is easily synthesized reagent and its diluted aqueous solutions ( $10^{-5}$ - $10^{-3}$  M) are stable in time. PMSA is stronger oxidizer than both widely used in the kinetic methods of analysis  $\text{H}_2\text{O}_2$  and  $\text{K}_2\text{S}_2\text{O}_8$ .

It is established that ferriin is oxidized slowly with PMSA and its solution becomes colorless. Ions Fe(III), Co(II), Ag(I), Pd(II), Cu(II), Ni(II) show significant and different accelerating activity in the reaction of ferriin with PMSA in low acidic medium. Ions Co(II) show their accelerating activity in absence of activators. The rest metals show accelerating activity only in presence of activators (substances which form active complexes with accelerator), for instance, 1,10-phenanthrolyne. Unlike Fe(III), Ag(I), Pd(II), ions Cu(II) and Ni(II) insignificantly accelerates investigated reaction.

Probably, active forms of accelerators mentioned above are capable to create compounds with PMSA and these forms are stabilized by activators. In such compounds the weakening of -O-O- bond of PMSA takes place, that causes a gap of this bond and free radicals  $\cdot\text{OH}$  and  $\text{SO}_4\cdot^-$  are created, which easily oxidize ferriin. Created free radicals can oxidize active forms of accelerators that lead to their deactivation.

The optimal conditions for accelerating of investigated reaction by ions Fe(III) and Ag(I) are the following: pH 5,0 (acetic buffer),  $C_{\text{ferriin}}=1,6\cdot 10^{-5}$  M,  $C_{\text{PMSA}}=4\cdot 10^{-4}$  M,  $C_{\text{phen}}=2\cdot 10^{-4}$  M. Under these conditions, factors of sensitivity for kinetic determination of metals mentioned above were established as a slope's tangent of the calibration curves that is a plot of reaction velocity (change of optical density of ferriin's solution for 4 minutes) versus analyte's concentration. Factors of sensitivity for determination of Mn(II), Fe(III), Ag(I), Pd(II), Co(II) are  $5,5\cdot 10^5$ ;  $1,1\cdot 10^5$ ;  $2,5\cdot 10^5$ ;  $2,0\cdot 10^4$ ;  $8,0\cdot 10^3$ , respectively.

The results of investigation are taken as a principle of kinetic determination of trace amounts of Fe(III) and Ag(I) in different objects.

# MULTISTAGE AZO COUPLING OF PHENOLS AND AMINES. ANALYTICAL ASPECT

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An azo coupling reaction of monatomic phenols with diazotized 4-nitroaniline has been investigated. By HPLC, NMR, elemental analysis, UV and IR spectroscopy it has been shown that the azo derivatives of o-guaiacol, o- and m-cresols interact with an excess of diazonium in pH interval of 4,5-9,5 and form corresponding 4,4-di(4-nitrophenylazo)-2,5-cyclohexadien-1-ones.

An azo coupling reaction of primary aromatic and aliphatic amines with diazotized 4-nitroaniline in water-organic solutions has been investigated. It has been demonstrated that depending on the nature of an organic solvent different azo derivatives are formed in neutral medium.

In the presence of proton-donative organic solvents (alcohols), aliphatic amines do not react with diazonium, whereas aromatic amines form mainly triazenes and also para-aminoazo compounds, which subsequently interact slowly with an excess of diazo reagent via N-coupling and form disazo derivatives.

In the presence of aprotic organic solvents, both aromatic and aliphatic amines interact with 4-nitrophenyldiazonium in the same way. The first stage yields fast in corresponding triazenes. At the second stage, irrespective of initial amine nature, triazenes interact with an excess of diazo reagent and form 1,3-bis(4-nitrophenyl)-triazene. Triazenes of aliphatic amines transform fast as well. In case of aromatic amines, the second stage yield depends on the inductive constants of substituents in an azo component.

The results obtained have allowed us to develop the analytical procedures for the preconcentration and determination of microquantities of the monatomic phenols, aromatic amines and total volatile primary amines by HPLC and photometric methods.

# **ANALYTICAL METHODS**

*Keynote lectures*

# AN IMPROVEMENT IN PERFORMANCE OF ETAAS BY METAL COMPLEX MODIFIERS

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Up to now, selection of the chemical modifiers to minimize matrix interferences is a complex multifactor task for an analyst in electrothermal atomic-absorption analysis. Conceptually new approach in choosing the suitable modifier involves the development of controllable chemical surrounding of the element to be analyzed and/or the atoms of the modifying element by their binding into the stable complex with organic N,O,S-donor ligands. In addition to the well-known factors favorable for elimination of the matrix interferences with the help of organic modifiers complexing organic modifiers provide chemical separation of analyte and matrix in the condensed phase; additional thermal stabilization of analyte at the initial stages of the pyrolysis (up to 500°C); possibility to form the target pre-atomization compound (oxide, sulfide); high-temperature solid-phase reduction of the element at the early stages of analysis involving the molecules of the modifier. The parameters for prediction of efficiency of organic complex-forming modifying agents have been proposed.

The advantages of novel additives – metal complex modifiers - are exhibited on introducing the chelated metal modifier into the solution under optimum conditions. Complexation of the metal ions in the modifier gives rise to change in reducing temperature of the metal-modifier and, hence, its capability for thermostabilizing the analyte; change in the form, size and the mode of the arrangement of the reduced particles of the metal modifier on the graphite surface of the furnace; decrease in concentration of the modifier with no change in its efficiency.

In this case the efficiency of metal complex modifiers is controlled not only by their thermal stability, the nature of the metal and the ligand used, but depends considerably on the reactions in the solution, mainly on exchange reaction like  $Me_I L_m + Me_{II}^{n+} = Me_I^{n+} + Me_{II} L_m$ , which variously affect the determination of the elements with the direct (Cd, Pb, Be) and inverse (In, Bi) atomization mechanism.

The use of complexing and metal complex modifiers in ETAAS provides:

- elimination of matrix interference and decrease in detection limit by one or two orders of magnitude;
- improvement in reproducibility of analyses;
- possibility for modification of extracts;
- analysis of oxidative matrices.



# MODERN STATE AND PROGRESS TRENDS OF CHROMATOGRAPHIC METHODS OF ANALYSIS OF TOXIC ORGANIC SUBSTANCES IN UKRAINE

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The modern state and progress trends of chromatographic methods of analysis of toxic organic substances (pesticides, substances migrant from polymeric materials, polychlorinated biphenyls (PCB's), polychlorinated dibenzo-p-dioxins (PCDD's) and other) in Ukraine is examined in the lecture. Criteria to which must satisfy analytical methods for determination of toxic organic substances at the level of hygienical norms is discussed. The methods of sampling agricultural and food raw material, food products and objects of environment and preparation to the analysis are examined (liquid and solid phase extraction, supercritical fluid extraction, microwave extraction, gel-permeation chromatography and other).

The chromatographic methods presently are the basic instrument of analytical chemistry of toxic organic substances in Ukraine. On the rates of development on the first places among them capillary gas chromatography, high performance liquid chromatography and combined chromatography-mass-spectrometry. Thin layer chromatography (TLC) continues to remain the most widespread method of screening in the analysis of trace amounts of pesticides. Possibilities of the TLC use for confirmation of identification of pesticides at their determination by other chromatographic methods are discussed.

The methods, which allow in one procedure of analysis to overcome, for example, most pesticides which are used in agricultural practice in the present time, get development and introduction in practice. The contribution of the Ukrainian scientists in field of chromatographic analysis of Persistent Organic Pollutants (POPs, chlorinated hydrocarbons, PCB's) and supertoxicants, such as PCDDs, is estimated.

Presently efforts of Ukrainian scientists in field of analysis of toxic organic substances directed on harmonization of the developed methods of analysis with the requirements of international standards and on wide introduction in practice of the quality control system in chromatographic researches.

# COUPLING UV-VISIBLE-NIR SPECTROSCOPY AND MAGNETIC STUDIES TO CHARACTERIZE ISOLATED AND COOPERATING SITES IN MATERIALS CONTAINING COBALT IONS

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The magnetic, optical, electrical and catalytic properties of transition metal ions (TMI) – based materials are strongly dependent on the *isolated* or *interacting* character of the TMI sites. In the case of cobalt, the tetrahedral and octahedral high spin (HS)  $\text{Co}^{2+}$  and octahedral low spin (LS)  $\text{Co}^{3+}$  species, indeed, are generally treated as *individual non-interacting sites*; but when these entities are close enough, they form clusters or tridimensional ensembles and they should be considered as *interacting components*; this is the case of  $\text{Co}_3\text{O}_4$ , which forms a *normal spinel lattice* composed of tetrahedral  $\text{Co}^{2+}$  and octahedral  $\text{Co}^{3+}$ . The present work describes the properties *cobalt-apatite materials* prepared by cation  $\text{Ca}^{2+}/\text{Co}^{2+}$  exchange or by impregnation of apatite by  $\text{Co}^{2+}$  solutions. It shows the evolution of optical spectra (UV-Visible-NIR) and magnetic data (SQUID) when going from isolated  $\text{Co}^{2+}$  ions to  $\text{Co}_x\text{O}_y$  clusters and  $\text{Co}_3\text{O}_4$  nanocrystals. When the metal cations of the host matrix oxide may change their oxidation state (*redox active matrices*, such as e.g.  $\text{TiO}_2$ ); metal-metal charge transfers occur and interpretations are not straightforward. Hence, model compounds of non-interacting cobalt species should then be found in *redox inactive oxide matrices*, such as  $\text{Al}_2\text{O}_3$ ,  $\text{SiO}_2$ , glasses,  $\text{MgO}$ .

# DEVELOPMENT OF INFRARED DETECTION IN FLOW INJECTION ANALYSIS (FIA) AND CAPILLARY ELECTROPHORESIS (CE)

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The potential of Fabry Pérot Quantum Cascade (QC) lasers for transmission measurements of aqueous samples using FIA was assessed. For this purpose two lasers, one lasing at  $1650\text{ cm}^{-1}$ , and the other at  $1080\text{ cm}^{-1}$ , were used in a flow injection system comprising a dedicated fibre-optic flow cell with an adjustable path length. As test analytes a nucleic base (adenine) and a nucleoside (xanthosine) were used. The heteroaromatic ring structure of both compounds gave rise to peaks employing both lasers, whereas the nucleic base, lacking the C-O stretching vibrations of the carbohydrate unit, only produced peaks with the laser emitting at  $1650\text{ cm}^{-1}$ . For the determination of xanthosine at this path length the limit of detection ( $S/N=3$ ) was determined to be  $0.07\text{ g/L}$ .

When applying CE a conventional mid-IR light source was used. To overcome the problem of total IR absorption by the fused silica capillaries that are normally employed in CE separations, a micromachined IR-transparent flow cell was made consisting of two IR-transparent  $\text{CaF}_2$  plates,  $150\text{ }\mu\text{m}$  wide and  $2\text{ mm}$  long, with a path length of  $15\text{ }\mu\text{m}$ . The connections between the fused silica capillaries and the flow cell were initially enabled by a small o-ring of UV-curing epoxy adhesive on the sharply cut ends of the capillaries but later on by using separate o-rings, commercially available. An application was finally developed for the separation and detection of natural sugars in orange fruit juices. The CE separation electrolyte comprised  $50\text{ mM}$  sodium carbonate buffer adjusted to  $\text{pH } 12.3$  with  $\text{NaOH}$ . Galactose was selected as an internal standard. The limits of detection ( $3S/N$ ) for all analytes were in the low millimolar range ( $0.7\text{-}1.9\text{ mM}$ ) or, in absolute amounts, the low nanogram range ( $1.5\text{-}3.2\text{ ng}$ ). The resolution ranged between  $1.14$  to  $3.15$  and the RSD of the proposed method was  $1.8\text{ - }4.4\%$ .

## FORENSIC APPLICATION OF LEUCO AND NEAR-INFRARED DYES

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Leuco dyes typically exhibit zero or very little fluorescence when applied to surfaces. If latent blood residues are present, leuco dyes are oxidized and become fluorescent dyes. One of the topics this presentation will discuss is a new chemistry for fluorescein latent blood detection that results in excellent contrast for several hours and in a significant number of cases the contrast remains for days or weeks. This new fluorescein chemistry requires no preparation at the crime scene and has been validated for use in the field. Several examples will be presented to illustrate how time and conditions affect contrast and false positive results. In addition to the visualization of latent bloodstains, it is also suitable for observing latent fingerprints or certain bodily fluid residues. This feature that is due to the delayed self-oxidation of the leuco dye does not interfere with latent bloodstain detection, because it appears at a later time. In addition to fluorescein, rhodamines can be prepared in their leuco form and are oxidized by latent bloodstains. The longer wavelength absorption and fluorescence properties of rhodamine can be very useful on certain substrates of high interference. Additional rhodamine chemistry utilizing photochromism will also be discussed. The second major topic of this presentation is the use of near-infrared dyes in forensic detection. The application of NIR dyes is advantageous due to their high molar absorptivities and the relatively low background interference of the long wavelength spectral region. NIR dyes possess advantages that make them an excellent reporter for forensic detection of latent chemical or biological residues left at crime scenes. Background interference is minimal in this spectral region, and excellent light sources and detectors are available to detect changes in NIR fluorescence as they interact with the latent residue. The use of night vision scopes or other NIR sensitive detectors permits sensitive and convenient detection. An additional advantage of NIR dyes in forensic detection is that very small amounts need to be applied. An NIR dye has been developed for detection of pepper spray residues. In addition latent fingerprints can be visualized by using bis(carbocyanine) dyes that open up their clamshell formation upon binding to latent fingerprints.

# ANALYSIS OF HIGH PURITY MATERIALS BY AES AND MS METHODS WITH PRE-CONCENTRATION OF MICRO-ELEMENTS

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At present time the use of oxide single crystals such as bismuth germanate ( $\text{Bi}_4\text{Ge}_3\text{O}_{12}$ ) and paratellurite ( $\text{TeO}_2$ ) as detectors in opto-electronics stimulate production of high purity Bi, Te, Ge and their oxides:  $\text{Bi}_2\text{O}_3$ ,  $\text{GeO}_2$ ,  $\text{TeO}_2$ . This requires development of analytical techniques for purity control of these materials. For survey trace analysis atomic emission spectrometry (AES) and mass spectrometry (MS) with inductively coupled plasma (ICP) is widely used. However, the detection limits of impurities achievable by these methods for the analysis of high purity solids are limited by necessity of sample dissolution in pure acids and dilution up to  $5 \cdot 10^3$  times for ICP-MS and 50-100 for ICP-AES. One of the most effective ways to improve the analytical performances of these methods is pre-concentration of micro-elements.

We have developed pre-concentration procedures based on distillation of matrix elements after its chemical transformation in a volatile form. Residues of matrix oxides were used as the collectors for micro-elements. Main advantages of distillation are: realization of process in the close volume, which let us to exclude a contamination; minimal quantity of chemicals used for sample pretreatment procedure; conservation up to 40 microelements in the concentrate; achievement the factor of concentration of about  $10^3$ ; easy solubility of the concentrates in nitric and hydrochloric acids.

The use of pre-concentration in combination with ICP-AES and ICP-MS let us to diminish a degree of sample dilution up to two orders of magnitude and essentially reduce the limits of detection of about 30 elements. In addition, low content of matrix element in the solutions prepared for ICP-analysis reduces the matrix influence and minifies the spectral interferences. Main limitation, especially for determination of widespread elements (Si, Ca, Fe, etc.) at the ppb and ppt levels is the purity of chemicals used for concentrate dissolution and dilution.

In the report analytical figures of merit of ICP-MS and -AES techniques in combination with pre-concentration of trace elements for survey analysis of high purity metals and their oxides used as the precursors for oxide monocrystals production will be presented and compared to that of direct ICP-MS and -AES techniques.

# SORPTION-CATALYTIC DETERMINATION OF MICRO-AMOUNT AND CHEMICAL STATE OF PALLADIUM ON SURFACE OF CARBON ADSORBENT

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The sorption evaluation of Pd(II) micro-amounts by active coals, ACs, from solutions with 50-500-fold excess of accompanying metals compounds was shown [1]. From the other hand catalytic action of Pd(II) in reaction of Mn(III) reduction by Cl<sup>-</sup> is used for Pd(II) micro-amounts determination by catalytic method [2]. The co-operation of sorption and catalytic determination of Pd(II) in one process was investigated.

Pd(II) was shown to be separated from Ni(II), Cr(III) and Co(III) by ACs completely, and only up to 3 % of Cu(II) and Fe(II) evaluate from solution together with Pd(II), this way practically pure palladium may be obtained by it's sorption from multi-component solutions. The selectivity of Pd(II) evaluation by ACs was explained by sorption mechanism, the main part of which consists in direct interaction of Pd(II) with  $\pi$ -conjugate electron system of carbon matrix and electrons transfer from carbon to Pd(II), last one can be reduced right up to Pd<sup>0</sup> in dependence on reducing capability of AC.

It was found that sorbed palladium might catalyse reaction of Mn(III) reduction by Cl<sup>-</sup> not only after it's removing from coal, but AC with palladium, Pd/AC, has also his own catalytic effect. On the base of dependence between characteristics of AC, chemical state of palladium on AC surface and catalytic action of Pd/AC in indicator reaction it might establish, that catalytic action concerns only to non-reduced or partly reduced palladium ions connected with chloride ions on coal surface. The presence or absence of catalytic action of Pd/AC in above-mentioned reaction may be proposed for determination of chemical state of palladium on AC surface. Catalytic effect was also used for palladium micro-amounts determination by sorption-catalytic method.

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# MODERN ATOMIC ABSORPTION SPECTROMETRY: ACHIEVEMENTS AND FUTURE PROSPECTS

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Atomic absorption spectrometry (AAS) started its career 50 years ago. During this time fundamentals of the method have been mostly discovered thus transforming AAS to very powerful but relatively simple method of analytical chemistry. Nowadays it is one of the most widespread methods in analytical labs.

The most important direction of its further development seems to be multi-element AAS. German-Brazilian team has received very interesting data using a prototype of serial multi-element atomic absorption spectrometer (e.g., [1]). In spite of advantages of diode laser AAS (the most attractive one is up to 3 orders of magnitude decrease in detection limits available) [2], it is still a field of interest mostly for physics rather than for analytical chemists. Spreading of hydride generation AAS to the determination of the elements that does not form volatile hydrides (such as Ag, Ir, Pd, Co, Cd, etc.) is of interest from viewpoint of development of extremely sensitive methods of analysis and of general chemistry [3]. Significant attention is paid to electrochemical rather than chemical generation of volatile hydrides that is prospective from viewpoint of reduction of blank values and, consequently, improvement in detection limits. As for flame AAS and mercury cold vapor technique, their development is generally completed. Although fundamentals of electrothermal AAS are mostly formulated as well, further works in chemical modifiers [4] and development of the methods of direct analysis of solids [5] are still actually. Very important point of activity of specialists in AAS is wider application of their achievements in the practice of service laboratories, via introduction of more AAS methods to international and national standards.

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# ELECTROANALYSIS WITH MESOSTRUCTURED ORGANO-SILICAS

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The elaboration of hybrid materials by bridging organic and inorganic chemistry at a molecular level is now wide field of investigation [1]. Among them, silica-based organic-inorganic hybrid materials become increasingly attractive for analytical and electroanalytical purposes by exploiting their advanced properties in aqueous suspensions or at an electrode/solution interface [2]. Such hybrids can be obtained either by post-synthesis grafting of porous silica samples or by sol-gel processing of a mixture of tetraalkoxysilanes and organo-trialkoxysilanes. Of particular interest are the nanocomposite materials displaying a regular mesoporous structure that can be functionalized with appropriate organic groups depending on the target application, which have been found very promising electrode modifiers [3]. The aim of this lecture is to highlight and discuss some recent achievements performed with using such new materials in analytical chemistry and electroanalysis.

After a brief overview of the actual developments of silica-based hybrid materials in (electro)analytical chemistry, special attention will be given to the particular example of  $\text{Hg}^{\text{II}}$  preconcentration on mesoporous silica samples functionalized with either aminopropyl or mercaptopropyl groups. Depending on pH and chloride concentration, the main forms of  $\text{Hg}^{\text{II}}$  in the environment ( $\text{HgCl}_4^{2-}$ ,  $\text{HgCl}_3^-$ ,  $\text{HgCl}_2$  and  $\text{Hg}(\text{OH})_2$ ) can be distinguished through their selective binding to amine, ammonium or thiol groups immobilized on the silica substrates. Upon incorporation of these materials in carbon paste electrodes, this selectivity effect can be exploited for the voltammetric detection of  $\text{Hg}^{\text{II}}$  species, in the anodic stripping mode subsequent to open-circuit accumulation. The influence of several experimental parameters was studied to optimize the uptake processes. In particular, the definite advantage of meso-structured organically-modified silicas (ensuring good accessibility to the binding sites and inducing fast transport of the analyte because of unrestricted diffusion) has been pointed out.

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*Oral presentations*

# SONOLUMINESCENCE SPECTROSCOPY. POSSIBILITIES AND PROSPECTS OF ITS USE IN ANALYTICAL CHEMISTRY

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There is luminescence named sonoluminescence during effecting of ultrasonic on solutions. Complication and transient of processes ( $<10^{-8}$  s) occurring in case of sonoluminescence, does not allow to create its theoretical model yet. However, there is enough information for the wide use of this phenomenon in analytical chemistry.

We carried out systematic researches of sonoluminescence as a source of analytical signal – emission spectrums of elements. It is shown that the sonoluminescence spectrums can be registered for elements which in the metallic state have boiling temperatures  $\leq 2700$  °C and energy of ionization  $\leq 7,65$  eV. The effect of increasing of sonoluminescence intensity and sensitiveness of determination of elements in sonoluminescence spectroscopy (in 5-10 times) was discovered at the use of simultaneous action of ultrasonic of high and low frequencies in comparison with using of ultrasonic low frequencies only. Theoretical bases of new spectroscopy method of analysis in sonoluminescence *spectroscopy* are developed. The method allows to conduct the direct analysis of solutions of elements' salts and natural brines in the range of concentrations from 5-10 g·l<sup>-1</sup> to saturated, with the presence in solution of salts to 50 g·l<sup>-1</sup>, presence considerable quantities of organic matters in natural brines and does not prevent to determine metals by this method also. The comparative analysis of determination methods of high concentrations of metals in water solutions showed, that the least error at the determination of high concentrations is provided by a gravimetric method, but it is tractable in expressiveness in the sonoluminescence method. The titrimetric method does not require the special apparatus. Nevertheless, it tracts in sonoluminescence and selective method in expressiveness. Thus, method of analysis of sonoluminescence spectroscopy is new spectral method for determination of high concentrations of elements. Now it uses in salt industry of Ukraine for the express analysis of brines on maintenance of basic matter (NaCl) and macroadmixture of metals (Ca, Mg). There is information about its use in medicine and galurgy industry in China and in France. Further development of method is linked, in our opinion, with the analysis of fusions of metals on maintenances of basic matter; it will be profitable for nuclear energy at determination of maintenance of basic matter in fusions of the alkaline metals used as liquid thermal vehicle.

# EXTRACTION OF ELEMENTS WITH POLYMETHINE DYES FROM WATER-ORGANICS MEDIUMS. CHEMICAL ANALYTICAL ASPECTS

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Realization of many photometric reactions in water-organics mediums often leads to substantial increasing their sensitivity and selectivity. However, the description of extraction of ion-associates (IA) of basic dyes from water-organic mediums practically is absent in scientific literature.

We have been investigated extraction of ion-associates, formed by polymethine dyes derivatives 1,3,3-trimethyl-3H-indolium with metal-ions (Zn, Co, Ag, Pd, Pt, Cu, Re, W). An introduction of the water-soluble donor-active organic solution (DAS) substantially increases the extraction of IA and suppresses simultaneously that of the ordinary dye salts. The concentration of DAS necessary for reacting the maximum extraction of IA reduced in the row of solvents: formamide > N-methylformamide > N,N-dimethylformamide > N,N-dimethylacetamide > N,N-diethylacetamide > hexamethylphosphortriamide. The correlation between the extraction level and the solvent donor capacity has been established by controlling the composition of water-organic medium, libev the selective extraction of metal-ions can be acheibed. It is important to pay attention to the fact that with increasing of concentration of thiocyanate-ions extraction of IA of elements is increasing and maximus extraction moved to the sphere of the most concentration of DAS. It can be explained by forming mixed complexes such as  $[Me(SCN)_x(DAS)_y]^{n-}$ . The influence of various factors on the formation of complexes and IA extraction has been studied and the optimal conditions have been found. The composition and the principal chemical-analytical characteristics of IA have been determined. The molar absorbtivity for various system is high as  $(3-24) \cdot 10^4$ . The new effective methods Cu, Ag, Pd, Pt, Re, W, Zn, Co of determination in alloys and semiconductors, in biological objects and objects in the environment have been worked out.

*Table.* Extraction-spectrophotometric methods of metals determination

Reagent	Analytical form of metals	Composition of water-organics phase	Organic phase	$\lambda_{max}$ (nm)	$\epsilon \cdot 10^{-4}$
PBR	$[Cu(SCN)_2]^-$	pH 5; 0,0005 M NaSCN	toluene	555	4,7
SBR	$[Zn(SCN)_4]^{2-}$	pH 5; 18 % DMFA	toluene	571	18,2
DIT	$[Ag(SCN)_2]^-$	pH 3; 0,0015 M NaSCN; 30% DMSO	toluene	659	15,8
DIC	$[HWO_4]^-$	pH 4; 16 % DMFA	benzene	560	2,8
BIC	$[Pd(SCN)_2]^-$	pH 0; 28% acetone;	toluene	553	13,3
NDIC	$[Co(SCN)_4]^{2-}$	pH 5; 10 % DMFA	toluene	552	24,4

# **X-RAY FLUORESCENCE INSTRUMENTS PRODUCED BY BOUREVESTNIC, INC.**

## **THE DESTINCTIVE FEATURES**

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At present the Bourestnik, Inc. manufactures the following X-ray spectrometers and analyzers:

- Benchtop short-wave automatic sequential spectrometer SPARK-1-2M with range of elements to be determined Sc ( $Z=21$ ) to U ( $Z=92$ ) and high energy resolution (to 7 eV on  $TiK_{\alpha}$ -line). The spectrometer is provided with developed software including qualitative-, quantitative-, standard-less semi-quantitative analysis programs, programs for spectral lines shift measurement, for material identification, and number of certified analysis procedures. The device is usually used for analysis of steels, alloys and ecology objects (soils, sediments and waters).
- Benchtop X-ray energy dispersive analyzer BRA-17-02 based on a gas-filled electroluminescent detector with an x-ray tube excitation and range of the elements to be determined from K ( $Z=19$ ) to U ( $Z=92$ ); an electroluminescent detector ensures two times better resolution compared with traditional proportional counters and possesses 20 times greater x-ray efficiency compared with semiconductor detectors. The device is used usually for grits concentration determination when analysing of aviation oils (certified analysis procedures are available) and in mining industry.
- Portable x-ray energy dispersive sulphur in oil analyser ASE-1 with measurement range 0.015 – 5% and a detection limit near 0.001%.

SPARK-1-2M, BRA-17-02 and ASE-1 have been certified as measuring devices and entered in the State Register of measuring devices.

Development of a benchtop energy dispersive analyser BRA-18 is carrying out which is based on Si-drift detector and x-ray tube with side window; range of the elements to be determined is extended from Mg to U. The distinctive feature of the device is that a specimen to be analysed is placed in the open air.

# NUCLEAR-PHYSICS METHODS IN CONTROLLING CONDITIONS AND DYNAMICS OF ENVIRONMENTAL POLLUTION

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Controlling environmental pollution has the purpose to investigate the content of elements and micro-elements in global and anthropogenic fall-outs of various aerosols on the underlying surface, the latter being different water reservoirs and ponds, agricultural grounds and timber industry lands, village territories, cities, etc.

The global geochemical background and enormous industrial environmental pollution have increased, thus, there are all the bases to speak about the beginning of biogeochemical formation development which has a direct influence on the ecological system condition in general as well as on the population health.

The existing variety of means and methods of micro-element analysis is used worldwide for the determination of element contents in atmospheric aerosols when they are collected at aspiration filters, sediment and natural surfaces and biota objects where toxic substances migration can be observed.

Instrumental neutron activation analysis (INAA) is considered the most informative and highly sensitive. Being applied, it allows detecting and determination of 30-40 elements with the sensitivity of  $10^{-8}$ - $10^{-10}$  g/g in one sample. The evident advantage of INAA is the ability to analyze samples of different nature (filters, soils, plants, biological tests, etc.) without any complex schemes of preliminary preparation.

Nuclear-physical methods are the basic ones in controlling environmental pollution which results from nuclear-power complexes and power plants work. Oil and gas production leads to the extraction of radio nuclides of natural origin in considerable amounts, which later spread from oil-slimes and water wastes in the neighborhoods of oil and gas producing enterprises. Similarly, toxic and radioactive elements can pollute environment in case of mineral deposits extraction.

The results of the work GNU "NPI at TPU" in foregoing directions it is enough packed are presented in proposed report.

# A NEW WAY TO CORRECT A NON-SELECTIVE LIGHT ABSORBANCE IN ATOMIC ABSORPTION SPECTROMETRY, BASING ON PRELIMINARY REGISTRATION OF MOLECULAR SPECTRA

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Atomic absorption analysis results are often burdened with systematic errors caused by a non-selective light absorption by molecular forms in gas phase. High molecular absorption values are typical for electrothermal atomizer. In previous works we have demonstrated the possibility of using spectrometer Saturn with electrothermal atomizer Grafit-2 to register the absorption spectra of gas phase of graphite furnace in spectral range 220...600 nm. The obtained in this way spectrum allow one to find the maximum molecular absorption regions and to estimate the systematic error probability.

In the present work we propose a new way of quantitative accounting for the non-selective absorption value. The systems considered here contain the sole molecular form: either iodide or chloride of potassium or sodium.

The absorption bands obtained for these systems are assigned using modern quantum-chemical methods. We demonstrate a good agreement of absorption peak positions obtained by experimental and theoretical methods. These allow to confirm the presence of the sole molecular form in gas phase.

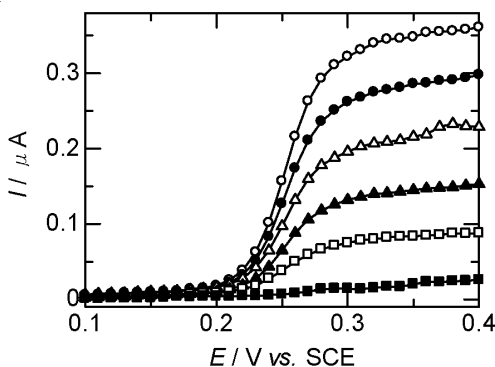
The molecular absorption spectra, registered at a lower temperature (e.g. 700 °C for iodide or chloride of potassium or sodium), enable one to find the absorbance ratio for any pair of wavelengths in the measurement range. These ratios can be used as a correction factor for analytical signal in atomic absorption analysis (at atomization temperatures above 2000 °C). The proposed method was tested by determination of beforehand known silicon and iron content in potassium chloride and sodium iodide respectively. The results are subject to random error only.

# VOLTAMMETRY WITH AN ELECTRODE SURFACE PERIODICALLY RENEWED BY LASER ABLATION

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The activation of solid electrodes has been an important subject in electroanalytical chemistry. The electrodes are frequently contaminated by electrolyzed products, and thereby they cannot stand long-term use as an electrochemical detector. In order to overcome the electrode contamination and moreover activate the electrode, we have developed a technique, in which the electrode surface is renewed by an ablation action of a strong laser pulse. The laser pulse can ablate a top surface of the electrode, and consequently contaminants are removed from the surface. Since the cleaning by laser ablation is available for an electrode remaining in a solution, it is very useful for analyses requiring long-term use of the electrode. In this work, a laser pulse from a Q-switched Nd:YAG laser was used for cleaning a Pt electrode of ( $\phi$  1 mm). A power of the pulse was adjusted to about 100 mJ/pulse and the pulse width was nominally 5 ns. A voltammogram was recorded, while firing the pulse every 2 seconds. Every current was sampled at 0.75 s after firing the pulse in order to avoid the charging current, and was plotted against the potential. As an example, voltammograms of ascorbic acid (AA) are shown in Fig. 1. All the voltammograms show an S-shaped curve, which suggests that the ablation action can renew not only the electrode surface, but also the diffusion layer growing during the electrolysis. The limiting currents were directly proportional to the concentration down to 0.01 mM, and the slopes obtained from the log-plot analysis were  $31.7 \pm 2.2$  mV in the concentration range from 0.10 to 5.00 mM. These facts indicate that the electro-oxidation of AA is a reversible two-electron process. It has been known that electrolyzed products of AA contaminate the electrode. Taking



this fact into account, the proposed voltammetry is a sensitive and practical method for the determination of AA.

Fig. 1. Voltammograms of AA in 0.1 M  $\text{H}_2\text{SO}_4$ . The top and bottom curves refer to voltammograms for a 0.5 mM AA solution and a blank solution, respectively. One increment in the concentration is 0.1 mM.

## THE ELEMENT'S FORMS OF PRESENCE DETERMINATION BY X-RAY EMISSION SPECTROSCOPY

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The potentialities of the new technique of the elements forms presence determination in condensed matter by emissive X-ray spectra are treated. The technique is based on the use of a new analytical signal – relative integral intensity of the last emission line (RII LEL) of given series of characteristic X-ray spectrum. RII LEL is the ratio of the integral intensity of LEL (line caused by electron transition between the external level and one of inner level) to the integral intensity one of the line of same series caused by inner electron transition (normalization line). The integral intensity of LEL is caused both the concentration of the determined element and its form of presence (valency, oxidation number etc.). On the contrary, the integral intensity of normalization line is caused by concentration of the element determined only. The matrix effects are the same for both lines. Therefore the RII LEL is a function of one parameter of the form of element's presence: the length of chemical bond, the radius of the first polyhedron, the coordination number etc. It is possible to determine this function with the help of RII LEL's measurements of an assembly of reference samples.

The employment of the technique suggested does not require ultra high resolution of spectrometer (in contrast to technique based on the chemical shift of X-ray line detection) and can be realized on the conventional analytical wavelength-dispersive devices.

The results of determination of the form of presence of As, Se, Nb, Mo, Ni, Cu in different solid compounds are given. The application of RII LEL for the study of structural transformations in chalcogenid glasses is shown. The X-ray spectral determination of crystal water, the possibility of studying of dissolution-crystallization processes and kinetics of some chemical reactions are discussed.

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## A NEW RETENTION MODEL IN MICELLAR LIQUID CHROMATOGRAPHY

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Mass-action model of surfactant micelle formation was used for development of the conceptual retention model in micellar liquid chromatography. The retention model is based upon the analysis of changing of the sorbat microenvironment in going from mobile phase (micellar surfactant solution, containing organic solvent-modifier) to stationary phase (the surfactant covered surface of the alkyl bonded silica gel) according to equation:

$$\{AR_n S_m\} = \{AR_p S_q\}_s + xR + yS,$$

where A – sorbat, S – surfactant, R – solvent-modifier.

The main equation of the model describes the dependence of retention factor,  $k$ , from surfactant concentration,  $c_s$  and modifier concentration,  $c_R$ :

$$\lg k = \text{const} - x \lg c_R + y \beta \lg c_s + x \lg \left( 1 + \frac{P v_s (c_s - \text{CMC})}{1 - v_s (c_s - \text{CMC})} \right) + y \beta \lg (1 - \beta),$$

and include the characteristics of the hybrid micelle formation (the critical micelle concentration,  $\text{cmc}$ ; the degree of counter ion binding,  $\beta$ ; the distribution coefficient of modifier between water and micellar pseudo-phase,  $P$ ) and also three fitting parameters: intercept and coefficients  $x$  and  $y$ , characterizing the differences in the sorbat microenvironment in the mobile and on the stationary phases.

The model was tested by the micellar liquid chromatography separation of the five rubomicin derivatives and four ethers of hydroxybenzoic acid. Micellar mobile phases were made with the sodium dodecylsulfate and 1-pentanol or isopentanol as modifier. In all cases the negative signs of the coefficients  $x$  and  $y$  indicate that at transition of the sorbat from the mobile on the stationary phase the number of surfactant monomers as well as the number of modifier molecules increases in its microenvironment.

A new type of functional dependence follows from the equation of the conceptual retention model:

$$\lg k = \text{const} + a \lg c_R + b \lg c_s,$$

where  $a$  and  $b$  are fitting coefficients.

The last equation was ensured the better description of the experimental data in whole variable space than the other known three-parameter equations.

# THE WAYS FOR INCREASING OF THE SENSIBILITY OF LANTHANIDES DETERMINATION BY LUMINESCENT METHOD

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It is well known, that in aqueous solutions the water molecules, which are in the inner coordination sphere of the complex, quench the lanthanide (Ln) luminescence in result of vibrations of the OH-groups (OH-oscillators). The use of D<sub>2</sub>O instead of H<sub>2</sub>O, the freezing of solution as well as the introduction of a second ligand to obtain a mixed-ligand complex leads to either partial or complete elimination of the H<sub>2</sub>O influence. The same effect may be achieved by water molecules replacement from the inner and outer coordination sphere at the addition of organic solvents or when the molecule of Ln complex is introduced into the micelle of the surfactant.

For elimination of intramolecular energy losses, we have synthesized ligands with high hydrophobisity - perfluoro-β-diketones R<sub>1</sub>-CO-CH<sub>2</sub>-CO-R<sub>2</sub> (R<sub>1</sub> = C<sub>6</sub>F<sub>13</sub> or C<sub>8</sub>F<sub>17</sub>; R<sub>2</sub> = phenyl or α-thienyl), that without second ligand eliminate completely water molecules from the inner coordination sphere. These ligands we have used in analysis at determination of Sm, Eu, Nd, Yb microamounts in high-purity lanthanide and yttrium oxides.

For elimination of intra- as well as intermolecular energy losses we have synthesized co-polymers – styrene or methylmethacrylate with β-diketones and used them in analysis for the same purpose. In this case the increase of sensitivity of Ln determination as well as selectivity was observed.

The solid matrix is used most effectively. Authors elaborated two ways of the polymer matrix application:

- 1) sorption Ln complex non-modified polymer – polymethylmethacrylate (PMMA) in organic solvent;
- 2) sorption by PMMA, modified by ligand.

Application of a modified sorbent is preferable, since in this case the intensity luminescence (*I*) of Ln, as well as the rate of its determination is higher about 6-7 times. The comparison of luminescence intensity of Ln – ligand complex solution before the sorption with results of *I* after sorption by both non-modified and modified PMMA showed that *I* increased in 30 and about 200 times, respectively.

## ADVANTAGES AND SHORTCOMINGS OF pH-STATIC TITRATION METHOD

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The pH-static technique, suggested lately for simple complexometric titrations, has been extended [1] on different areas of titrimetric analyses, where different complexo(no)metric, redox and/or precipitation reactions are accompanied by generation (or consumption) of protons. The titrimetric procedure is based on alternate and successive additions of primary (PT) and auxiliary (AT) titrants into D+AD solution (D) containing an analyte (or analytes), a buffer, and a solution adjusting (AD) pH of the solution to a pre-assumed  $\text{pH}_0$  value. Every time, PT added in portions shifts pH from  $\text{pH}_0$  to  $\text{pH}_0 - \Delta\text{pH}_j$  (in the case of proton generation) and then pH is returned to the initial  $\text{pH}_0$  after addition of AT according to titrimetric mode (PT is added in portions). Total volumes ( $V_{\text{Pj}}$ ,  $V_{\text{Aj}}$ ) of PT and AT added are plotted in ( $V_{\text{P}}$ ,  $V_{\text{A}}$ ) co-ordinates. In the desired case, the resulting curve obtained for single analyte consists of two rectilinear parts. The point of intersection of these parts gives the end volume ( $V_{\text{e}}$ ) that should be sufficiently close to the equivalence volume ( $V_{\text{eq}}$ ).

To find the best *a priori* conditions of analysis, the equilibrium analysis, based on material balances and all physicochemical knowledge involved with an electrolytic system, has been done with use of iterative computer programs. The effects resulting from (a) a buffer chosen, (b) its concentration and (c) complexing properties, (d)  $\text{pH}_0$  value established were considered in simulated and experimental titrations. Further effects tested were: tolerances in (e) volumes of titrants added in aliquots, (f) pre-assumed pH values on precision and accuracy of concentration measured from intersection of two segments obtained in such titrations.

It was indicated that the original method can be extended on systems where two or three analytes can be determined from a single titration curve. The shifts  $\Delta\text{pH}_j$  affected by j-th PT addition should be sufficiently high; it depends on  $\text{pH}_0$  value, a kind and concentration of the buffer chosen and its properties. The criterion of choice of the related conditions of analysis has been proposed. A computer program (written in MATLAB and DELPHI languages), that enables the pH-static titration to be done automatically, has also been prepared.

[1] T. Michałowski, M. Toporek, M. Rymanowski, *Talanta*, **65** (2005) 1241

# **ANALYSIS OF THE SIGNAL FORMATION IN DOUBLE STAGE ELECTRO-THERMAL ATOMIZER FOR ATOMIC ABSORPTION ANALYSIS**

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The process of signal formation in the double stage electro thermal atomizers for atomic absorption analysis significantly differs from the signal formation in the classic electro thermal atomizer. As this process determines efficiency of the application of the method it is necessary to have the understanding of the details of that process and the effect of the design parameters of the atomizer on the efficiency of analysis.

In classic electro-thermal atomizer the process of formation of the analytical signal is combination of two processes: the analyte supply (in the process of evaporation) and the analyte removal (by diffusion of the analyte from the atomizer). In double stage atomizer a very significant role plays the process of conductive transfer of the analyte from the evaporator to the atomizer itself and this makes the main and a principle difference of these devices. Additionally to the named difference arises the problem with optimization of the double stage atomizer as the amount of design parameters and possible combination of operation parameters significantly increases.

The full 3D analysis of the flow in this type of device is rather complicated. That is why in parallel with the 3D simulation that gives description of some important details, that result from 3D character of the flow, was developed 1D model that provided a very efficient and rather accurate description of the analyzed process with minimum expenses on the analysis.

On the base of the developed mathematical models was developed regression model of the atomizer efficiency via main design parameters such as linear dimensions and operation temperatures.

Comparison with experimental data confirmed efficiency of presented models, which enabled proper explanation of some uninterpreted experiment facts.

# ON-LINE MONITORING OF HYDRODYNAMIC FLOW PROFILES IN MICROFLUIDIC CHANNELS BASED UPON MICROELECTROCHEMISTRY

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Miniaturisation of various devices and systems has become a popular trend in many areas of modern nanotechnology such as microelectronics, optics, etc. In particular, this is very important in creating chemical or electrochemical sensors where the amount of sample required for the analysis is a critical parameter and must be minimized. In this work we will focus on a micrometric channel flow system. We will call such miniaturised flow cells 'microfluidic systems', i.e. cells with one or more dimensions being of the order of a few microns. Such microfluidic channels have kinetic and analytical properties which can be finely tuned as a function of the hydrodynamic flow. However, presently, there is no simple and *direct* method to monitor the corresponding flows *in situ*.

We propose an *indirect* method for reconstructing any hydrodynamic flow profile occurring locally within a rectangular microfluidic channel based on experimental currents measured at single or double microband electrodes embedded in one channel wall. A perfectly adequate quasi-conformal mapping of spatial coordinates and an exponentially expanding time grid in conjunction with the solution of the corresponding variational problem approached by the Ritz method are used for the numerical reconstruction of flow profiles. The concept of the method is presented and developed theoretically and its validity is tested based on the use of pseudo-experimental currents emulated by simulation of the diffusion-convection problem in a channel flow cell, to which a random Gaussian current noise is added. The flow profiles reconstructed through our method compare successfully to those introduced a priori into the simulations even when these include significant distortions vis-a-vis classical Poiseuille or electroosmotic flows.

# FEATURES OF ECOLOGICAL-ANALYTICAL MONITORING OF SURFACE WATER OBJECTS

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For solution of one of the main eco-monitoring task – identification of technogenic impacts on ecological state of water body under natural changes – it is necessary to improve ecological-analytical monitoring methodology. It is considered as chemical analysis of state and ecosystem parts: molecules, cells, organisms, bio-geocinose, landscapes and bio-sphere.

Main tasks on theoretical grounds and development of methodology for chemical analyses of ecological state of surface water bodies under regulation of heavy metal ions discharges in the bodies. It is necessary to:

- show analytical problems of chemical analysis of ecological state of water bodies and ways of their solution, ground methodology on laboratory and on-site researches;
- develop and improve voltammetric methods for detection of ion (free) forms of heavy metals in water, show their potential in evaluation of ecological state of water;
- develop application of biological methods in analytical chemistry for study of response of test-system “natural water – phytoplankton – higher water vegetation” on impact from heavy metal ions with application of natural analytical systems and chemical ways of control of biota response reactions under conditions of on-site modeling;
- show possibilities of voltammetry in researches of main factors and processes, caused heavy metal ions detoxication and their distribution among water ecosystems components;
- show possibilities of atomic-absorption spectroscopy in detection of background heavy metal ions in water, bottom sediments, aquatic life and waste water sediments and ground chemical-analytical criteria for ecological interpretation of obtained chemical analyses results.

Specific ways of the above-mentioned tasks are shown on the example of regulation of waste water discharges from galvanic units in water object.

# SPECTROPHOTOMETRIC DETERMINATION OF PHOSPHATE AND ARSENATE IONS BY MEANS OF IONIC ASSOCIATES OF CYANINE DYES WITH POLYOXOMETALATES

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A reaction of mixed molybdenum polyoxometalates (POMs) with cyanine dye has been used for highly selective and sensitive spectrophotometric determination of phosphorus(V) and arsenic(V). Color of the solution is considerably changed by reaction of Keggin POMs with styrene cyanine dyes. Derivatives of 1,3,3-threemethyl-3*H*-indol – astrazone violet (AV 3R), astrazone rose, astrazone yellow, astrazone red were investigated.

In accordance with these data, ionic associates (IA) can be precipitated at phosphate concentrations more than  $10^{-6}$  M. Below this concentration stable supersaturated solutions of IA are formed. Colour of IA appears immediately after mixing of the solutions and remains constant during several hours. There is a new band in spectrum at 570-590 nm. Appearance of color is caused by formation of stable solid phase in the solution.

Sensitivity of the proposed method correlates with molar absorptivity of the cyanine dye. Mixed POMs  $\text{PMeMo}_{11}\text{O}_{40}^{5-}$  ( $\text{Me}=\text{Ti}^{4+}, \text{Sb}^{3+}, \text{Bi}^{3+}$ ) were chosen as analytical form because of its higher stability as compared with 12-molybdophosphate. Only  $2\text{-}3\cdot 10^{-3}$  concentration of molybdate is enough for complete formation of POM avoiding in this way formation of IA with polymolybdate ions. In addition, mixed POMs are stable in wider interval of pH. Increasing of anion charge from 3 to 5(6) is also favorable. Constant absorbance of IA is observed in the acidity range of 0.12-0.28 M.

The calibration graph was found to obey Beer's law in the range  $2.0\cdot 10^{-8}$  to  $4.0\cdot 10^{-7}$  mol·l<sup>-1</sup> P(V) or As(V) ( $l=5$  cm). Molar absorptivity was equal to  $1.17\cdot 10^5$  l·mol<sup>-1</sup>·cm<sup>-1</sup> for AV 3R. Reproducibility is at satisfactory level (1-3%). Phosphorus was determined in high pure chemicals with a 36 detection limit of  $\sim 10^{-6}$  %.

Most of ions do not interfere to the determination of P(V) or As(V). Big access of colored transition metals can be tolerated by using those metals solution as reference solution. It was already shown that high selectivity of the proposed method with respect to metal ions gave the opportunity to determine phosphorus in a number of nonferrous (brass, bronze) and ferrous alloys without preliminary separation.

# CHEMILUMINESCENCE REACTIONS IN HETEROGENEOUS SYSTEMS FOR TRACE DETERMINATION OF BIOLOGICALLY ACTIVE ANIONS

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Present research is devoted to investigation of application of luminol reactions in heterogeneous systems. Systems of rapid consecutive reactions usable for the determination of biologically active, toxic anions have been studied. Anions were quantitatively converted into chemiluminescing solid or gaseous products detectable on solid / liquid or gas / liquid interface. Methodology developed made it possible to combine concentration of microcomponents with chemiluminescence detection and to achieve high sensitivity of determination.

Sorbability of heteropoly acids of P, Si, Ge and other heteropoly forming elements by a number of sorbents from water solutions has been elucidated. Heteropoly acid concentrates as analytical forms were detected by luminol directly on sorbent surface. On the other hand, heteropoly acids in water solutions react with cationic surfactants forming insoluble ion associates (IA) which like corresponding heteropoly acids react with chemiluminescence indicators with light emission. Ion associates are also separated from matrix by filtration and concentrates are detected on sorbent surface. Chemico-analytical features of sorbed species have been elucidated as well as their composition, solubility products of some IA. Correlation has been found between length of surfactant hydrocarbon chain and stability of corresponding IA as well as between stability of IA and place of the central atom of corresponding heteropoly acid in Periodic Table of elements. Off-line combined analytical procedures have been developed with detection limits at the level of 0.02 – 0.1 µg/L for P, As, Si, Ge which belong to solid phase – chemiluminescence trace analysis.

Anions of another group were derivatized with formation of gaseous chemiluminescing species. Chemical reaction – gas extraction has been used with chemiluminescence detection in the stream of carrier gas in “on-line” mode. Rate of a number of reactions has been studied as well as kinetic curves of extraction of gaseous products. Highly sensitive and rapid hybrid procedures have been developed for the determination of  $\text{IO}_3^-$ ,  $\text{BrO}_3^-$ ,  $\text{ClO}_3^-$ ,  $\text{ClO}_4^-$ ,  $\text{NO}_2^-$ ,  $\text{NO}_3^-$ ,  $\text{CrO}_4^{2-}$ ,  $\text{ClO}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$ ,  $\text{S}^{2-}$ ,  $\text{SO}_3^{2-}$  with detection limits at the level of µg/L, duration of analysis 3 min.

Procedures proposed possess substantial advantages compared to known ones and are being used in water monitoring.



*Poster presentations*

# THERMODYNAMIC VALUES FOR THERMOSTABLE COLUMNS

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High temperature liquid chromatography using water-rich and superheated water eluents was used to separate polar compounds with different function groups and phenol homologues on different hybrid phases, including XTerra MS C18 and XTerra phenyl columns. The retention factors and relative retentions at a range of temperatures were determined. In addition, methylene selectivity and efficiency were studied. The enthalpy, entropy and free energy for solute transfer from the mobile phase to the stationary phase values were compared.

## MILLIPROBE XRF ANALYSIS OF SINGLE MINERAL GRAINS (XRF MP/SG)

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Large scale investigations in fields of geochemistry of accessory minerals especially during the area selection and target evaluation on the base of regional heavy mineral sampling require fast, cheap, sensitive and precise analytical methods and procedures which will allow analyzing a small quantity of substances (single micro crystals).

Such methods as LA-ICP-MS, EMPA and SIMPS are used for this purpose now. All of them have good analytical characteristics: low detection limits, high precision and spatial resolution. But these methods require expensive hardware and time-consuming sample preparation. As the method without disadvantages mentioned above, the milliprobe XRF analysis of single micro crystals (XRF MP/SG), which require no sample preparation is presented. It was realized on original XRF instrument with two thin X-Ray beams from two independent X-ray tubes, which irradiate the sample by turns [Savenok, 2005]. The beam of first tube (Mo anode) is monochromatic by cylindrical crystal-monochromator (LiF, plane 200) for MoK<sub>α</sub> line, the beam of second tube (Ag anode) is filtered by different changing filters. Both of beams are collimated to diameter 0.5 mm. Characteristic X-ray of a sample is detected by energy-dispersive spectrometer with Si(Li) detector cooled by liquid nitrogen. The sample is placed on thin (10 μm) polyethylene film without any preparation. The main problems of quantity analysis of such samples in the measurement condition are considered. Prior calculations and experimental testing of two versions of Sr, Y, Hf, Pb, Th, U quantitative analysis in zircon, monazite and apatite grains size from 0.01 to 0.5 mm are carried out. First, one is based on a comparison of the elements fluorescence with scattered by sample primary radiation; second, one is based on comparison of the elements fluorescence with fluorescence of main mineral cations (Zr, Ca, LREE respectively). In last case, the iteration procedure of elements concentration calculation is needed, but the possibility of more small crystals analysis is present. The technique approbation shows good adaptability of described method for above mentioned tasks solution and potential possibility of area its utilization expansion.

**THERMOANALYTICAL RESEARCH OF CRYSTALLINE  
HYDRATE OF COMPOSITION  $Zn_{2-x}M^II_xP_2O_7 \cdot 5H_2O$   
( $M^II = Mg, Mn, Co$ )**

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Thermoanalytical method is one of the widespread methods of physical and chemical researches. Considerably broadens its possibilities combination with methods differential-thermal (DTA), differential-thermogravimetric (DTG), thermogravimetric (TG) analyses.

In given work the possibilities enumerated above of varieties of thermal analysis used to research of solid solutions of hydrated diphosphates with diverse composition. So, for example, the results of differential-thermal analysis  $Zn_{1,5}Co_{0,5}P_2O_7 \cdot 5H_2O$  showed, that it steady in the time of heating on air to 333 K. A further rise of temperature in interval 333 – 725 K is accompanied with the masses loss, which takes place in two basic stages, registered on crooked TG by two clear degrees, attendant to removal 4,0 and 1,0 mole  $H_2O$ . On crooked DTA these stages dehydration registers by two endothermic effects. In interval 603 – 725 K on crooked DTA is observed an exothermal effect.

Complex analysis of standards, got on all dehydration stages of  $Zn_{1,5}Co_{0,5}P_2O_7 \cdot 5H_2O$ , showed, that products of its partial dehydration are trihydrate with composition  $Zn_{1,5}Co_{0,5}P_2O_7 \cdot 3H_2O$  (408 K) and monohydrate –  $Zn_{1,5}Co_{0,5}P_2O_7 \cdot H_2O$  (488 K).

Considerably complicated realizes ablation of water from  $Zn_{1,5}Co_{0,5}P_2O_7 \cdot H_2O$ . Heating of it to 603 K is accompanied with practically full destruction of diphosphate structure. In composition of X-ray amorphous solid phase take place the processes of anion condensation. On their realization indicates formation of triphosphate with linear anion structure (5,6 mas.% in count on  $P_2O_5$ ) in composition of burning products.

Further heating of heterophase X-ray amorphous system to 725 K lead to simplification of composition of burning products and to formation only phase - crystalline anhydrous diphosphate of zinc-cobalt with composition  $Zn_{1,5}Co_{0,5}P_2O_7$ .

Heating  $Zn_{1,5}Co_{0,5}P_2O_7$  to 1173 K is furthered to perfection of crystalline structure of anhydrous diphosphate.

# QUALITY CONTROL OF AGROCHEMICAL FORMULATIONS BY DIFFUSE REFLECTANCE NEAR INFRARED SPECTROMETRY

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A solvent free, fast and environmentally friendly near infrared-based methodology was developed for the determination and quality control of 11 pesticides in commercially available formulations. This methodology was based on the direct measurement of the diffuse reflectance spectra of solid samples inside glass vials and a multivariate calibration model to determine the active principle concentration in agrochemicals. The proposed PLS model was made using 11 known commercial and 22 doped samples (11 under and 11 over dosed) for calibration and 22 different formulations as the validation set. For Buprofezin, Chlorsulfuron, Cyromazine, Daminozide, Diuron and Iprodione determination, the information in the spectral range between 1618 and 2630 nm of the reflectance spectra was employed. On the other hand, for Bensulfuron, Fenoxycarb, Metalaxyl, Procymidone and Tricyclazole determination, the first order derivative spectra in the range between 1618 and 2630 nm was used. In both cases, a linear remove correction was applied. Mean accuracy errors between 0.5 and 3.1% were obtained for the validation set.

Results found by the NIR method compared well with those obtained by the reference chromatographic procedures. The developed PLS/NIR method does not consume any solvent as no sample preparation is necessary, improving the laboratory efficiency without sacrifice the accuracy.

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# PHOTOACOUSTIC-FTIR DETERMINATION OF MANCOZEB IN PESTICIDE FORMULATIONS

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Mancozeb is a dithiocarbamate pesticide with a very low solubility in organic and inorganic solvent. In this work we have developed a solvent free, accurate and fast photoacoustic FTIR-based methodology for Mancozeb determination in commercial fungicides. The proposed procedure was based on the direct measurement of the solid samples in the middle infrared region using a photoacoustic detector. A multivariate calibration approach based on the use of partial least squares (PLS) was employed to determine the pesticide content in commercially available formulations.

The PLS calibration set was built mixing in an agate mortar different amounts of Mancozeb standard with kaolin, a coadjuvant usually formulated in agrochemicals. Cluster analysis was employed for sample classification and to select the adequate PLS model according with the characteristics of the sample matrix and the presence of other components.

The proposed PAS-FTIR procedure allows the determination of 30 samples  $\text{h}^{-1}$ , does not require any sample pre-treatment and avoids waste generation. So, it can conclude that the PAS-FTIR methodology is a reliable alternative to long and tedious classical method of analysis of Mancozeb and improves the sample frequency achieved by the FTIR procedure based on the measurement of KBr disks using internal standard.

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## DIRECT POTENTIOMETRIC DETERMINATION OF SULFATE CONTENT IN BIOLOGICAL FLUIDS (URINE)

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Sulfate is the final metabolite of sulfur-containing proteins; therefore, its content determination appears to be a very informative test in diagnostics of some diseases. However, duration and laboriousness of traditional procedures of sulfate determination prevent use of this test in everyday laboratory practice of clinical analysis. In this case, method of direct potentiometry, widely used in the determination of biological fluids electrolytic composition, seems to be very promising. In this work, the possibility of sulfate determination in urine using specially manufactured sulfate-selective electrode is discussed.

Urine is highly mineralized mixture which, along with sulfate, contains chloride (15 times more than sulfate), hydrophosphate (in amount comparable with sulfate), as well as oxalate, urate and some other organic anions influencing the potential of ion-selective electrode (ISE). It has been shown that effect of all ions mentioned, except chloride, can be eliminated by acidification of the sample with phosphoric acid up to pH 2–2,5. Therefore, the selectivity coefficient of sulfate towards chloride becomes the critical parameter determining the possibility of sulfate-selective electrode application in analysis. The influence of the nature of anion exchanger, plasticizer and neutral anion carrier – hexyl 4-trifluoroacetylbenzoate (**I**) – on the chloride-sulfate selectivity has been studied, and the results show that membrane containing monomethyldioctyl-tris-(2,3,4-dodecyloxybenzyl)-ammonium sulfate – 7,5%, (**I**) – 20%, bis-(2-ethylhexyl)sebacate – 39,5%, poly(vinyl chloride) – 33%, has the best selectivity ( $\lg K_{\text{SO}_4, \text{Cl}} = -1,43$ ). Dilution of the sample (200–250 times) leads to complete elimination of the influence of chloride ions. The influence of calcium and manganese ions, caused by their complexation with sulfate, is eliminated this way as well.

Several sulfate determinations in model solutions and urine samples were carried out. The results are of sufficiently good reproducibility (within 10% rel.) and are in agreement with gravimetry and nephelometry data. This fact allows us to recommend this method for express-determination of sulfate in urine.

# APPLICATION OF ADSORPTIVE STRIPPING VOLTAMMETRY FOR SIMULTANEOUS DETERMINATION OF COPPER (II), BISMUTH (III) AND LEAD (II)

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Copper (II), Bismuth (III) and lead (II), are important elements in the environment and they have essential roles in different biological systems. Lead is widely distributed in nature and exhibits severe deleterious effects on human [1]. Copper is an essential element for the normal metabolism of many living organisms. Bismuth has been used in medicines for the treatment of helicobacter pyloric-induced gastritis [2, 3]. Therefore trace analysis of these elements is important for monitoring their concentration in the environment.

A novel sensitive and selective adsorptive stripping procedure for simultaneous determination of copper, bismuth and lead is presented. The method is based on the adsorptive accumulation of thymolphthalexone (TPN) complexes of these elements onto a hanging mercury drop electrode, followed by reduction of adsorbed species by voltammetric scan using differential pulse modulation. The optimum analytical conditions were found to be TPN concentration of 4.0  $\mu\text{M}$ , pH of 9.0, and accumulation potential at  $-800$  mV vs. Ag/AgCl with an accumulation time of 80 seconds. The peak currents are proportional to the concentration of copper, bismuth and lead over the 0.4-300, 1-200 and 1-100  $\text{ng mL}^{-1}$  ranges with detection limits of 0.4, 0.8 and 0.7  $\text{ng mL}^{-1}$  respectively. The procedure was applied to the simultaneous determination of copper, bismuth and lead in real and synthetic samples with satisfactory results.

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# FT-IR POLARIZED SPECTROSCOPY OF 9-FLUORENONE AND DEUTERATED 9-FLUORENONE ORIENTED IN NEMATIC LIQUID CRYSTAL

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*Dedicated to Professor Bojidar Jordanov*

In previous work [1] linearly polarized FT-IR spectra of 9-Fluorenone dissolved and oriented in the nematic liquid crystal ZLI-1538 was studied. The information obtained from spectra show that this molecule aligns its long axis very well along the nematic director and permit us to make vibrational assignments for the detected bands. In this work we use the nematic liquid crystal ZLI-1695, which presents the advantage to be anisotropic at room temperature. Polarized FT-IR spectra of 9-Fluorenone and 9-Fluorenone-d<sub>8</sub> were measured. Results permit us to make complete assignments for the observed bands. A number of earlier assignments, which were doubtful, have been corrected.

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# SIMULTANEOUS SPECTROPHOTOMETRIC DETERMINATION OF BROMIDES AND IODIDES IN BROMIDE-PREVALENCE SYSTEMS

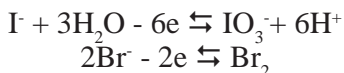
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One of the most required methods of determination of iodide-ions in practice of chemical analysis is photometric determination of products of iodination of organic compounds. The oxidation of iodide to iodine can be carried out sufficiently selectively. But in case of presence of great abundance of bromide-ions the selective oxidation of iodide-ions is problematic. The variants of determination of iodide-ions with different organic reagents are known, but the absence of bromide-ions in a system is supposed in most of them. In natural objects these halides are present simultaneously.

The selective method of determination of iodide-ions in the bromide-prevalence systems is suggested. The variant is realized this way:

The electrochemical oxidation of solution containing iodide- and bromide-ions in  $\text{HClO}_4$  is carried out. Work and auxiliary electrodes are platinum. At this potential such reactions are running:



When the electrochemical oxidation has been finished the analyzable solution is boiled till almost removal of bromine. Then the halogenation of fluorescein by two aliquots of determined solution at  $\text{pH} \sim 5.5$  is carried out. Abundance of iodide-ions is added to one of the aliquots and abundance of bromide-ions – to the other. The dependence  $A(\lambda)$  is measured for every solution.  $C(\text{I}^-)$  is calculated from received data supposing that two light-absorbing forms - fluorescein and dihalide-fluorescein are present at this condition.

The comparison of this variant of determination of iodide-ions with the method of spectrophotometric determination of iodide-ions with Iodinephenol Red is carried out. The selectivity of determination of iodide-ions with Iodinephenol Red is measured. The systematic errors appear significantly of  $C(\text{Br}^-)$  of  $6 \cdot 10^{-4}$  mol/l.

Supposed method allows determining in KBr the iodide-ions in the range of  $\omega(\text{I}^-) = 0.05-0.1\%$ . Variants of extension of effective range of the method are discussed.

# EXPERIMENTAL UNITS FOR PLANAR CHROMATOGRAPHY WITH EXTERNAL CONTROL PROPERTIES OF THE CHROMATOGRAPHIC SYSTEM

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Experimental units for horizontal and vertical thin-layer chromatography (TLC) with external control properties the chromatographic system were designed and made. This control is based on injection of additional gaseous components, of either acidic or basic nature, into the chromatographic chamber in the course of chromatographic process in order to change the properties of all the components of the chromatographic system, namely, the mobile and stationary phases and the analyte. This version of horizontal TLC includes eluent feed on the plate through filter paper or fine-porous cloth. The version of vertical TLC is implemented in the classical way. In both cases, gas is conveyed to the hermetic chamber through gas-supply pipes. The technical simplicity of the design, the capability of carrying out analysis on several chromatographic plates simultaneously with the aim to eliminate the effect of uncontrollable factors at serial analyses is advantages of our unit for upgoing chromatography.

The designed units were used for chromatography of some organic compounds of the xantene series (namely, fluoresceine, eozine, erhytrozine, Bengal rose). Chromatography was conducted in water-organic eluents on Sorbfil plates in the presence or absence of gaseous components in the chamber. The application of the new modification of upgoing TLC with a controllable gaseous phase has been found to enhance the separation selectivity in the systems under study.

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# THIN-LAYER CHROMATOGRAPHY OF BENZOIC ACIDS WITH EXTERNAL CONTROL PROPERTIES OF THE MOBILE PHASE

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A modification of the thin-layer chromatography (TLC) technique with external control over the chromatographic system is proposed.

In the course of mixture separation, the composition and properties of both mobile phase (MP) and stationary phase (SP) are purposefully altered by means of introduction of some active components into the MP, which are absorbed by it and then sorbed by the SP (e.g. on a silica gel layer). This procedure enables a new principle of control over chromatographic process to be implemented, which enhances the selectivity of separation. As a possible way of controlling the chromatographic system's properties in TLC, the pH of the mobile phase and sorbent surface may be changed by means of partial air replacement by ammonia (a basic gaseous component) or carbon dioxide (an acidic one).

The influence of NH<sub>3</sub> and CO<sub>2</sub> on the chromatographic behaviour of benzoic acid and its derivatives (o-, m-, p-hydroxybenzoic, nitrobenzoic, aminobenzoic, chlorobenzoic acids) was studied. The work was carried out by means of upgoing TLC on Sorbfil plates. Isopropanol- and ethyl acetate-containing water-organic eluents were used as mobile phases in the absence or presence of gaseous modifiers in the MP. The novel modification of TLC has been found to separate benzoic acids with different values of their dissociation constants more effectively than water-organic mobile phases.

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# DETERMINATION OF ALBUMIN IN URINE BY CAPILLARY ELECTROPHORESIS

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The separation of proteins and peptides mixtures is the objective of protein biochemistry. Albumin (Mr 66 000) concentration in a biological fluid (serum, urine or cerebrospinal fluid) is assayed as markers for a series disease, such as nephritic syndrome or chronic glomerulonephritis. In diabetic patients the progression of microalbuminuria is accompanied by an increase in urinary concentrations of human serum albumen. In normal the excretion of albumin is 20 µg/ml, in pathology - 20-200 µg/ml.

Typically, quantitative protein determination is done on the one hand by colorimetric or nephelometric methods, on the other hand for more difficult analytical problems by more sophisticated techniques such as high performance liquid chromatography (HPLC), gel-electrophoresis and immunoassay. However, these methods are tedious, time-consuming and expensive.

An alternative method is capillary electrophoresis (CE).

We have developed the method for quantitative analysis of urinary albumin with CE. A capillary electrophoresis systems “Nanophor 01” (Institute of Analytical Instrumentation, Russian Academy of Sciences, Saint-Petersburg) equipped with a UV-detector was used to determine analyte. Separation was achieved using 45 cm×30 µm I.D. fused silica capillary column with UV-detection at 214 nm.

Desalting and depigmentation of urine sample was carried out by gel-filtration on Sephadex G25 with cut mass 10 kDa.

The major problems in assay of protein by CE are the low efficiency and reproducibility by presents of protein adsorption on the inner surface of a capillary, and poor concentration sensitivity UV-detection.

There are several methods of buffer and capillary surface modification used to prevent electrostatic interactions. Two modes have been examined: run buffer with pH >10 in the uncoated capillary and anionic polymer coating capillary, developed in IAI.

The way to solve the second problem is the use of different techniques of on-line concentration of probe in CE (stacking, sweeping, etc.). The best results were achieved with the stacking with reversed polarity. Detection limit of albumin was 10 µg/ml.

# ELECTROOXIDATION, QUANTUM CHEMICAL CALCULATIONS AND CHEMILUMINESCENT ANALYSIS OF DIHYDROPYRIDINES DERIVATIVES

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Electrochemiluminescent method and technology provides unique possibility for different assays having obvious distinguished features in comparison with known electrochemical and luminescent analytical methods. In a case when assay is demanded of analytes having non-electrochemiluminescent properties an original new diagnostic method of "light spin traps" developed by us should be used, e.g. catching by electrogenerated electrochemiluminescers ion-radicals of intermediate labile radical products - free radicals of complex organic compounds (analyte) in different liquid-phase systems, bioobjects including.

In this paper the electrode anodic reactions of a number of dihydropyridine (DHP) derivatives, quantum-chemical calculations of reactions between DHP cation-radicals and electrochemiluminescers anion-radicals (aromatic compounds) and DHP indirect ECL assay were investigated. The actuality of this work and its analytical value follow from the fact that objects of investigation - DHP derivatives - have pronounced importance due to its pharmacology properties as high effective hypertensive medical product.

All electrochemical, ECL and analytical investigations were carried out with the help of home-built ECL analytical apparatus "ELAN-2". We obtained a set of ampere, volt-intensity (ECL) curves for different analyte and reactant (electrochemiluminescer) concentration, on a base of which the graduated graphs for DHP ECL definition were built. The *ab initio* quantum-chemical calculations of bimolecular reactions in systems under investigation were carried out and reactions rate constants and activated complex profile were obtained too. There exists good correlation between theoretical rate constants and their values obtained using R. Marcus theory for electron-transfer reactions with experimental electrochemical data of systems under investigation.

## VOLTAMMETRY OF Zr(IV) IONS WITH SOME AZODYES

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Zirconium is used in a wide range of industries, and with advances in modern technology. The diversity of their applications has increased. Therefore, determined of zirconium are very important. The direct determination of zirconium are practically impossible by polarographic method because the reduction potential of Zr(IV) in aqueous solutions is more negative than that of H<sup>+</sup>. However, zirconium can be determined with use of certain organic ligands, which are form electroactive complexes. Perceptivities from this point of view are complexes of Zr(IV) with azodyes. One of this azodyes is calces, which reduce on the dropping mercury electrode in wide within of pH. One peak corresponds to reduction of calces in the all acidity medium. In the presence of Zr(IV) ions the appearance of addition peak ( $E = -0.36 \div -0.69V$ ) is observed on the voltamperograms of calces within the limit of pH 0.7-8.0. The additional peak is observed with more negative potential than reduction peak of the free ligand.

The value of current of the addition peak on concentration of dye and metal, ionic strength of the solution, influence of solvent and temperature were investigated.

Nature of current of additional peak was determined. It's multiple depending on the rate of polarizing tension. The absence of anodic peaks on the voltamperograms of calces testifies that the reduction of the compound is an irreversible process.

Linear dependence of current of additional peak  $I_p^k$  on concentration of Zr(IV) can be used for elaboration sensitive and selective determination of zirconium with detection limit of  $1.7 \times 10^{-7}$  mol/l.

# DETECTION OF AROMATIC AMINES BY SURFACE-ASSISTED LASER DESORPTION-IONIZATION

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An application of surface-assisted laser desorption-ionization (SALDI) method for practical, ultrahigh sensitivity detection of aromatic amines by GC-MS is reported. The prototype analytical device for trace detection of different organic compounds is created.

The analytical properties of the GC/MS detection of aromatic amines with different structure of carbon skeleton between benzene and amino group are represented. It is shown, that the main ions are in the form of  $(M+H)^+$  (protonated molecules) or  $(M-H)^+$ . All compounds also give two or three very specific positively charged fragments of analyte molecules. The simultaneous monitoring of a major fragments ion peaks and the molecule ion peak dramatically increases the ability to discriminate a targeted analyte from interfering chemical noise.

It was found, that at standard gas-chromatograph sampling of 1  $\mu$ L of analyte solution the limit of detection for different amines was measured as 0.1-3 ng/ml, or of about 1 femtomole of analyte in the probe. This detection limit is better of published data, obtained by conventional GC-MS technique. Evidently, that both the increasing of the laser spot size and the optimization of GC-capillary position can strongly improve the detection limit.

The possible mechanism of ionization, fragmentation of studied compound as well as their desorption by laser radiation is discussed. It is shown that the formation of analyte ions is a result of a multi stage complex process included surface activation by laser irradiation, the adsorption of neutral analyte and proton donor molecules, the chemical reaction on the surface with proton or electron transfer, production of charged complexes bonded with the surface and finally laser desorption of such preformed molecules.

The reported data demonstrate the high analytical potential of the SALDI method. It is shown that this method may be realized in a comparatively simple, affordable, and highly efficient instruments.

# RESEARCH OF DEPENDENCE OF INTENSITY OF X-RAY RADIATION FROM PHYSICAL AND CHEMICAL PROPERTIES OF THIN-FILM SPECIMENS

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At X-ray fluorescence analysis (XRF) of samples of the limited weight is perspective to prepare for specimens as polymeric films on a basis of methylcellulose [1]. By the example of definition of heavy metals in film specimens have studied dependence of intensity of X-ray radiation from their chemical compound, surface density ( $P_s$ ) and the size (D) particles of the powder introduced to polymer. Have theoretically established, that the basic source of an error of results XRF is dependence of intensity ( $I_1$ ) analytical lines of determined elements from  $P_s$  a specimen. Thus the best account of variations  $P_s$  provides a method of the internal standard: at change  $P_s$  from 2 up to 6 mg/sm<sup>2</sup> the coefficient of variation  $V_t$  describing an error of definition Mo, Zn, Cu, Co, Fe and Mn in a method of the direct external standard, reaches 40 %, and at use of a method of the internal standard (an element of comparison Ga) value  $V_t$  does not exceed 2,2 %. Experiment within the limits of a casual error ( $V_c$  changes from 2,9 up to 7,4 %) has confirmed theoretical conclusions.

Have compared intensity  $I_1$ , measured from the films prepared by introduction of an analyzed material to polymer in a various aggregative stations: as a powder, a solution and a mix of a powder with a solution. The weight of an introduced material (in recalculation on superficial density  $P_{sm}$ ) changed from 0,14 up to 0,43 mg/cm<sup>2</sup>. Have established, that in some cases the value  $I_1$ , measured from films with a powder, it is essential (~40 %) less the value  $I_1$ , measured from films with a solution, containing identical quantity of determined elements. By using of methods of a standard - background and internal standard this decrease is saved.

The dependences of intensity  $I_1$  from the size D particles of the powder introduced to polymer for the films, described various values  $P_{sm}$ , have studied. The difficult character of dependences  $I_1 = f(D)$  are established. Researches on finding-out of reasons of observable effects are carried out.

1. The patent of Russia No. 2239170. A method of the preparation of standard samples of the atmospheric aerosols loaded on the filter / Korzhova E.N., Smagunova A.N., Kuznetsova O.V., Kozlov V.A.



# **ELECTROTHERMAL ATOMIZATION IN GRAPHITE FURNACE: A KINETIC MODEL WITH TWO INDEPENDENT SOURCES**

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To understand the causes of signal change and therefore to explain the influence of physico-chemical factors on its shape and magnitude, the mathematical models are employed. A multitude of different and often contradictory models were proposed to describe the atom formation in ET AAS, but they do not take into account a number of effects influencing appreciably the atomic absorption profile. The surface effects (such as structural changes in graphite tubes, surface porosity, analyte penetration into graphite etc.) are very important.

We developed an original kinetic model based upon the solving of the differential equation of diffusion with two independent sources, which describes the form the atomic absorption signal with high precision. The first source describes the atomization from the surface of graphite furnace; the second describes the formation of atoms inside the walls of the graphite furnace and its outflow into the analytical zone. So, the following model of the dynamics of an analyte within electrothermal atomizers can be proposed. On the surface and inside the walls the atom formation occurs with the same activation energy but with different values of the atomization rate constants. Atoms, which initially were situated on the furnace surface, desorb from surface and diffuse in inert gas towards the open ends of the furnace, whereas the atoms, which initially were inside the walls, pass through heated graphite. Thus the shape of atomization profile is influenced by such parameters: kinetic parameters – atom formation energy, atomization rate constants for atoms inside furnace walls and for atoms on the surface, diffusion parameters – diffusion activation energy of metal vapor in graphite, pre-exponential factor.

Employing the proposed model, the behavior of the experimental signals of Cu, Ag, and Zn at different temperatures was described. The model explains increased tailing of the back edge of Cu profiles.

A new interpretation for the shift of absorbance maximum as the initial mass of Ag increases is proposed. The most probable mechanism of the shift is more rapid increase of atomic absorption signal from the source, which describes the formation and outflow of atoms from graphite compared with the signal from the source, which describes the atomization from the furnace surface.

# IR SPECTROMETRICAL DETERMINATION OF VOLATILE ORGANIC SUBSTANCES IN WATERS AFTER EXTRACTION INTO GASEOUS PHASE

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The essential advantage of IR spectra measurements in the gaseous phase is the proximity of the experimental data to the theoretically calculated. It gives the possibility to obtain simpler spectral curves with less number of absorption's maximum and their undistorted form because of absence of molecular interactions, polymerization etc. This fact gives the highest selectivity between molecular spectrometric methods and provides to increase of precision. In this paper we discussed the ways of the further perfection of the IR gaseous measurements and widening of the method possibilities. So we investigated the gaseous extraction using IR spectra for the wide range of organic volatile substances from the water solutions. It allowed us to make such conclusions:

- The sensitivity of analyses may be increased by variation of parameters what provides the rise of the completeness of gaseous extraction –  $t^\circ$ ,  $v$ , for hydrophilic organic substances – the presence of salting-out agents. It has been determined that the most effective extraction of aliphatic alcohols is a characteristic feature for high concentration alkaline solutions.
- IR spectra of gaseous phase contain exclusively most intensive spectral lines without the widening because of influence of hydrogen bonds and different molecular interactions. It facilitates the choice of analytical signals. In such conditions the matrix effect is minimized. There is observed inversely proportional dependence between boiling points (bp) and time of desorption of analytes. The difference of bp in 20-30°C gives the possibility of fixation in dynamic conditions the resolution of analytical signals as a function of time for different substances in multicomponent systems. So, it's possible to analyze extracts of organic substances from the ecoobjects both in static and dynamical conditions with the decreasing of the limit detection about 2-3 orders.
- Another way to increase of sensitivity is the using of IR-FT measuring. Comparison traditional and IR-FT versions for hydrocarbons shows the growth of analytical signal value on more then 2 orders.
- And finally, the further improvement of high selectivity of analytical IR spectrometry is the using the chemical modification. There is possible to realize the fast and total transformation unvolatile and volatile analytes to the vapour phase. In those cases there is also essentially increased the number of analyzed compounds.

## **SOME FEATURES OF AN INDIRECT SORPTION-PHOTOMETRIC DETERMINATION OF NONIONOGENIC SURFACTANTS**

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Because of a wide use of nonionogenic surfactants (NIS) in many areas of production, medicine and in a life, they have become known hydrosphere pollutants. As a result there is a necessity of the control over their contents in natural waters. Now there exist a sufficient number of methods of NIS determination with different detection limits. As a rule, a preliminary concentration is used for surfactants various classes detection limits decrease.

In this work the results of investigation of Sintanol DT7, the representative of oxiethylated alcohols class, sorption regularities on Si(IV), Sn(IV) and Al(III) oxihydrates to choose the most suitable sorbent for extraction of its microamounts and its strong keeping on a surface are presented. The researches carried out have shown silica L5/40 to answer to such requirements. It is well-known, NIS of oxiethylated alcohols class to be able to form stable cationic complexes with alkaline earth metals ions, particularly with barium ions, in aqueous solutions. At the same time their physical and chemical properties and behavior in aqueous solutions remind the corresponding cationic surfactants (CS) ones that allows to use the same methods of determination. First of all it is the ability of CS to form stable ionic associates of stoichiometric composition with anionic dyes.

The worked out sorption-photometric method of NIS determination calls preliminary sorption concentration of NIS microamounts from aqueous solutions on silica L5/40. The concentrate obtained is put in a solution with precise concentration of bromthymol-blue (BTB) anionic dye and  $\text{BaCl}_2$  excess. As a result the ionic associate 1:1 is formed and is kept comparatively strongly on a surface. The BTB excess remains in an aqueous phase and it is easy to determinate it photometrically. The linear dependence of optical density of BTB solutions after sorption on NIS concentration in an interval  $1 \cdot 10^{-6} - 2,5 \cdot 10^{-5}$  M is observed. The indirect way of the given method is caused by the fact the calibration plot does not come from a zero point of coordinates, and NIS zero concentration corresponds to initial BTB concentration in a solution.

## IONOMETRY POLYELECTROLYTES DETERMINATION

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Surface-active substances (SAS) are the most widespread contaminants of sewage and natural waters. They translate in small dispersion condition liquid and firm polluting substances – chlororganic, mineral oils, pesticides. Therefore, the SAS contents determination in water solutions is now one of actual tasks of analytical chemistry.

The potentiometry sensor (ion-selective electrode) controls application for determination of polymeric surface-active substances now gets the increasing value. Potentiometry sensor controls are actively used due to simple instrument registration, a wide range of determined concentrations, and opportunity of continuous substances contents definition. That less, the ionometry application for the cation polymeric SAS analysis in a solution is limited by complexity of polycation charge determination and ion-exchanger synthesis.

For diagnostics of the cation polymeric SAS contents with average molecular weight less than 10000 ion-selective electrodes with a film membrane on the basis of polyvinyl chloride are offered. As opposed ion of ion-exchanger both inorganic complex anions and organic anion dyes are used. The membrane structure and solution ionic force influence on electrode characteristics of the suggested electrodes is investigated. The special attention at measurements was given to membrane condition: surface morphology, porosity, swelling at long use and ageing of polymeric films, containing ion-exchanger. Time of the synthesized membranes life made 60-90 day. Membranes which used after 90 day of storage in paper packing showed the electrode characteristics similar renewed films. After 120-130 measurements the electrode function steepness of the some electrodes decreased half that, apparently, is caused by swelling of a polymeric film and washing away ion-exchanger from membrane. Thus, after 100 measurements there was a necessity of membrane replacement on an electrode.

As during diagnostics the major is a selectivity of the suggested devices, the electrode selectivity factors were defined by fixed preventing ion method. As preventing used one polymeric substance to another and synthetic washing means “Lotus” and “OMO” that contains cation SAS. The received values of selectivity factors varies in  $1,1 \cdot 10^{-3}$ - $2,2 \cdot 10^{-2}$  interval.

# CHEMICAL-ANALYTICAL PROPERTIES OF POLYAMINES ASSOCIATES AND APPLICATION IN ANALYSIS

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For the last years the polymer surface-active substances have found new application as modifying agents of properties of organic reagents. Besides polyamines will be used as flocculants, corrosion inhibitors, stabilizer of the medicines, in cosmetic, latex manufacture, at clearing of sewages. Metacide has properties of a cationic polymer surface-active substance and it's widely applied in a rubber industry. The control of it contents is necessary both different stages of manufacturing process and during its synthesis from monomers of hexamethylene diamine and diciandiamide.

Metacide can be shown by the formula  $\text{NH}_2-[(\text{CH}_2)_6-\text{NH}-\text{C}(\text{NH}\cdot\text{HCl})-\text{NH}]_n$  with molar weight about 10000, polyguanidine -  $[(\text{H}_2\text{N})_2\text{C}=\text{NH}]_n$  with molar weight 5000.

The interaction of polyamines with 4 groups of organic reagents is established: triphenylmethane dyes (chlorphenol red (CPR), bromkrezol magenta (BKM)); oxyfluorone (phenylfluorone (PF), eosine (EO), bromopyrogallol red (BPR)); phenolcarbonic acids of triphenylmethane series (chromasuroil S (CAS)); azo dyes (stilbazo (SB), alizarine yellow (AY), thoron (TH), magneson (MG), calcion (CC)) with formation of the coloured associates.

In presence of polyamines the maximum of light absorption of indicated triphenylmethane dyes displaces on 10-30 nm, for azo dyes the shift of the band reaches 50-80 nm. The greatest difference of light absorption of associates and reagents is watched for BKM at pH 5,05, for BPR at pH 4,20, for CPR in an interval pH 5,05-5,45. At these pH dyes are anions, it promotes interaction with a cationic surface-active substance. The ratios between polymer and BKM, BPR, CPR are established by spectroscopy method, its equal 1:20, 1:20 and 1:30 accordingly.

It is possible to determine the metacide content with the use of ionic associates of metacide with BKM, BPR, CPR; polyguanidine with azodyes SB and MG by spectrophotometry. The monomers, from which one synthesizes of metacide and polyguanidine, and which are present in actual objects of the analysis, do not react with dyes. 0,01-0,20 mg metacide at use BKM (0,01-0,10 mg at use CPR) is determined in 25 ml of solution. It's possible to determine 9-16 mg/l of polyguanidine (pH 4-5) and 35 - 400 mg/l (pH 11-12) using magneson.

# INFLUENCE OF SYNTHETIC AND NATURAL POLYMERS ON ANALYTICAL PROPERTIES OF AZODYES

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Last years the polymeric surface - active substances began to use as modifiers of organic reagent properties. In our work the behavior of synthetic polymers (polysulphonilpiperidinilmethylenhydroxide (PSPMH), polyvinylpyrrolidone (PVP), polyamines - polyguanidine and metacide) and natural polymers (starch, gelatin) for various molecular masses are investigated.

The interaction of polymers with azodyes methyl red, methyl orange, alizarine yellow R, gallion, lumogallion, magnezon, tropeoline 0, 00 and 000, congo red, brilliant yellow (BY), stilbazo, thoron, calcion, eriochrome black T, eriochrome blue-black is investigated by UV-, VIS- and IR-spectroscopy. The introduction of polymer in solutions of azodyes results, as a rule, in change of maximum and intensity of light absorption bands, displacement of dissociation constants of dyes in acidic and alkaline areas (table).

Table. The characteristics of brilliant yellow adducts with polymers

Brilliant yellow form	Polymer	pH interval	$\lambda_{\max}$ , nm	$\Delta\lambda$ , nm	pK (pH <sub>1/2</sub> )	$\Delta$ pK (pH <sub>1/2</sub> )
(HR <sup>-</sup> ) <sub>2</sub>	-	1,5-8,5	400	-	0,89	-
	gelatin	0,4-8,9	398	-2	0,23	0,66
	starch	0,5-8,2	396	-4	0,30	0,59
	PVP	0,1-7,8	420	20	-0,15	1,04
	PSPMH	0,3-7,1	428	28	-	-
(R <sup>2-</sup> ) <sub>2</sub>	-	> 9,3	484	-	8,93	-
	gelatin	9,8-13,7	486	2	9,38	-0,45
	starch	9,1-13,0	483	-1	8,62	0,31
	PVP	8,7-13,0	520	36	8,25	0,68
	PSPMH	7,9-12,0	532	48	7,73	1,20

It is established, that the natural and synthetic polymers influence on spectrophotometrical, protolytical and complex-formating properties of azodyes in different degree. The result of interaction between anions of organic dyes and polymers is formation of specifical hydrophobic-hydrated adducts. Express spectrophotometrical methods of polymer content determination in water solutions with the help of polymer adducts have been elaborated.

# SOME NEW POSSIBILITIES IN THE APPLICATION OF TETRAIODOMERCURATE FOR THE PHOTOMETRIC ANALYSIS

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A number of organic compounds prevent ammonia from being detected by photometrical method with the use of Nessler reagent (a mixture of solutions of  $K_2HgI_4$  and KOH or NaOH) for they themselves bring about a coloration or dimness of Nessler reagent. Among aliphatic amino compounds the polyamines: guanidine, alkylene diamines, polyethylene polyamines are especially active. We took ethylene diamine to study a nature of the products of reactions of those amines with tetraiodomercurate and the possibilities of such reactions to be used for analysis of water.

In the absence of ammonia and the concentration of polyamines being  $\geq 20 \mu M$  the production of sediments take place. Ethylene diamine reacts with Hg(II) in the form of diimide -HNRNH- to form the insoluble complex  $IHgHNRNHHgI$ . In the presence of ammonia the production of sediments having complex composition is also possible. Given concentration of  $K_2HgI_4$  1 - 2 mM, NaOH 60–120 mM and comparable amounts of ammonia and ethylene diamine the products of reactions are only the soluble green-coloured complexes, bearing ammonia in the form of nitride and ethylene diamine in the form of diimide. Those complexes are polymers, with their absorption spectrums being different from those of the similar polymeric “ammonia” complexes.

The methodology of photometric determination of polyamines in the form of soluble complexes described was developed. To take into account both the absorption of the light by the products of reaction of Nessler reagent with ammonia and admixtures of coloured substances and suspended particles in the sample being analyzed the two-wave photometric technique in combination with chemical differentiation of optical density (the disruption of the coloured complexes by thioglycolic acid was used). The detection limit was equal to  $1 \mu M$ . The procedure proposed may be useful in detecting polyamines in some sewage and in controlling quality of the drinking water.

# INVESTIGATION OF ANTHOCYANIN COMPLEXATION WITH METAL IONS BASED ON THE COLOR MEASUREMENT

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Anthocyanin complexation with metal ions is one of the properties that determine their function as natural pigments. Binding of these bioligands to biogenic metals causes a co-pigmentation effect of plant tissues. Chelating of toxic metal ions considered to be one of detoxifying processes. Complexation effects cause a problem of color modification when pigments are used as natural colorants in food industry. This problem challenges needs for developing of analytical approaches to estimate anthocyanin metal binding ability. To date usability of colorimetry as instrumental method for pigmented samples color measurement has not been characterized.

The work was aimed at colorimetric investigations of anthocyanin complexation in solution and in vivo in plant tissues. Pigments with different number of hydroxyl groups in chelating center (pelargonidin, cyanidin, delphinidin) were investigated. The measurements were made using standard colorimetric systems XYZ and CIELab 76. To prove complexation effect spectrophotometric analysis of solutions and their differential spectra were additionally used along with reflectance spectroscopy of complexes in solid phase. Solution pH influenced on structure modification of pigment flavylium form resulting in chinoid base that possesses metal-binding activity. Using preparative isolation of metallochelates special characteristics were established that allow to identify chromatophore system modified by metal binding. This data explain the shift in dominant wavelength and color tone purity based on physical theory of color vision. The correlation between colorimetry parameters and concentration of metal ion was established.

Based on experimental results the method for identification of anthocyanin metallocomplexes was suggested.



# GENERALIZED DESCRIPTION OF POWDER AND POWDER SLURRY-LIKE MATERIALS IN X-RAY FLUORESCENCE SPECTROMETRY

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Our communication describes grain size effect in XRF of powder and powder slurry-like substances in terms of the generalized model:

$$I_f = kI_0 \frac{\omega \sum C_j^v C_{mi}^j (\tau_{mi} \rho_j) (g_j / \mu^j)}{\sum C_j^v g_j}, \quad g_j = \frac{1 - \exp(-\mu^j d_j)}{d_j}, \quad \mu^j = \mu_\lambda^j + \mu_i^j$$

Here  $C_j^v$  is the volume concentration of  $j$ -phase particles;  $C_{jm}$  is the mass concentration of the analyte in the  $j$ -phase particles;  $\omega$  is the x-ray fluorescence radiation yield;  $\tau_{mi}$  is the mass absorption coefficient of the analyte for the primary radiation;  $d_j$  is the  $j$ -phase particle effective size;  $\rho_j$  is density of  $j$ -phase;  $\mu_\lambda^j, \mu_i^j$  are the linear absorption coefficients for the primary and characteristic x-rays of  $j$ -phase, respectively.

This model is based on the calculation of probability  $p_j$  of x-ray photon impact on the  $j$ -kind particle, referred to fixed size class:

$$p_j = V_{tot} C_j^v \frac{S_j}{V_j} = V_{tot} C_j^v / d_j,$$

where  $V_{tot}$  - is the volume of sample;  $S_j$  and  $V_j$  are cross section and volume of  $j$ -kind particle, correspondingly.

The expressions provide the limiting transition. When  $d_j \rightarrow 0$  for all  $j$ -phases,  $g_j \rightarrow \mu^j$  and the above expression transforms to the expression for a homogeneous sample. In case of the two-component powder, consisting of fluorescent and non-fluorescent particles, when size of the non-fluorescent particles  $d_0 \rightarrow 0$ , the above expression transforms to the expression for slurry-like substance (A.L. Finkelstein, T.N. Gunicheva, e. a. // X-Ray Spectrom. 1992. V. 21. p. 287-292). In case of the multicomponent powder with the equal size particles the expression transforms to the well-known Berry-Furuta-Rhodes formula.

Comparison with literature experimental and calculation data showed that the model proposed ensures the accurate behavior of the functional dependence of x-ray fluorescence intensity on the particle size. Its main advantage is the possibility to estimate the effect of particle size for polydispersive multicomponent substances.

# DETERMINATION OF POLYPHENOLIC ENANTIOMERS IN GREEN TEA EXTRACT BY CAPILLARY ZONE ELECTROPHORESIS

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Nonalcoholic and strong drinks (tea, wine) contain a number of aromatic substances with amino and hydroxyl groups (first of all, there are polyphenolic compounds and alkaloids) which defined sort and quality of drinks.

Catechin and epicatechin are two flavanols of the catechin family. They are enantiomers. The capillary zone electrophoresis (CE) methods with UV-detection were developed for quantitative determination of this flavanols in green tea extracts. For this purpose following conditions were varied: running buffers, pH and concentration of chiral additive ( $\beta$ -cyclodextrin was chosen as a chiral selector). Borate buffers improve selectivity of separation because borate can make complexes with *ortho*-dihydroxy groups on the flavanoid nucleus.

Extraction of the catechin and epicatechin from the green tea was carried out by liquid extraction with methanol.

A capillary electrophoresis systems "CAPEL 103R" ("Lumex" Ltd, Saint-Petersburg) equipped with a UV-detector was used to separate and quantify analytes.

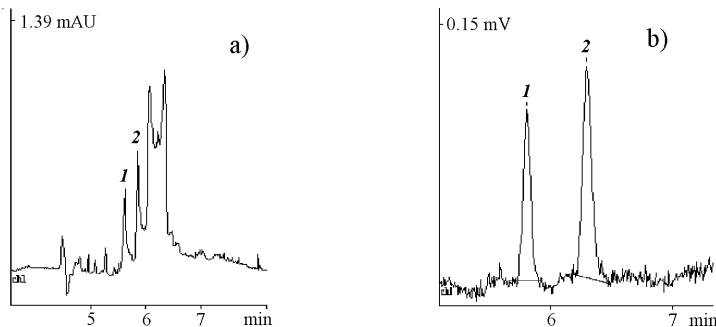


Fig. Electropherogram of a) catechin standards, b) green tea sample prepared in 50 % methanol using liquid extraction

Electrophoretic condition: 60 cm (effective length of 50 cm) $\times$ 75  $\mu$ m I.D. fused capillary column, run buffer borate buffer pH 9,0,  $\beta$ -cyclodextrin, electrophoresis voltage 20 kV, detection at 254 nm.

Sample is in deionized water. Peak identification: (1) (-)-epicatechin, (2) (+)-catechin

*This work was supported by the Foundation for Assistance to Small Innovative Enterprises*

**ADVESICLE MEDIATED EXTRACTION BASED ON SUPPORTED  
VESICULAR AGGREGATES AS NOVEL MEDIA FOR THE  
ISOLATION OF POLAR AND NON-POLAR ORGANIC  
COMPOUNDS PRIOR TO LIQUID CHROMATOGRAPHY**

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The ability of vesicle-coated silica to aid the extraction of organic compounds from water prior to liquid chromatographic analysis is presented for the first time. The method is based on the formation of silica supported cationic multi-lamellar vesicles of gemini surfactants inherently ensuring the presence of hydrophilic and hydrophobic sites for the partitioning of analytes bearing different properties. Method development is illustrated by studying the adsolubilization of UV absorbing chemicals from swimming pool water. Due to the requirement for external energy input (intense mixing) a method based on solid phase dispersion was applied producing better results than off-line SPE. Meticulous investigation of the experimental parameters was conducted in order to elucidate the mechanisms behind the proposed extraction pattern. Analyte recoveries were quantitative under the optimum experimental conditions offering recoveries higher than 96% with RSD values below 5%.

# POLYCYCLIC AROMATIC HYDROCARBONS LUMINESCENCE DETERMINATION USING MICELLAR SOLUTIONS

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Polycyclic aromatic hydrocarbons (PAHs) are a class of organic compounds consisting of two or more condensed aromatic rings. The main source of PAHs are fossil fuels such as crude oil or coal. Therefore, the distribution of these organic compounds is mainly carried out by oil and coal products, such as heating oil, vehicle fuels, coal coke and creosote. The pollutants can enter the environment directly, for example in spillages of oil and oil products or by slow dissolution of protective coatings, such as tar coatings on ships, creosote coatings on riverbanks or harbours, and coal tar coatings in drinking water pipes. Present-day standard methods for the detection of PAHs include liquid-liquid extraction, solid phase extraction and supercritical fluid extraction in combination with high performance liquid chromatography, liquid or gas chromatography. These approaches require expensive instrumentation, experienced analysts, extensive sample treatment (purification, derivatization, pre-concentration) and often large amounts of toxic solvents and chemicals. Thus, since the social interest for monitoring of samples contamination with PAHs is continuously increasing, the development of screening methods that will be fast, technically simple, inexpensive and useful for the routine analysis of a large number of samples is of great importance.

The aim of this work is the development of pyrene determination in gasoline and contaminated soils. For this purpose we used room temperature phosphorescence (RTP) in micellar solutions of sodium dodecylsulphate (SDS). For pyrene extraction from contaminated soils hexane was used. Then extracts carried in glass and dried. After that remains was dissolved in SDS solution in the presence of sodium sulphite as deoxygenation agent and thallium (I) nitrate as "heavy atom". For pyrene RTP excitation 337 nm wavelength was used. To check the accuracy of the procedures proposed for pyrene determining by RTP, the pyrene concentrations in the same gasoline samples were also measured by GC-MS.

For fluorescence PAH determination in tap water acid-induced cloud point extraction was used. This kind of extraction based on the phase separation into two isotropic liquid phases: a concentrated phase containing most of the surfactant (surfactant-rich phase), where the solubilised solutes are extracted, and an aqueous phase containing a surfactant concentration closes to the critical micellar concentration.

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# PROPERICIAZINE AS A SELECTIVE AND SENSITIVE REAGENT FOR THE SPECTROPHOTOMETRIC DETERMINATION OF MICROGRAM AMOUNTS OF PLATINUM

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Propericiazine forms a pink complex with platinum(IV) at room temperature ( $26\pm 2^\circ\text{C}$ ) in hydrochloric acid – sodium acetate buffer medium containing copper(II) ions. The complexation is complete within 10 min. The complex exhibits an absorption maximum at 520nm with a molar absorptivity of  $1.204\cdot 10^4 \text{ L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$ . Beer's law is obeyed over the concentration range 0.5 – 12.2 ppm of platinum. A 50 - fold molar excess of the chromogenic reagent is necessary for the development of maximum colour intensity. Job's method of continuous variation, the molar ratio method, and the slope – ratio method indicate a 1:1 composition for the complex. The effects of pH, time, temperature, reagent concentration, order of addition of reagents and interference for various ions are reported. The reagent has also been used successfully for the determination of platinum in minerals and alloys.

Procedure: To an aliquot of the sample solution containing 12.5 – 305  $\mu\text{g}$  of platinum(IV) were added 5 ml of hydrochloric acid – sodium acetate buffer of pH 2.1, 1 ml of 0.1M Cu(II) sulphate solution, and 3.0 ml of 0.5% propericiazine solution. The solution was diluted to 25 ml with distilled water, mixed thoroughly, and the absorbance measured at 520 nm against a reagent blank solution after 10 min. The platinum concentration of the sample solution was determined using a standard calibration curve.

## VOLTAMMETRY OF IRIIDIUM(IV) WITH TRIPHENYLMETHANE- AND AZO- DYES

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The thesis is research to study of voltammetric properties of Ir(IV) in the presence of the different nature dyes with following analytical application of the results obtained. It has been found the possibility to increase the sensitivity of iridium polarographic determination in the presence of some organic dyes, on particular, pyrocatechol violet, eriochrome cyanine R, chromazurol S, xylenole orange, (due to their catalytic action on the reduction process) and acid chrome dark blue (due to their formation complex compounds). The process of reduction Ir(IV) in the presence of triphenylmethane (tritan) dyes is a catalytic reaction with irreversible transfer of the charge. The nature of reduction current in these systems is diffusive with considerable kinetic limitations. Limitative stage of the reduction process takes place in near-electrode layer. The mechanism of the appearance of hydrogen catalytic currents in iridium solutions in the presence of tritan dyes has been proposed. The method of Iridium determination in complex compositions with  $C_{\min} \sim 1-2 \times 10^{-7}$  mol/L in the presence of tritan dyes has been elaborated.

Electrochemical reduction of iridium solutions in the presence azodye (acid chrome dark blue [ACDB]) on slowly dropping mercury electrode is accompanied by occurrence of additional peaks on background acetic-ammonium buffer solutions except for waves of reduction azodye. Potentials of these peaks are displaced to cathode region of the potential compared to the respective peaks of reduction of the azodye. The nature of reduction current in iridium solutions in the presence ACDB is diffusive with considerable adsorptive limitations. The method of voltammetric determination of iridium with ACDB has been developed ( $C_{\min} \sim 1-2 \times 10^{-7}$  mol/L).

The voltammograms of complex compounds of iridium with azodye appears considerably more clear separate than in the case of tritan dyes, but a sensitivity and selectivity of this method is considerably less.

## **FAST TEMPERATURE GRADIENTS BY RESISTIVE HEATING FOR LC APPLICATIONS**

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Interest in the use of temperature as a modifier in HPLC separations has increased markedly recently with the introduction of a range of stable hybrid stationary phases and the use of superheated water as an eluent. To maximise the benefit from these new advances requires a HPLC capable of rapid and reproducible heating/cooling of columns during the separation. Hence, this has led to the development of a chromatography oven based on resistive heating, capable of consistent heating patterns, which has been tested with RP columns. Highly efficient heat transfer to various column geometries has been accomplished giving temperatures from ambient to 200°C with ramping rates up to 30°C/min. The heater includes design features that allow for the preheating and post column cooling of the eluent.

The separation of a complex mixture of pharmaceutical compounds has shown that temperature programming can generate a separation equivalent to gradient elution. The gradient results in the sharpening of late eluting peaks and significantly improved separation efficiency. The analysis time is reduced allowing for high sample throughput and greater peak capacity. Added benefits have encompassed hyphenation with MS where temperature gradients with a fixed eluent composition are much more desirable as the detector background remains unaffected.

# DIMERKAPTOTIOPIRON AS REAGENT FOR SPECTROPHOTOMETRIC AND ELECTROCHEMICAL DETERMINATION OF OSMIUM

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The difficulties of the osmium determination are connected with its different degrees of oxidation in solutions, existence in various chemical forms, which can pass one into another. The analytical problem can be successfully solved in many cases by using of selective organic reagents. Among these reagents leading role belongs to the sulfur containing ones.

Interaction between osmium(IV) and osmium(VI) and derivatives of dimerkaptotiopiron (**DT**) has been studied by amperometric, potentiometric and spectral photometric methods in different mediums. It has been found out that in reactions of methyl dimerkaptotiopiron (**R**) with Os(IV) and Os(VI) complex formation prevails. It has a step-like nature, being revealed by such change of ratio of Os:R in the course of titration as: Os(VI):R - from 1:1 to 1:4 in acid medium and from 2:1 to 1:4 in weak alkaline medium; Os(IV):R - from 1:1 to 1:5 in medium of H<sub>2</sub>SO<sub>4</sub> and from 1:1 to 1:6 - in HCl medium.

Spectral photometric titration has been carried out in binary systems of Os - Pt, Os - Pd, Os - Ru at optimum wavelength of 490 nm.

Consequent potentiometric titration of osmium(IV) and ruthenium (IV) in their mixtures has been carried out in broad range of concentrations: from 1 mkg to 200 mkg in samples of 20 ml. It has been shown the possibility of amperometric determination of osmium(VI) in binary and triple systems with silver(I), platinum(IV), palladium(II), gold(III), founded on formation of corresponding compounds with dimerkaptotiopiron, having a different solubility. The determination of Os(VI) is possible under tenfold - hundredfold excess of above mentioned metals.

The extraction of osmium(VI) and osmium(IV) compounds with dimerkaptotiopiron by polar solvents has been researched. 50 - 100 - multiple concentrating has been carried out in acid solutions regardless from chemical form of Os(VI) and Os(IV) with the following determination of each of them from one sample by amperometric titration of reextracts by means of DT. A methodic of atom absorption determination of osmium has been suggested.



## INDUCED DECREASING PH GRADIENTS IN CHELATING CHROMATOGRAPHY

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The eluent acidity is one of the important parameters affecting on separation efficiency and on column loadability in liquid chromatography. The pH-gradients are widely used for separation or purification of biological zwitter-ionic compounds, and lately - for preconcentration and separation of metal ions on chelating sorbents. Two approaches exist for pH gradient formation within ion-exchange columns: the chromato-focusing technique and inducing technique. For decreasing pH gradient formation in the chromatofocusing technique, an anion-exchange column are equilibrated by start buffer under higher pH, and then passed the buffer eluent with noticeably (greatly) lower pH through the column. The smooth decreasing of eluent pH is observed as a result of consecutive titration of sorbent basic groups by acidic eluent. The alternative technique consists of periodical injection of 1-2 ml of inducing solution at higher pH in flow of buffer eluent. The concentration of inducing solution as a rule is higher in 10-100 times, that leads to quick re-equilibration of sorbent and to following smooth changing pH at column outlet. The inducing technique allows to reduce the time of pH gradient formation in 3-4 times.

The induced decreasing pH gradients were pioneered in the use for the separation of metal ions within the column, packed with chelating sorbents (olygoethyleneamines bonded silica and carboxylated polymer matrixes). The separation is based on complexation of metal ions with ionogenic groups under initially higher pH and subsequent chelates dissociation during linear pH decreasing in sorbent layer. The adjustment of high ionic strength in both mobile phases allows to form smooth quasi-linear induced pH gradients even using single-component eluent (i.e., citric or acetic acid).

The possibility of inducing of pH gradients within thin long capillaries with flowing retentive stationary phase based on propylamine or polyethyleneimine was shown.

The applicability of induced pH gradients for separation of metal ions within anion- and cation-exchange columns was verified.

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## DETERMINATION OF COATINGS THICKNESS BY MEANS OF DESK-TOP XRF SPECTROMETERS

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For direct measurement of coatings thickness on some basement it is necessary to have a set of reference samples, but practical preparation of that set meets with serious problems. Much more simple procedure of coatings thickness measurement may be realized on the base of comparison of the intensity of the characteristic line from the coating with the intensity of the bulk sample, having the same composition ( $I(d)/I(\infty)$ ). In this case coating thickness determination by means of XRFA is realized on the base of solution of the equation between the intensity of characteristic line and the thickness of the coating and its composition as well as the composition of the material of the basement as the scattering in it as well as its characteristic emission may cause a significant input into intensity of the coating characteristic line emission.

In case if coating material consists only of a single element (that is the most typical case) it is not very complicated to calculate the calibration curve for any characteristic line of coating element. This calibration curve sets relation between ( $I(d)/I(\infty)$ ) and coating thickness D. The estimations demonstrate that by means of such approach is possible to make the measurements of the coatings in the range of 10 - 60 micrometers. The calibration curves were calculated for the measurements on the spectrometers SPECTROSCAN MAX-G, and SPECTROSCAN MAX-GV.

But more interesting and accurate possibility of coating measurement may be realized on the base of the measurement of the intensity of the characteristic line not of the coating but of the bulk material forming the basement. The estimations made for Ka and Kb lines of iron plated by zinc has demonstrated that in this case is possible to carry on the measurements of coating thickness up to 40-50 micrometers. The usage of beta lines, having higher energies then alpha lines, is more preferable. It is only necessary to keep in mind that in realization of that analysis is necessary to take into account possible excitation of basement material characteristic lines by means of characteristic lines of coating excited by the initial tube spectra. In case of iron coated by zinc this effect may be very significant, especially for rather thick coatings. In case of zinc thickness of about 40 micrometers the increase of iron lines intensity may be 4 or 5 times due to this effect.

The experiment testing was realized on the steel samples having zinc coating. The samples were made of steel tape used for cables protection having surface density 100 and 200 g/m<sup>2</sup>, which corresponds to the thickness of zinc costing about 14 and 28 micrometers. The measurements on the base of the presented above procedure has given the thicknesses of 20 and 25 micrometers.

# **ELECTROCHEMICAL STUDIES ON INHIBITION OF MILD STEEL CORROSION BY NICOTINAMIDE**

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Nicotinamide (pyridine 3-carboxylic acid amide) is effective inhibitor for mild steel corrosion in acidic solution. The effect of nicotinamide on mild steel dissolution in sulfuric acid has been investigated by electrochemical methods like steady state galvanostatic polarisation measurements, potentiodynamic polarisation measurements, impedance measurement and cyclic voltammetry. The dissolution parameters like corrosion currents, passive current, flade potential, open circuit potential, cathodic and anodic Tafel slopes and inhibition efficiencies were determined. Passivating parameters have also been obtained and it is revealed that these are strongly Passivating additives. Synergistic effects of I ion in these have a strong impact on the performance of these additives. These results were also verified by weight loss methods. The surface analysis studies carried out with the help of SEM also supplement the electrochemical results.

## DETERMINATION ORGANIC COMPOUNDS BY DIFFUSE REFLECTION SPECTROSCOPY

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Trinitrophenol as well as other polyderivations is an associated additive of polynitroaromatic explosives. Normally, sample preparation of these compounds is provided by solid face extragents (SPE) which show strong affinity to many organic compounds, so for the further accurately analysis separation of nitrophenols with the use of HPLC/MS method is needed. To quickly collect data in a forensic analysis on criminal and terroristic activities, where there is often a need of express field methods, we propose a selective solid phase reagent. It allows to combine sample concentration steps with a visual-test or more precise solid phase spectrophotometric method. As a matrix of SPE we used silica with ion-exchange ethylsulfonic acid groups. A selective photometric reagent for nitrophenols determination – 2,3,5-tripheniltetrasolium chloride ( $\text{Ph}_3\text{Taz}^+\text{Cl}^-$ ) - was used as a modifier. Optimal sorbtion-desorbition conditions of modifier and its hydrolytic stability were determined. Kinetic performance and optimal acidity of polynitroaromatic phenols sorbtion were studied. Interphase interaction research was realized through a diffusive reflection spectroscopy method. Increase of the analytical signal was determined in a reflection spectrum with polynitrophenols content growth on the surface of SPE. With these data we determine the chemical character of polynitrophenols sorbtion with  $\text{Ph}_3\text{Taz}^+\text{Cl}^-$  immobilized on their surface as a result of molecular complex formation between the electron acceptor (analyt) and electron donor (modifier). Influence of organic and inorganic compounds on nitrophenols determination results was studied.

# EXTRACTION-SPECTROPHOTOMETRIC DETERMINATION OF PHOSPHATE AND ARSENATE USING IONIC ASSOCIATES OF POLYOXOMETALATES WITH BASIC DYES

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Different extraction-spectrophotometric procedures were proposed for the P(V) and As(V) determination as ionic associates (IA) of polyoxometalates with basic dyes. Main disadvantage is difficulty in separation of reagent excess. Flotation, centrifugation or extraction does not allow to create sufficiently sensitive procedures due to worsening of reproducibility.

Two procedures for the extraction-spectrophotometric determination of P(V) and As(V) have been developed.

First procedure consists of several stages. 11-molybdo-bismuthphosphate (MBP) is formed and extracted with butyl acetate, stripped with ammonia or acetate buffer solution and determined in aqueous solution using reaction of MBP with Astro Floxine (AF) or other polymethine dyes. Full separation from molybdate excess is not necessary in this procedure as spectrum of IA differs considerable from dye spectrum. Therefore separation is simplified and used only as preconcentration step. Concentration factor 50 and good reproducibility make possible determination of low P(V) concentrations at  $10^{-8}$  mol/l level and lower.

Extraction and flotation separation of POMs as ion-pair with a bulky cation of Astrazone Violet (AV) with different organic solvents is investigated. Conditions for separation of dye excess from ion-pair  $\text{PMo}_{11}\text{TiO}_{40}^{5-}$  with polymethine dye AV are found.

Procedure has been proposed for the P(V) and As(V) determination based on the selective extraction of ionic associate of Crystal Violet with reduced molybdophosphate with mixture of inert (toluene) and active (methyl isobutyl ketone) solvents. Extraction of reagent is negligible. After concentration determination lower than  $10^{-7}$  mol/l of P(V) and As(V) is possible.

# SIMULTANEOUS DETERMINATION OF ORGANIC COMPOUNDS IN MIXTURE USING THE SUBSEQUENT EXTRACTIONS

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In practice of chemical analysis of organic substances, for some classes of compounds measuring of summary concentration in re-count to one of representatives is used. In the case of need of information about the content of each component, the chromatographic methods are applicable.

However, it is possible to use two-dimensional spectra in spectrophotometry as an alternative. In this case, the pH value of the water phase in extracting systems is used as a supplementary coordinate.

The procedure of simultaneous extracting-spectrophotometric determination of nitrophenols in wastewater is proposed on the example of the analysis of mixtures of mono-, di-, and trinitrophenols. The procedure consists of extraction concentrating in an acid medium, and sequential back-extractions under various pH. Such procedures give possibility for isolation *o*-, *m*-, *p*-nitrophenols,  $\alpha$ -,  $\beta$ -,  $\gamma$ -dinitrophenols and trinitrophenol in separate groups. Simultaneous determination is carried out by summary light-absorption of nitrophenol-ions. The error of determination concentrations on maximum contaminant level in natural waters doesn't exceed 10%. The peculiarities of application of the sequential extractions under fixed pH were studied on the example of mixture of simplest phenols (phenol, *o*-, *m*-, *p*-cresols). The procedure of their determination is based on the extraction to carbon tetrachloride, subsequent back-extraction and spectrophotometric measurement of interaction products with diazo-*p*-nitroaniline.

The system of anionic surfactants is another example of organic compounds' mixtures. The procedure of their determination is proposed using coordinate pH in two-dimensional spectra of ionic associates' anionic surfactants with rhodamine 6G. This procedure was tested on the analysis of surfactant waters and domestic detergents.

# OPTIMISATION OF MICROBAND ELECTRODE SIZES AND LOCATIONS WITHIN A RECTANGULAR MICROFLUIDIC CHANNEL FOR ELECTROCHEMICAL MONITORING OF HYDRODYNAMIC FLOW PROFILES

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We have previously proposed a method for reconstructing any hydrodynamic flow profile occurring locally within a rectangular microfluidic channel based on experimental currents measured at single or double microband electrodes embedded in one channel wall. This is of great interest since we have reasons to believe that flow profiles in microfluidic systems might not conform to the classical hydrodynamics which predicts a parabolic flow. The flow reconstruction was achieved by the solution of a variational problem which resulted in a flow profile function based on experimentally measured currents at single or double microband electrodes. However, it was found that the performance of the reconstruction procedure strongly depends on the geometry of channel flow cell and local hydrodynamics. For instance, when the size of an electrode is very small the diffusion layer extends only over a small fraction of channel height and thus the electrode ‘sees’ only the gradient of flow profile at channel floor and its current is insensitive to the shape of flow profile in the most of channel height. On the other hand, when the electrode is very large as compared to channel height and corresponding rates of convection and diffusion the situation resembles that of a thin-layer cell and the current is proportional to average flow velocity regardless of actual shape of flow profile.

In this work, we determine constraints on the dimensionless parameters of the system (dimensionless electrode widths, gap size and Peclet number), first qualitatively and then quantitatively, which ensure that the proposed flow reconstruction approach is sufficiently sensitive to the shape of the flow profile. The results can be readily applied for identification of hydrodynamic regimes or electrode geometries that provide best performance of our flow reconstruction method.

**DETERMINATION OF 1-[2-OXO-2-(TRIFLUOROMETHYL-10-PHENOTHIAZINYL)-ETHYL]-4-HYDROXYIMINOMETHYL-PYRIDINIUM CHLORIDE BY DERIVATIVE UV-SPECTROPHOTOMETRY**

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Some phenothiazinyl phenacylpyridinium oximes, characterized by the hydroxyiminomethyl group in the position 4 of the pyridine ring, were synthesized and checked for antidotal activity in poisonings by highly toxic organophosphorus compounds, such as pesticides or nerve gases. As continuous of our investigation on determination of this type of compounds, in present work suitable conditions for direct second derivative spectrophotometry determination of 1-[2-oxo-2-(trifluoro-methyl-10-phenothiazinyl)-ethyl]-4-hydroxyiminomethyl-pyridinium chloride in solution were established.

Spectrophotometric curves were recorded on a GBC Cintra 20 UV-Visible spectrophotometer over the spectral range 225-400 nm, against a corresponding blank. Values of pH were determined by PHM 62 Standard pH-meter (Radiometer, Copenhagen). Ultraviolet absorption spectra of oxime has been examined in Britton-Robinson buffer solutions in pH range between 2.2 and 10.0. In the pH range between 2.2 and 7.0 exists one maximum of absorbance, and the other in alkaline medium. Although both of them can be used for analytical determination, the second order derivative UV-spectrum was chosen for analysis because the absorbance band in the zero order spectrum of investigated oxime is broad, in acid medium.

The calibration graph was constructed by plotting 1-[2-oxo-2-(trifluoromethyl-10-phenothiazinyl)-ethyl]-4-hydroxyiminomethylpyridinium chloride concentration versus peak to-peak amplitude in the second-derivative UV spectrum between 240-330 nm. The Beer's law was verified over the concentration range from  $2 \cdot 10^{-6}$  to  $2 \cdot 10^{-5}$ M. The regression equation was  $y=0.00409x-3.425 \cdot 10^{-5}$  with correlation coefficient (r) of 0.99989 indicating good linearity. The precision of the method was determined at three different concentrations of oxime. From the results obtained it might be concluded that the proposed method is simple and fast, allow precise and accurate results, and it can be applied to assay of small amounts of 1-[2-oxo-2-(trifluoromethyl-10-phenothiazinyl)-ethyl]-4-hydroxyiminomethyl-pyridinium chloride.



# HPLC DETERMINATION OF PHENOLS WITH PHOTOMETRIC AND AMPEROMETRIC DETECTORS

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For selective estimation of phenols pollution of environment such chromatographic methods as gas chromatography with flame-ionization detector (ISO method 8165) and high performance liquid chromatography with UV-detector (EPA method 625) is recommended. For determination of phenol, cresols, chlorophenols in environmental samples application of HPLC with amperometric detector is perspective. Phenols and chlorophenols can be easy oxidized and determined with high sensitivity on carbon-glass electrode.

The comparison of analytical characteristics HPLC methods of determination of phenols with application amperometric and photometric detectors was carry out in this work. Experiment was executed with use liquid chromatograph "Zvet-Yauza" and 100 mm-3mm; 150mm-3mm column with Silasorb C18 (5; 10  $\mu\text{m}$ ). With amperometric detector phenols were detected in oxidizing regime on glass-carbon electrodes. With photometric detector phenols were detected at 254 nm.

The influence of such factors on sensitivity of amperometric detector as voltage of work electrode and eluent composition was investigated. Although peak of phenol presence on chromatogram even with acetonitrile – water mobile phase, the high sensitivity of amperometric detector can be achieved with acetonitrile – acetate buffer or acetic acid solution. Maximum response of electrochemical detector was obtained at +1200 mV voltage of work electrode. In the optimal conditions comparison of characteristics of amperometric and photometric detectors was carry out. Optimization of mobile phase composition allow to separate some mixture: phenol, 2-chlorophenol, 4-chlorophenol, 2,4-dichlorophenol, 2,4,6-trichlorophenol; cresols and guaiacol; hydroquinone, resorcinol, pyrocatechol, phenol; phenol and aminophenols.

HPLC method with amperometric detection was applied for determination of phenols in sea sediment and some drug preparation. Peaks of phenol, guaiacol, cresols, hydroquinon and resorcinol were identified on chromatogram of birch tar. The HPLC method with electrochemical detectors was used for determination of some drug preparation of aminophenol derivate. So *p*-acetaminophenol (paracetamol) was determined in some drug.

# CHROMATOGRAPHIC BEHAVIOUR OF PYRETHROID PESTICIDES

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Synthetic pyrethroids is one of the group of modern insecticides of cyclopropanecarboxylic acid derivative. The pyrethroids preparation is the racemic mixture of optical isomers or mixture of *cis*- or *trans*-isomers.

This peculiarity of pyrethroids needs to take into account during gas chromatographic determination.

The specialities of chromatographic behaviour of cypermethrin, permethrin,  $\lambda$ -cyhalothrin, deltamethrin and fenvalerate were investigated in this work. Gas chromatographic determination was carried out with use of packed column with stationary phase of different polarity (OV-101, OV-210; OV-17) and capillary and polycapillary columns with non-polaric stationary phase. Chromatographic peak identification was realized with attraction GC-MS method.

It was shown that on cypermethrin chromatogram with packed column (1m-2mm; Chromaton-N-super + 5%OV-101) present one peak, although preparation is the mixture of eight isomers. But with use of capillary column (25m-0,32 mm; HP-5) on chromatogram present four peak. With assistance GC-MS this peaks were identified as cypermethrin isomers. The permethrin is the mixture of two geometric isomers (*cis*- and *trans*-). With packed column with non-polaric stationary phase on chromatogram isomer peaks are not separated. In that time with application of packed column with medium-polaric stationary phase (OV-210; 1,5%OV-17 + 1,95%QF-1) or capillary column separated peaks *cis*- and *trans*-isomers were presented on chromatogram. Their identification was confirmed GC-MS method assistance. Preparation  $\lambda$ -cyhalothrin is the mixture of *R*- and *S*-isomers, but on packed column with non-polaric stationary phase was obtained single peak on chromatogram. The application of capillary column (HP-5) was permitted separate of isomer peaks. Gas chromatography of deltamethrin was realized with capillary column and packed column with 2 mm diameter, although GC-method as methyl ether derivative was recommended for deltamethrin. In case capillary column two peaks present in chromatogram and with assistance of GC-MS methods these peaks were identified as deltamethrin isomers. By analogy with other pyrethroids separation of *R*- and *S*-isomers of fenvalerate is not possible in packed column, but is going in capillary column.

## PROBLEMS OF SIMILAR COLUMN IN QUANTITATIVE ANALYSIS BY REVERSED-PHASE HPLC

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Except for the high molecular weight range, nearly all substances can be separated by reversed-phase (RP) HPLC. The many different separation mechanisms in RP HPLC, based on hydrophobic, hydrophilic and ion-pairing interactions, and size exclusion effects together with the availability of a large number of high quality stationary phases, explain its great popularity. At present approximately 90% of all HPLC separations are carried out by reversed-phase mode of HPLC, and an estimated 800 different stationary phases for RP HPLC are manufactured worldwide.

The understanding of retention and selectivity behaviour in reversed-phase HPLC in order to control and predict chromatographic properties are interesting for both academic scientists and manufacturers. A number of retention and selectivity models are the subject of ongoing debate. The theoretical understanding of retention and selectivity, however, still lags behind the practical application of RP HPLC. In fact, many users of RP HPLC techniques very often select stationary phases and other experimental conditions by experience and intuition rather than by objective criteria.

Having wide and increasing quantity of RP HPLC sorbents in disposal the main question in RP HPLC is their interchangeability. Column characteristics that are usually described by their manufacturers are not full enough for the analytic to choose a suitable column for the specified resolutions or he ought to choose other similar column used before. In fact, nomenclature of reversed-phase stationary phases is too unsophisticated and is a source of confusion in their application.

In this work the state-of-the-art and perspectives of column characterization and comparison have been presented and discussed. All information about physico-chemical properties of RP HPLC C18 and C8 columns as porosity, average surface area, free silanol concentration, binding ligand density and others, were summarized. The points of views about column classifications, its advantages and disadvantages were discussed. It was shown that C18 and C8 HPLC column classification processes do not allow selecting the column with the same or prearrange selectivity.

## VOLTAMMETRIC DETERMINATION OF Co(II), Ni(II) AND Pd(II) IN THE COMPATIBLE PRESENCE

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In practice of analytical chemistry during the long period of time the opened is the problem of compatible determination of elements with near chemical, analytical characteristics. Among them there is a cobalt, nickel and palladium, which are used in different types of industrial products, semiconductor materials, medical preparations, and also biological substrates. It is heavy to find methods that would not be used for the analysis of these materials now. However majority from the known methods of determination of microamounts of nickel, cobalt and palladium is needed previous concentration and separation from concomitant elements. Deciding this problem is succeeded using correctly neat organic reagents that allow to conduct not only separate determination of elements but also to promote the sensitiveness of their determination.

It is set that the ion of Pd(II) forms polarographic active complex compound with *o*-hydroxysubstituted azodyes – tropeolin 0 (acetate buffer solution  $E = -0,58V$ ). The limit of detection Pd(II) ions is  $2 \times 10^{-7}$  mol/l. Instead complexforming between the ions Co(II), Ni(II) and tropeolin 0 in the optimum terms of the Pd(II) determination in general is absent. It enables to conduct the Pd(II) determination in presence the 200-multiple surpluses Co(II) and 80-multiple surpluses Ni(II).

For the increase of sensitiveness of the voltamperometric determination Co(II) use *o,o'*-dihydroxysubstituted azodyes (eriochrome red B and calces). The Co(II) determination can be conducted at potential of reduction of coordinating connection of Co(II)-azodye ( $E = -0,9V$ ) and directly the Co(II) ( $E = -1,2V$ , ammonia buffer solution) ions. The results of researches show that selectivity of the Co(II) determination in presence the Ni(II) and Pd(II) ions more high with the use of analytical signal at the potential  $-1,2V$ . It is thus succeeded move aside potentials of peaks of reduction of the Ni(II) and Co(II) ions on a background ammoniac buffer solution from  $\Delta E = 0,2V$  to  $\Delta E = 0,4-0,5V$ . The Co(II) determination can be conducted in presence 50-100 multiple surpluses Ni(II). Palladium in these conditions does not prevent to 60 multiple surplus.

# DETERMINATION OF SODIUM ACYLISETHIONATE IN THE COMBI SOAP BY REVERSED – PHASE HIGH – PERFORMANCE LIQUID CHROMATOGRAPHY

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The combined soap (CS) is a mix of fatty acids salts (FAS) and different surfactants. The surfactants usually sodium acylisethionats (AIST), which are derivates of fatty acids, as a rule, coconut oil or lauric fraction.

The method of the analysis of the CS described in the international standard ASTM (D 820 – 93) is a long time, multi-stage procedure. Accuracy of AIST determination is low, since surfactants determined by an indirect method of subtraction. Thus, the objective of our research was to develop an exact and express method of AIST determination in CS.

As a method of research, has been used high-performance liquid chromatography in reversed - phase regime (RP HPLC). The advantage of the present method is the following: the additional information about AIST and FAS composition (homologous distribution); simple preparation of samples (dilution of a CS sample of in a mobile phase).

The research has been carried out by the liquid chromatograph Perkin-Elmer (Series 200), which has tandem detectors: the diode array ( $\lambda=210$  nm) and the refractometer. The temperature of a column was 30°C, speed of a mobile phase is 1.5 ml/ min. As a mobile phase, mixtures of solvents methanol - water and acetonitrile - water with addition of sodium perchlorate. The columns with the modified silica gel C8 and C18 (4.6×220 mm, 5  $\mu$ m) were used for separation of the AIST and FAS components. In order to make the identification of AIST and FAS components more reliable the ratio of the values of the above-mentioned detectors signals of each substance analyzed.

We have found out, that a mobile phase methanol - water and a column of the sorbent C8 should be used for separation AIST and FAS components. The duration of the analysis has been 20 minutes. The error of AIST determination does not exceed 2 percent.

# ON DEPENDENCE OF THE PRIMARY RADIATION FILTRATION EFFECTIVENESS ON THE DETECTOR RESOLUTION IN AN ENERGY DISPERSIVE X-RAY FLUORESCENT ANALYSIS

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The main factor limited x-ray fluorescent energy dispersive analysis sensitivity is a background due to scattering of x-ray tube continuous spectrum on a sample. To lower the background a monochromatic and/or polarized radiation is using in many devices. However these methods result in considerable lowering of the spectrometer efficiency and require corresponding increase of the exciting radiation power. For small-sized (benchtop or portable) devices a more economical method for image contrast increasing is considering as advanced one – primary radiation filtration being provided by introduction of a proper filter between the X-ray tube and a specimen to be studied. His way is realized in many energy dispersive instruments. The optimum thickness and the filter material are determining by an specimen to be analyzed, spectral composition of the exciting radiation and a detector characteristic, in the first place, by its resolution.

In the presented work an algorithm for the primary radiation filter optimization has been developed and realized in the Mathcad envelope which provides a minimal detection limit of a critical element both at the given X-ray tube power and at the given maximal acceptable count rate.

The algorithm is based both on a mathematical simulation of a spectrum of secondary radiation emitted by a sample to be studied and the detector response function. The detection limit  $C_0$  is given by criteria 3s:

$$C_0 = C \frac{3\sqrt{B}}{I_C \sqrt{T}},$$

where B and  $I_c$  – count rates of the background and the line at C concentration near 0 (in the linear range), T – exposure time.

The results of simulation have been confirmed by determination of Fe traces in quartz sand, Cu and Mo in flotation tails and Ag in waste fixing waters on BRA-17-02 analyzer based on X-ray gas-filled electroluminescent detector and on BRA-18 analyzer based on Si-drift detector. The results of the simulation conform satisfactory with the experimental data: in the mentioned cases the optimum filtration results in 2 to 5 times lowering of the detection limit.

# FLOW INJECTION ELECTROCHEMICAL HYDRIDE GENERATION ATOMIC ABSORPTION SPECTROMETRY FOR THE DETERMINATION OF ARSENIC

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A flow-injection system with electrochemical hydride generation and atomic absorption detection for the determination of arsenic is described. This technique has been developed in order to avoid the use sodium tetrahydroborate, which is capable of introducing contamination. The sodium tetrahydroborate ( $\text{NaBH}_4$ ) - acid reduction technique has been widely used for hydride generation (HG) in atomic spectrometric analyses. However, this technique has certain disadvantages. The  $\text{NaBH}_4$  is capable of introducing contamination, is expensive and the aqueous solution is unstable and has to be prepared freshly each working day. In addition, the process is sensitive to interferences from coexisting ions.

A simple electrochemical flow-through cell with powder carbon as cathodic material was used and optimized. The influence of the generation current, concentration of the catholyte, carrier stream, flow rate of the sample and interferences by other metals on the generation of hydrogen arsenide were studied. This system requires only a small sample volume and is very easily automatized. The electrochemical HG technique combined with AAS is a well-established method for achieving the required high sensitivity and low detection limits.

A Perkin-Elmer 5000 AAS was used, with an electrically heated quartz tube atomizer. The electrolyte is continuously conveyed by peristaltic pump. The sample solution is introduced into the loop and transported to the electrochemical cell. A constant current is applied to the electrolytic cell. The gaseous reaction products, hydrides and hydrogen, formed at the cathode, are flowed out of the cell with the carrier stream of argon and separated from the solution in a gas-liquid separator. The hydrides are transported to an electrically heated quartz tube with argon and determined under operating conditions for hydride forming elements by AAS.

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# A KINETIC METHOD FOR DETERMINATION OF 2,4-DINITROPHENOL

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A kinetic method for the determination of 2,4-dinitrophenol is proposed. The method is based on the inhibiting effect of 2,4-dinitrophenol on the Mn(II) catalysis of the oxidation of malachite green with potassium periodate. The reaction was followed spectrophotometrically at 615 nm. The optimal experimental conditions for the determination of 2,4-dinitrophenol were established under the optimal reaction conditions:

$$C_{\text{MG}} = 1.6 \cdot 10^{-6} \text{ mol} \cdot \text{dm}^{-3}, C_{\text{CH}_3\text{COOH}} = 2.5 \text{ mol} \cdot \text{dm}^{-3},$$

$$C_{\text{Mn(II)}} = 2 \cdot 10^{-6} \text{ mol} \cdot \text{dm}^{-3}, C_{\text{KIO}_4} = 2 \text{ mol} \cdot \text{dm}^{-3}, t = 25 \pm 0,1^\circ\text{C},$$

the 2,4-dinitrophenol concentration was varied from 92 - 920  $\text{ng} \cdot \text{cm}^{-3}$ .

A linear dependence was established between  $\text{tg}\alpha$  and the concentration of 2,4-dinitrophenol:

$$\text{tg}\alpha = 0,061 - 0,0416 \times C_{\text{DNP}} \quad r = 0,998$$

The calibration line which can be used for the determination of the 2,4-dinitrophenol concentrations in the interval mentioned.

Kinetic expression for the reaction in the presence and absence of 2,4-dinitrophenol are postulated. The effects of certain foreign ions upon their action rate were determined for the assessment of selectivity of the method.

The method was applied for the determination of 2,4-dinitrophenol in urine. The reproducibility was very good. The results obtained by the proposed method also agreed well with the values obtained by standard methods.



# X-RAY FLUORESCENCE ANALYSIS OF COLLOIDAL SYSTEMS

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A lot of natural as well as technological objects of analytical control are colloidal systems, i.e. human blood, biological liquids, sol and suspension forming in different technological processes (ore-dressing, electrochemical deposition, catalysis and other), food, paint-and-lacquer materials, sewage water and other.

If the colloidal systems are considered as objects of X-ray fluorescence analysis, some special features are to be mentioned.

1. Density of colloids and concentration of determined elements in them are lower than in the solid samples but a little more than in the solution.
2. Light elements predominate in the colloid's composition.
3. Colloid systems are heterogeneous.

Thus, the contribution of coherent and non-coherent (Compton) scattering in attenuation of primary radiation and fluorescence increase in comparison with the solid samples.

The goal of our investigation was to develop the X-ray fluorescence analysis procedure for the determination of heavy metals in the paint-and-lacquer materials.

The procedure of determination of metals in the thin layer without elimination of the non-volatile organic components for different paints containing inorganic pigments was developed. Several techniques of sampling from paint-and-lacquer materials for X-ray fluorescence analysis were proposed. For the study of nonhomogeneity of metal distribution in the thin layer we used additionally the local method of X-ray fluorescence analysis.

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# APPLICATION OF SYNTHETIC CALCIUM HYDROXOAPATITE IN LIQUID CHROMATOGRAPHY

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Selectivity of chromatographic separation is known to be varied by changing both the nonstationary phase composition and adsorbent nature. It is shown that the less are the values of the reached selectivity coefficient the higher are the requirements to column effectiveness. In this connection the choice of stationary phase with high and predicted selectivity coefficient for the compounds being separated is still remains a topical problem of high-performance liquid chromatography.

The hydrogen bonding between sample and solute molecules in polar solvents can also play an important role in affecting sample retention and solvent selectivity. The strength of retention polar molecules appears to be caused by the strength of surface hydrogen bonds. Since POH-groups of calcium hydroxyapatite are capable of forming the strongest hydrogen bonds it can be expected that organic bases will be hold more strongly and selectively on calcium hydroxyapatite surface than on, say, silica gel surface.

A theoretical description of hydrogen bonding effects can be made from model of charge-controlled adsorption. It was found that the energy of adsorption of organic molecules are determined by the ratios between the effective charges of their atoms and atoms in polar solvent molecules:

$$E_{\text{ads}} = E_{12} - E_{23} - E_{13} \approx Q_1 Q_2 / \epsilon R_{12} - Q_2 Q_3 / \epsilon R_{23} - Q_1 Q_3^* / \epsilon R_{13},$$

where the indexes 1, 2 and 3 designate adsorbent, adsorbate and solvent;  $E_{ij}$  is the Coulombic energy;  $Q_{ij}$  is the greatest effective charges of atoms; and  $R_{ij}$  are the interatomic distances in the adsorption and solvation complexes.

It was shown that selectivity of adsorbents in liquid chromatography might be considered as sum of nonspecific and specific parts. The angular factor of dependence  $E_{\text{ads}} = f(Q_2)$  determines nonspecific charge-controlled selectivity of adsorbents:

$$\alpha = \gamma_2 / \gamma_1 \exp(Q_1 / R_{12} - Q_3 / R_{13})(Q_N - Q_K),$$

where the indexes N and K designate different adsorbates;  $\gamma_i$  is the molecule size. The specific selectivity is determined by the additional orbital interactions between adsorbent and adsorbate.

The value of  $Q_j$  for calcium hydroxyapatite can be defined by charge of  $\text{Ca}^{2+}$  and  $\text{PO}_4^{3-}$  ions. From this point of view calcium hydroxyapatite can be used as high-selective adsorbents for high performance liquid chromatography because with increasing of  $Q_j$  will be rise a selectivity coefficient  $\alpha$ .

# KINETIC METHOD FOR DETERMINING ANTIOXIDANT DISTRIBUTIONS IN MODEL FOOD EMULSIONS

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The activity of antioxidants in food [1] emulsions and in some biological systems [2] is depends on a multitude of factors including the localisation of the antioxidant in the different phases of the system. The aim of this study is determining antioxidant distributions in model food emulsions. For the purpose, we measured electrochemically the rate constant of hexadecylbenzenediazonium tetrafluorborate (16-ArN<sub>2</sub>BF<sub>4</sub>) with the antioxidant, and applied the pseudophase kinetic model to interpret the results.

The reactions are carried out under first-order conditions, i.e., the stoichiometric concentration of the antioxidant,  $\alpha$ -tocopherol, is in large excess over that of 16-ArN<sub>2</sub><sup>+</sup> such that the concentration of  $\alpha$ -tocopherol does not change significantly throughout the time course of the reaction. The emulsion employed was prepared by mixing the non-ionic emulsifier Brij 30, octane and HCl (3 mM, pH = 2.5). The resulting emulsion is opaque, thus  $k_{\text{obs}}$  values were obtained electrochemically by employing Linear Sweep Voltammetry (LSV).

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# APPLICATION OF SURFACE-ASSISTED LASER DESORPTION IONIZATION TO THE DETECTION OF BIOMOLECULES

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Matrix-assisted laser desorption/ionization (MALDI) is widely used for the detection of organic molecules. One of the limitations of the method is a strong matrix background in low-mass (up to 500-700 Da) range. In present work an alternative approach based on the application of rough matrix-less surfaces and known as surface-assisted laser desorption/ionization (SALDI), has been applied.

The study of surfaces of various nature (polished, etched and grinded silicon, graphite of different porosity and density, grinded and sputtered germanium) and comparison of sensitivity, desorption/ionization efficiency of analytes, nature and intensity of background, surface morphology etc., shown, that analytical signal from thermolabile biomolecules can be obtained for the surfaces of different materials with various roughness (in part, non-porous), and signal value differs in an order of magnitude for masses of 500 Da. Maximum amplitudes were observed for rough non-porous silicon and different types of graphite, minimum – for germanium sputtered on the silicon substrate. The best uniformity and integral signal values were obtained from rough non-porous silicon and graphite surfaces. Graphite substrates allow to obtain ion signal in more wide mass range with lower laser energy threshold. Probably, this is connected with the differences in a protonation mechanism of molecules as well as in the strength of their adsorption binding with the surfaces of different nature. At the same time, unlike silicon surfaces, graphite surfaces are characterized by higher background. To eliminate the negative properties of the surfaces, their chemical modification was tried. Modified surfaces demonstrate higher sensitivity and uniformity as soon as lower background.

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# TRANSMITTANCE-NIR AS AN ENVIRONMENTALLY FRIENDLY TOOL FOR QUALITY CONTROL AT PESTICIDE INDUSTRY

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A critical study has been carried out in order to evaluate the capabilities of Near Infrared spectroscopy for the analysis of commercial pesticide formulations using transmittance measurements. In this sense, it has been evaluated the determination of active ingredients in agrochemical formulations after extraction with an appropriate solvent.

The number of accumulated scans and nominal resolution have been tested in order to ensure a compromise between sensitivity and sampling frequency.

Different calibration models, such as classical least squares and multivariate calibration approaches have been considered.

Moreover recovery studies on commercial spiked samples were developed in order to assess the no contribution of the matrix and evaluate the accuracy of the proposed procedure.

Results obtained by the developed procedures were statistically comparable with those obtained by reference chromatographic techniques.

On considering the solvent consumption and waste generation, it is clear that NIR measurements reduce drastically the amount of  $\text{CH}_3\text{CN}$  consumed compared with the HPLC procedure. On the other hand, the sample frequency obtained by the NIR methodology was higher than those obtained by HPLC.

We can conclude that transmittance near infrared based methodology provides an accuracy and precision agree with those required by CIPAC for the pesticide analysis in commercially available formulations.

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# DETERMINATION OF NUTRITIONAL PARAMETERS OF YOGHURT SAMPLES THROUGH PARTIAL-LEAST-SQUARES ATTENUATED TOTAL REFLECTANCE FOURIER TRANSFORM INFRARED SPECTROMETRY

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The aim of this work is the determination of several nutritional parameters, such as Energetic Value, Protein, Fat, and Carbohydrates content, in commercially available yoghurt samples by using Attenuated Total Reflectance Fourier Transform Infrared (ATR-FT-IR) spectrometry and a partial least square approach.

62 yoghurt samples, covering an important wide range of available types of yoghurts, were obtained from the Spanish market in order to develop the study and were directly measured after homogenization by manual shaking.

In order to select the instrumental conditions for carrying out the ATR measurements several parameters including the number of accumulated scans per spectra or nominal resolution were tested. To avoid the cross-contamination and to establish an appropriate strategy for cleaning the ATR cell between samples, several procedures were tested using background and blank controls. Moreover, the possible sample sedimentation on the ATR plate cell due to the complexity of the sample matrix during the spectra acquisition was also checked.

In order to evaluate possible classes among samples considered, a clustering analysis was carried out before PLS treatment for selecting properly a reduced but well representative calibration set.

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## 3,5-DIBROMO-PADAPH AS THE REAGENT FOR PLATINUM METALS DETERMINATION

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The purpose of the research - creation of a photometric technique of definition of Pt(II) at the presence of a Pd(II) and Rh(III) with the help 3,5-di-Br-PADAPH - 2-(3',5'-dibromo-2'-pyridilazo)-5-diethylaminophenol - the most perspective reagent from analogues of PAR-s.

In the table are submitted spectrophotometric characteristics of color reactions of platinum metals with a 3,5-diBr- PADAPH

*Table.* Color reactions of platinum metals with a 3,5-diBr-PADAPH  
( $n=3, P=5$ ).

Element	Media	$\lambda_{\max}$ , nm	$\Delta\lambda_{\max}$ , nm	$\varepsilon \cdot 10^{-4}$	M:R
Pd	pH 1,5±0,5 M H <sub>2</sub> SO <sub>4</sub>	610	140	3,6±0,2	1:1
Pt	pH 2,5±0,5	580	120	2,6±0,2	1:1
Rh	pH 4,2±0,4	590	140	2,1±0,3	1:1
Rh	pH 4,2±0,4	590	140		1:2
Ir	pH 5,2±0,4	580	130	2,3±0,3	1:1
Ir	pH 5,2±0,4	580	130		1:2

Reactions occurs in aqua-organic media: ~ 20-25 % isopropanole is optimal.

Full complexation with Pt(II) is reached at the presence of an ascorbic acid (optimum 4 mg/cm<sup>3</sup>) during 10-15 min at 65±5°C. At these conditions complexes of Pd lose stability and within a day there is their full destruction accompanying with decolouration of solutions. That makes possible definition of a Pd and Pt at joint presence, including at H<sub>2</sub>SO<sub>4</sub> media.

For maintenance of optimum values pH at definition of Rh and Ir used the acetic buffer mixes, prepared with addition of isopropanole. Colour of complexes develops within 2 h at 65±5°C or during 5 min under influence of microwave radiation.

Introduction at a reactionary mix up to 4 cm<sup>3</sup> conc. H<sub>3</sub>PO<sub>4</sub> on 25 cm<sup>3</sup> of a solution masks reaction of Rh(III) and does not prevent development of color reactions of a Pd(II) and Pt(II), that makes possible definition of Rh at the presence of a Pd and Pt.

By development of techniques for full removal of ignoble metals used sorbtion on sorbent POLIORGS(IV).

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## ELECTROCHEMICAL DETERMINATION OF GUAR IN COPPER ELECTROWINING PROCESS

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According to the results of copper electro wining process, for obtaining homogeneous and pure precipitation guar must be added to electrolyte. There for determination of guar are important. In this study considered the polarization potential and concentration has a logarithmic relation. These relation were study by using D.P.V (differential pulse voltammetry) technique different parameter such as copper and acid concentration, temperature, pulse height and scan rate were studied and optimum condition are:  $C_{H^+} = 176.99$  g/l,  $C_{Cu^{2+}} = 36$  g/l,  $T = 40$  °C,  $H_{pulse} = 50$  mv/s, scan rate = 10 mv/s. Then with optimum condition calibration curve was plotted and standard deviation of 10 replicated was  $S = 5.3 \cdot 10^{-3}$ . This method was applied in real sample.



# ENHANCED SIGNAL-TO-BACKGROUND RATIO WITH A HIGHLY ORDERED PYROLYTIC CARBON FILM AS AN ELECTROCHEMICAL INTERFACE

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Carbon has been most widely used electrode material in electroanalysis, electrocatalysis and electrosynthesis [1-3].

There are several methods for the fabrication of thin-film carbon electrode including sputtering [4, 5], electron beam evaporation [6], pyrolysis of polymeric thin film [7] and pyrolysis of gaseous hydrocarbons [8].

In this work we have fabricated a pyrolytic carbon film by chemical vapor deposition method (CVD) under specific deposition condition to obtain a carbon film with significant ordering of graphitic planes parallel to the hot substrate. We called this obtained pyrolytic carbon film "highly ordered pyrolytic carbon" (HOPC) in which high ordering of graphene layers has occurred. Therefore HOPC is structurally similar to pyrolytic graphite (PG) and highly ordered pyrolytic graphite (HOPG) that in their structures high ordering of graphitic planes is observed [2]. However the size of these graphitic planes in HOPC is very smaller than PG and HOPG as indicated by Raman spectroscopy.

The HOPC were characterized by Raman spectroscopy and scanning electron microscopy. In addition cyclic voltammetry was performed on the HOPC and the results were compared to glassy carbon (GC) for evaluating the electrochemical utility. Low background current and capacitance was observed. Also the rate of charge transfer were determined via cyclic voltammetry and the very interesting observation was that the signal-to-background (S/B) ratio was a factor of ~30 larger at as-deposited state HOPC than at freshly polished GC electrode for hexacyanoferrate redox couple.

The effect of electrochemical pretreatment was evaluated. We observed that electrochemical anodization at 1.9 V vs Ag/AgCl for 2 min and reduction step at -0.1V vs Ag/AgCl for 30 sec can improve the rate of charge transfer about one order of magnitude for hexacyanoferrate redox couple and also change surface microstructure. We used Raman spectroscopy to probe these changes.

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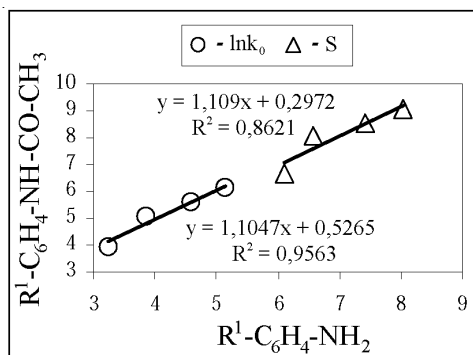
# APPLICATION METHANOL ELUENT RP-HPLC ANALYSIS FOR ESTERS OF 4-AMINOBENZENTHIOSULFINIC ACID AT PROCESS OF THEIR SYNTHESIS

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The esters of thiosulfinic acid  $R^1-SO_2-S-R^2$  are used as fungicides and antibacterial preparations. These compounds have similar structure fragments to allicin – natural insecticide from garlic with following structure  $(CH_2=CH-CH_2)_2[SO-S]$  (<http://www.ALLICIN.com>). For determination of ethyl S-ester of 4-aminobenzenthiosulfinic acid (esulan) in the ointment RP-HPLC was proposed [1] with acetonitrile : water=30:70 as eluent. For searching bioactive compounds the synthesis of new esters of thiosulfinic acid is perspective that was confirmed by results of recent studies as instance [2]. Therefore requirements are existed for investigation HPLC separations of these substances.

With eluent MeOH : H<sub>2</sub>O = 40:60% w (flow rate -1 ml/min) full separation was achieved within acetylated and non-acetylated on amino group of eight thioesters of 4-aminobenzenthiosulfinic acid with retention in next order for  $R^2 = -CH_3, -C_2H_5, -CH_2-CH=CH_2, -C_3H_7$  by RP-HPLC on Spherisorb-ODS-2 (250×4,6 mm). The chromatograms were obtained at 254 and 289 nm. Retention was generalized by  $\ln k = \ln k_0 - S \cdot \phi$  ( $\phi$  - MeOH volume part in range near 0.4-0.6) as shown in Fig.



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## POSSIBILITY OF USING GRASING EMISSION IN WAVE DISPERSION X-RAY SPECTROMETRIES

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Opportunities of definition of small impurity levels by means of X-ray spectral analysis are limited due to presence of the considerable background caused by that the primary radiation is reflected and disperses by the analyzed sample and gets on the detector. The contribution of a background to an analytical signal increases errors of obtained results. X-ray fluorescence analysis (XRF) is characterized by the reduced background. It is based on an irradiating of the analyzed sample by a X-ray tube. Available constructions of X-ray spectrometers allow to carry out such analysis only in one of modes: in a traditional mode when angles of incidence primary irradiation and picking out of fluorescent one are great enough, and also in modes of the total reflection (TR-XRF) or grazing-exit (GE-XRF). In last two cases the background is much less, than in the traditional mode, and the ratio a signal / background (contrast) is maximum.

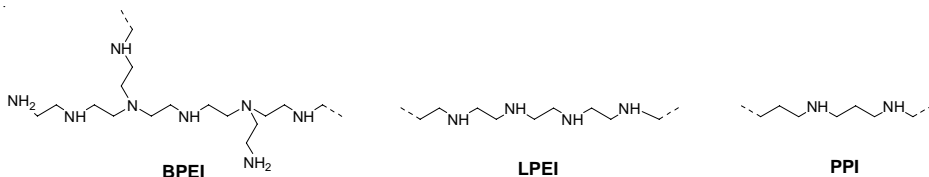
We succeeded to adapt the portable X-ray spectrometer SPARK 1, intended for measuring in a traditional mode, for work in the mode of GE-XRF (without changing the construction and X-ray optics of the spectrometer). For this purpose, it is offered the special cartridge which allows to reduce an angle of picking out of a characteristic X-rays up to 1-2 degrees instead of standard cartridge for the sample interposed into the socket of the specimen holder. It is shown, that using such cartridge causes the contrast increasing in 3-5 times in comparison with the contrast obtained using standard cartridge. This reception appeared efficient in the case of determination of small impurity levels in a sample. One should carry out XRF analysis in a traditional mode with standard cartridge for determination of major impurities levels.

# MICROCALORIMETRY AS A FACILE WAY TO SHOW PROPERTIES OF POLYAMINES

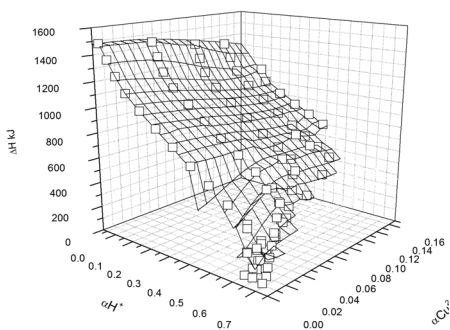
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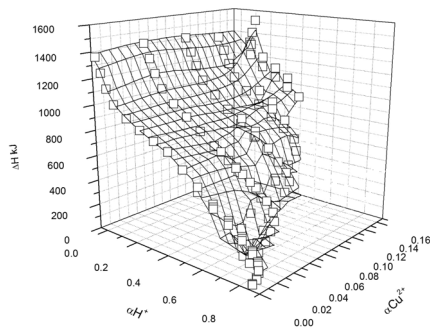
Usually the acid-base properties of polyelectrolyte are studied by potentiometric titrations. However it is well known, that understanding of polyelectrolyte properties in solution is based on the knowledge of the thermodynamic properties. Up to now, there is only a small number of microcalorimetry titrations of polyelectrolyte solutions published. Therefore we carried out potentiometric and microcalorimetric titrations of hydrochloric form of the linear and branched polyamines at 25°C and 65°C, to study the influence of the structure on the acid-base properties.



In addition we studied the complexation of  $\text{Cu}^{2+}$  by the polyamines using microcalorimetry and potentiometry. The enthalpy changes measured are presented as function of the degree of protonation and the amount of  $\text{Cu}^{2+}$  bound.



LPEI- $\text{Cu}^{2+}$



BPEI- $\text{Cu}^{2+}$

The thermodynamic parameters DH, DG and TDS were calculated as a function of the degree of protonation and the amount of  $\text{Cu}^{2+}$  bound at high ionic strength of LPEI, BPEI and PPI. The different behaviour of LPEI, BPEI and PPI is discussed.

## APPLICATION OF EXTRACTION IN COULOMETRY

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Extraction is widely used in analytical chemistry due to its simplicity, rapidity and ability of using to separate as well as concentration and trace compounds. Extraction is applied to concentrate the detecting components. The combination of extraction and photometry or voltampermetry is known, however it was not used in coulometry.

Coulometric determination of Cu(II) and Ni(II) was carried out applying such reagents as 8-hydroxyquinoline and 8-mercaptoquinoline. Electro-generated bromine was used as a titrant.

8-Hydroxyquinoline forms the complex with Cu(II) in ratio 1:1 at pH 5-7. The composition of the complex is changed on 1:2 at pH>7. 8-Hydroxyquinoline accepts bromine therefore its excess has been removed with NaOH solution. The complex was extracted with chloroform. It was shown that double extraction was enough to extract the complex. The detection limit is  $5 \times 10^{-7}$  M during 10c and at current generation  $1 \times 10^{-3}$  A.

8-Mercaptoquinoline is not dissolved in chloroform but forms 8,8'-diquinolyldisulfide as a contaminant at storage which is dissolved in chloroform and interferes to following coulometric determination of the complex compounds. 8-Mercaptoquinoline was rinsed by same portions of chloroform to remove the contaminants.

Cu(II) and Ni(II) form the complexes 1:2 with 8-mercaptoquinoline extracted with  $\text{CHCl}_3$ .

Acetohydrazidines are interesting for the analytical usage. They were proposed as the reagents for the determination of Ni(II) in different environmental samples. 2-(4-methoxybenzoyl)-4-(2-nitrophenyl)acetohydrazidine forms the blue complex 1:1 with Ni(II). The extraction was carried out with n-butanol saturated with water. The reagent excess was excluded by  $\text{CCl}_4$ .

Bromine electrogeneration was carried out from tetrabutylammonium bromide in 0,1 M  $\text{NaClO}_4$  acetonitrile solution with 100 % current yield.

# THE STUDY OF KYNURENIN PATHWAY BY CAPILLARY ELECTROPHORESIS

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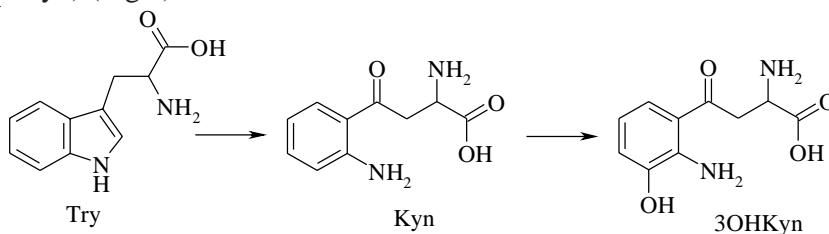
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Tryptophan is a precursor for a series of metabolic reactions. Two tryptophan catabolizing pathways are well characterized: (i) tryptophan converts to serotonin; (ii) tryptophan is also converted to kynurenine.

Our attention is focus on the biochemical defects of kynurenine pathway. The concentration of metabolites changes under various diseases, such as neurodegenerative disease, memory loss, chronic renal failure, eyes disease.

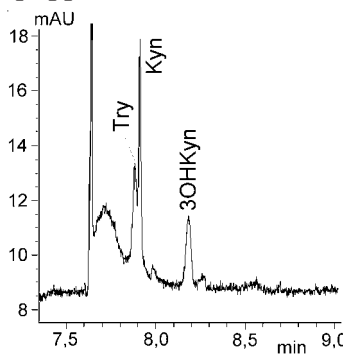
The kynurenine pathway metabolites are kynurenine, kynurenic acid, xanthurenic acid, 3-hydroxykynurenine, anthranilic acid and quinolinic acid. The more important are kynurenine (Kyn) and 3-hydroxykynurenine (3OHKyn) (Fig 1).



**Fig.1.** The more important metabolites of tryptorhan

Degradation of the tryptophan accompanied with increasing in 10 times of kynurenine level in the case of renal failure. As the result of 3-hydroxykynurenine's ability of easy oxidize neurotoxin compounds form.

A capillary electrophoresis systems "Agilent CE 1100" (HP, USA) equipped with a diode array detector was used to separate and quantify



analytes. Separation was achieved using an 60 cm (effective length of 50 cm)×50 μm I.D. fused capillary column with UV-detection at 227 nm and 30 kV of voltage. Injection was performed using pressure at 50 mbar, for 20 s.

**Fig. 2.** Electropherogram of real sample (homogenize of *Drosophila* flies heads). Electrolyte solution: 7 mM sodium tetraborate, pH 8.14

*This work was supported by the Foundation for Assistance to Small Innovative Enterprises*

# **ELECTROANALYTICAL APPLICATIONS OF SOME COMPLEX COMBINATIONS WITH SCHIFF BASE. COPPER AND NICKEL IONS DOSAGE IN INDUSTRIAL WATERS**

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The paper presents the experimental and theoretical data regarding the realization and characterization of three liquid-membrane electrodes, which have not been mentioned in the specialized literature so far. The active substances whose solutions in nitrobenzene have constituted the membranes on a graphite rod, are simple complex combinations of the Cu(II) and Ni(II) ions with Schiff base N-[2-thienylmethylidene]-2-aminothiophenol (TNATPh).

Cu<sup>2+</sup>-selective and Ni<sup>2+</sup>-selective electrodes have been used to determine the copper and nickel ions in aqueous solutions, both by direct potentiometry and by potentiometric titration with EDTA. They have also been used for determining the Cu<sup>2+</sup> and Ni<sup>2+</sup> ions in industrial waters by direct potentiometry.

The following characteristics were studied in this order:

- the electrodes response to Cu<sup>2+</sup> and Ni<sup>2+</sup> ions concentration;
- the influence of pH on the response to Cu<sup>2+</sup> and Ni<sup>2+</sup> ion selective electrodes;
- the selectivity of the electrodes;
- the dynamic response and reproducibility of the electrodes.

The study of these electrodes has proved primary and secondary characteristics favorable to their practical utilization in potentiometric titrations and in direct potentiometric determinations.

The electrodes have a wide linear response range to Cu<sup>2+</sup> and Ni<sup>2+</sup> ions concentration. For this reason, they are adequate for the potentiometric determinations of copper and nickel ions in diluted solutions (dilutions may go down to 10<sup>-5</sup> M) as well as in checking the industrial waters.

# METHODICAL TECHNIQUES FOR RESEARCH OF RARE-METAL AND RARE-EARTH MINERALS WITH X-RAY MICROANALYSIS

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The X-ray microanalysis is the basic method of study of rare-metal and rare-earth minerals of micron size. The multi-component composition, instability of minerals under the electron beam, overlap of X-ray characteristic lines, absence of reference samples of adequate composition present difficulties in the research of mineral composition.

The technique was created to analyze fersmites, baotites, ortites, ferriallanite, toernebohmit, monazit, ankylite and other accessory minerals from carbonatit associations. It was based on using microanalyser JCXA-733 of Jeol Company to analyze the following elements: Nb, Ta, Ba, Sr, Ca, Ti, Fe, Mn, Si, Al, Mg, P, Cl, F, U, Th, Y and 14 rare-earth elements ( $Z = 57-71$ ). Synthetic single oxides of rare-earth elements, metallic Nb and Ta, and oxides of other elements analyzed were used as reference samples. The experiments showed that optimum conditions for production analytical signal are: accelerating voltage 20 kV, the beam current 20 nA, time of counting 10 s, the electron probe 10 mm in diameter. To register  $L\alpha$  and  $L\beta$  lines of rare-earth elements, the crystal analyzer LiF was applied. The correction of analytical signal for overlapping of analytical lines was made through coefficients of overlap, provisionally defined with the samples not containing the element analyzed. The recalculation of intensities in the concentration was performed by PAP-method with mass coefficient of Marenkov using MARSHALL software.

The evaluation of metrological characteristics of the technique, performed with minerals of different composition, showed that technique developed for reliability and precision satisfies the requirements offered for quantitative determinations, category II. The detection limits are acceptable for solving the problems posed and amount to 0.1 – 0.4 wt. %, depending on the element analyzed.

The comprehensive studies of rare-metal – rare-earth minerals of carbonatit associations were carried out. Some rarest mineral species were investigated. Two minerals were attested by the Commission on new minerals of International Mineralogical Association as new.



# USING OF ION SELECTIVE ELECTRODES FOR THE DETERMINATION OF THE IONIC LIQUIDS SOLUBILITY IN WATER

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Ionic Liquids (ILs) are non-volatile, non-flammable and thermally stable, they have high ionic conductivity. These features make ILs very promising in use as solvents in organic synthesis, catalysis, separation and extraction processes. Thus ionic liquids are able to replace traditional solvents that could be potential environment pollutants. The only way for them to be lost to the environment is to contaminate a wastewater stream. Hence, it is important to develop the inspection methods of ILs' components content in water solutions. One of the most convenient, cheap and fast analytical methods is potentiometry with ion-selective electrodes (ISE). ISEs are applicable for the determination of broad range of concentration (typically, four orders of magnitude). Consequently, may be used to estimate the solubility of both well-soluble and poorly soluble ILs. Two different types of the ISEs have been developed. There were an anion selective electrode based on tributylhexadecylphosphonium bromide and a cation selective one based on sodium tetraphenylborate as a cation-exchanger in PVC-plasticized membranes with 2-nitrophenyloctyl ether as a plasticizer. As an example, we have fabricated and tested ISEs for the widely used alkylimidazolium ionic liquids. Aqueous solubility of typical ILs at 21°C have been determined:  $0.075 \pm 0.001 \text{ mol} \cdot \text{l}^{-1}$  (1-butyl-3-methylimidazolium, BMIm, hexafluorophosphate);  $0.018 \pm 0.001 \text{ mol} \cdot \text{l}^{-1}$  (BMIm *bis*(triflylimide));  $0.054 \pm 0.007 \text{ mol} \cdot \text{l}^{-1}$  (1-butyl-2,3-dimethylimidazolium, BDMIm, hexafluorophosphate);  $0.014 \pm 0.001 \text{ mol} \cdot \text{l}^{-1}$  (BDMIm *bis*(triflylimide)). The electrodes have demonstrated good potentiometric characteristics: they can be used in a wide pH-range, have a high selectivity and are suitable for the most practical cases. Also the electrodes developed were applied for ethyldodecyl-diphenylphosphonium *bis*(triflylimide) solubility in water determination. This liquid is noticeably more hydrophobic than imidazolium derivatives mentioned above, nevertheless this method is acceptable to estimate the solubility, but has a little bit low sensitivity.

*This work was supported by Russian Foundation for Basic Research (grant 02-03-32340-a)*

# INDIRECT DETERMINATION OF ASCORBIC ACID BY ELECTROTHERMAL ATOMIC ABSORPTION SPECTROMETRY

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Ascorbic acid commonly known as vitamin C, is one of the most important water soluble vitamins. Ascorbic acid is involved in many biological processes and it is an essential compound in the human diet [1]. The determination of ascorbic acid has gained increase significance in pharmaceutical, clinical, and food applications. So far, different methods have been developed for determination of ascorbic acid [2, 3].

In this work, a method based on the reduction potential of ascorbic acid was developed for the sensitive determination of trace of this compound. In this method ascorbic acid was added on the Cr(VI) solution to reduced that to Cr(III). Cr(III) produced in solution was quantitatively separated from the remainder of Cr(VI). The conditions were optimized for efficient extraction of Cr(III). The extracted Cr(III) was finally mineralized with nitric acid and sensitively analyzed by electro-thermal atomic absorption spectrometry. The determinations were carried out on a Varian AA-220 atomic absorption equipped with a GTA-110 graphite atomizer. The results obtained by this method were compared with those obtained by the other reported methods and it was cleared that the proposed method is more precise and able to determine the trace of ascorbic acid. Table shows the results obtained from the determination of ascorbic acid in two real samples by the proposed method and the spectrometric method based on reduction of Fe(III).

Table. Determination of ascorbic acid in real samples

Sample	Number of analysis	Proposed method ( $\mu\text{g/g}$ )	Spectrophotometry ( $\mu\text{g/g}$ )
Garlic	5	$186 \pm 1.6$	$179 \pm 2.9$
Green peper	5	$539 \pm 1.9$	$533 \pm 5.1$

1. M. C. Yebra, R. M. Cespon, and A. Moreno-Cid, *Anal. Chim. Acta.*, 2001, **448**, 157.
2. M. A. Memon, M. H. Memon, M. U. Dahot, and I. A. Ansari, *Med. j. Islamic Academy of Sci.*, 2000, **13**(2), 69.
3. Y. Miura, M. Hatakeyama, T. Hosino, and P. R. Haddad, *J. Chrom. Sci.*, 2002, **956**, 77.

# **SORPTION-SPECTROPHOTOMETRIC AND VISUAL TEST-DETERMINATION OF OXO-ANIONS OF IODINE AT THE SILICA GEL MODIFIED BY QUATERNARY AMMONIUM SALTS**

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Iodine belongs to group of irreplaceable microelements. The degree of morbidity of people with goiter increases after Chernobyl disaster, at unfavourable ecological conditions and iodine deficit. Owing to these facts government program of iodification (iodination) of food has been accepted and problem of determination of iodine compounds is very urgent.

Last time development of methods of iodine determination, which include preliminary sorption preconcentration of microcomponents and their subsequent determination in phase of concentrate get great practical significance. Silica gel (SG) with adsorptively modified quaternary ammonium salts (QAS) gets properties of anion-exchange resin. The sorbents modified in this way can be used successfully for determination of different anions.

Interaction of periodate with immobilized on the silica gel surface QAS – trinonyloctadecylammonium chloride has been studied. The optimal conditions of periodate sorption have been investigated. Interference of main components of sea water has been examined. 16500-fold excess of  $\text{Cl}^-$ , 11000-fold excess of  $\text{Na}^+$ , 380-fold excess of  $\text{K}^+$ , 420-fold excess of  $\text{Ca}^{2+}$ , 500-fold excess of  $\text{Mg}^{2+}$ , 60-fold excess of  $\text{HCO}_3^-$ , 20-fold excess of  $\text{BO}_3^{3-}$ , 280-fold excess of  $\text{SO}_4^{2-}$  do not interfere with the determination of periodate.

After sorption of anion and its reduction to free iodine on the SG surface sorbents get intensive color. Using absorption spectrum the calibration curve has been obtained. Its equation is:

$$A = (0,019 \pm 0,001) \times 10^6 C, \text{ mol/L.}$$

Detection limit of periodate determination is 1,35  $\mu\text{g}$  per sample. The color scale for visual test-determination has been constructed in working range 5-50  $\mu\text{g}$  periodate-ion per sample.

Developed methods have been checked up by analysis of kitchen salt which contains potassium iodate. Preliminary oxidation of iodate in the salt to periodate was performed by hydrogen peroxide in the acidic solution. The results of analysis coincide with certificate data of iodinated kitchen salt.

# ELUCIDATION OF THE HETEROPOLYBLUE NATURE AND EXTRACTION-SPECTROPHOTOMETRIC DETERMINATION OF PHOSPHATE USING MIXED HETEROPOLYANIONS

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Spectrophotometric methods based on an enhancement of the blue color produced on reduction of 12-molybdophosphate (arsenate) in the presence of antimony(III) are widely used for the determination of phosphorus(V) or arsenic(V). However, nature of heteropoly blue, their spectra, mechanism of the reaction are obscure. In addition, mixed POMs were shown as very efficient analytical forms for the determination of P(V) and As(V).

It is shown that both Sb(III) and Bi(III) can speed reduction of 12-molybdophosphate (12-MPC) to the corresponding heteropoly blue (12-MPB) by ascorbic acid (AA). It is found that mixed polyoxometalates can be formed in solution which reduce considerably more rapidly than 12-MPC. Complete formation of mixed POM is observed only if significant excess of Me(III) ions is used in the reaction. POM responsible for blue color was synthesized by selective extraction. Chemical analysis of tetrabutylammonium salt is in accordance with formula of  $(TBA)_6PMe(III)Mo_{11}O_{40}$  (Me = Sb, Bi). IR spectrum of mixed POM is identical to 12-MPC.

Electronic spectra of reduced mixed POMs (RMC) are identical with spectra obtained in conditions of analysis. Spectrum of RMC having two bands at 720 nm in visible region and another at 890 nm differs from the spectrum of 12-MPB in which only one prominent band is present at 800-840 nm. Spectra in organic solvents were displaced to 670 nm for RMC and to 720 nm for 12-MPB.

Mechanism for RMC formation is proposed. Transfer of electrons from ascorbic acid proceeds through Me(III) atoms to molybdenum atoms in mixed POM. Me(III) atoms in heteropolyanion can be oxidized to Me(V) by Mo(VI) making possible easy oxidation of AA.

RMC can be selectively extracted into butyl acetate. Concentration coefficient 50 was achieved. Factors affecting accuracy and reproducibility of the proposed method were investigated. Method is simple and fast. Detection limit is 0,3  $\mu\text{g/l}$  for P(V).

# OXIDATIVE LUMINESCENCE OF UV ABSORBING CHEMICALS. APPLICATION TO THEIR DETERMINATION IN SUNSCREEN PRODUCTS BY REVERSED PHASE LIQUID CHROMATOGRAPHY WITH CHEMILUMINESCENCE DETECTION

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Sunscreens are a class of compounds that absorb UV radiation and attenuate the deleterious effects of solar radiation on the human skin. Several methods have been developed to determine UV filters in suncare products, such as UV spectroscopy [1] and high performance liquid chromatography with diode-array detection [2]. In this study, a new method deploying Reserved-phase liquid chromatography (RP-HPLC) with chemiluminescence (CL) emission is developed for the simultaneous determination of 6 organic sunscreen products: Octyl Methoxycinnamate (Eusolex 2292), Phenylbenzimidazole Sulfonic Acid (Eusolex 232), 4-Methylbenzylidene Camphor (Eusolex 6300), Butyl Methoxy dibenzoylmethane (Eusolex 9020), Benzofenone-2 and Octyl Dimethyl PABA. The analytes are separated isocratically in a C<sub>18</sub> column with methanol-water (80-20) and then delivered to the CL cell. In order to overcome the interference of methanol in the CL measurement a new manifold employing a two-line double-flow injection analysis system is arranged to accomplish preoxidation of the organic solvent. Once pre-oxidised, the mobile phase containing only small amounts of the solvent is delivered to a second FIA manifold where light emission is generated through reaction with a stronger oxidant (acidic permanganate). It is proved that the CL reaction in combination with the pre-oxidation step offers the ability of developing many alternative analytical procedures while enabling its conjunction with liquid chromatography. The calibration curves were linear for Eusolex 2292, Eusolex 232, Eusolex 6300, Eusolex 9020, in the concentration range of 5-1000 µg l<sup>-1</sup> and for Benzofenone-2 and Octyl Dimethyl PABA in the concentration range of 1-1000 µg l<sup>-1</sup>. Relative standard deviation (R.S.D) of the determination was within 5%. The limits of detection were equal to 46.1 µg l<sup>-1</sup>, 52.9 µg l<sup>-1</sup>, 74.7 µg l<sup>-1</sup>, 18.4 µg l<sup>-1</sup>, 29.9 µg l<sup>-1</sup> and 16.4 µg l<sup>-1</sup>, respectively.

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# OPTICAL DENSITY DIFFERENTIATION FOR THE MIXTURES OF Cu, Zn, Co, Ni COMPLEXES WITH 4-(2-PYRIDYLAZO)-RESORCINOL

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The differentiation of analytical signal in the photometry enables one to use non-specific reagents for the sensitive, selective and express determination of metals in the form of their intensively coloured complexes. The typical representative of such reagents is 4-(2-pyridylazo)-resorcinol (PAR). We have developed the methodics for the determination of some metals in the drinking water which employ the PAR as the photometric reagent and the differentiation of optical density of the mixture of coloured complexes by means of combined multiwave photometry and the specific destruction of the complexes caused by the change of the reaction medium.

Simultaneous determination of Cu and Zn in the form of coloured PAR complexes is performed at pH 10 in the presence of pyrophosphate which binds the admixtures of Al, Fe and Mn into the inactive complexes. The measurements of the change in the optical density are made at 520 and 550 nm before and after the destruction of the complexes by EDTA, or at 530 nm before and after the destruction of the copper complexes by the thioglycolic acid and the destruction of the zinc complexes by EDTA. The detection limit for Cu is 2-5, for Zn - 3  $\mu\text{g}/\text{dm}^3$ . The application of these methodics at pH 8 enables one to determine simultaneously Cu and Zn at high excess of the latter.

The simultaneous determination of Co and Ni is also made at pH 8 in the presence of pyrophosphate. The EDTA is added to the mixture of coloured complexes of these metals to bind the Cu and Zn admixtures into the inactive complexes. The optical density of the solution is measured at 530, 555 and 580 nm. The solution is heated to the boiling point to destruct the complex formed by Ni with PAR, and then is cooled. Again the measurements of optical density are performed at the same wavelengths. The Ni concentration is calculated from the variation in the optical density, and the Co concentration is calculated from the final values of optical density. The detection limits for these metals are 4 and 2  $\mu\text{g}/\text{dm}^3$ , respectively.

# **SORPTION-X-RAY-FLUORESCENCE DETERMINATION OF TOXIC METALS WITH THEIR PRECONCENTRATION ON COMPLEXING CHEMICAL MODIFIED SILICA**

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Under the conditions of increasing antropogenic environmental pollution monitoring of toxic metals (Pb, Cd, Zn, Al, Mo, Cr, Bi) is a very actually. The big number and difficult of analyzes which necessary for solving this problem need new express and effective methods.

One of the best methods of the express complex monitoring of toxic metals is separation and concentration on sorbents with following analysis of the sorbents faze. For chemical sorbtion of toxic metals ion-retarding resin and complexing polymeric organic and inorganic sorbents are widely used. Among them is distinguished complexing chemical modified silica, which separate toxic metals forming persistent complexes with molecules immobilized on the surface.

In this work the results of research common sorbtion-X-Ray-fluorescence analysis of Pb(II), Cd(II), Zn(II) and Mo(VI) with preconcentration on complexing chemical silica gel modified with mercaptane groups and modified with 8-hydroxyquinoline were described. The conditions and limits of determination of the X-Ray-fluorescence method in the “thin” lawyers are discussion.

It was shown that X-Ray-fluorescence method do possible to separate metals in the multycomponents samples by different methods of synthesis chemical modified silica and different ways of coordination of ion metals on the surface.

# THE INFLUENCE OF SURFACTANTS NATURE AND CONCENTRATION ON THE ANALYTICAL SIGNAL IN THE ATOMIC ABSORPTION DETERMINATION OF LEAD, CADMIUM AND CHROMIUM

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Nowadays in the light of finding the ways of solution of ecological problems, with the improvements in standards of micro quantity definition of metals in new materials, with the intensification in food products and water quality standards the problem of limits of micro quantity determination of metals and the accuracy of the definition methods becomes important. Lead, cadmium and chromium are super toxicants and their concentration in waste, waters, air, soil and food products has to be controlled. One of the basic methods of these elements definition in objects of complex chemical composition is the atomic absorption spectrometry. At present customary water solutions become inferior to other mediums. Aqua-organic and non-aqueous solutions have been used for a long period of time; currently the use of ultra decisive fluids, ionic liquids and so-called organized mediums such as aqua micellar surfactant solutions is more common. Therefore the object of presented work is the sensibility and selectivity intensification of lead, cadmium and chromium atomic absorption determination as well as the establishment of possibility of air-acetylene flame–low-temperature flame (propane-butane-air) transition. The systematic research of surfactants (kation, anion, non-ion) nature and concentration influence on analytical signal in atomic absorption determination of lead, cadmium and chromium has been successfully conducted on models. The established results have been compared. The mixtures of modifiers that maximize the analytical signal have been sorted. The surfactant-based modifier addition to analyzed solutions reduces viscosity, surface stretching and the drop size of sprayed solution, boosts the effectiveness of spraying and transforms oxidation-reduction eminence of flame. The ion redistribution of defined components takes place, which leads to their saturation primarily in small size drops. The sensibility of metals atomic absorption determination increases in 2 or 3 times. Mineral acids and other attendant components influence on lead, cadmium and chromium analytical signal during their atomic absorption determination in low-temperature flame has been studied. The modifier addition to analyzed solutions intensifies selectivity of atomic absorption determination. The modifier-based methodology of cadmium and chromium atomic absorption determination in food products, of chromium in sewage waters. The detection limit has been evaluated.



# STUDY OF THE FCH<sub>2</sub>CHF RADICAL BY VUV PHOTOELECTRON SPECTROSCOPY AND COMPUTATIONAL CALCULATIONS

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HeI photoelectron spectra have been recorded for the reaction of atomic fluorine with 1,2-difluoroethane at different reaction times. Fluorine atoms have been generated by microwave discharge of F<sub>2</sub> molecules in flowing He. The spectra have been recorded using a photoelectron spectrometer specifically designed to study short-lived species in the gas phase. A structured band associated with either CH<sub>2</sub>CH<sub>2</sub>F or FCH<sub>2</sub>CHF as a short-lived primary reaction product was recorded at an optimum mixing distance of 15 mm above the photon beam. The experimental first adiabatic and vertical ionization energies were measured as  $(8.86 \pm 0.04)$  eV and  $(9.36 \pm 0.03)$  eV respectively. The average vibrational separation of  $(1070 \pm 30)$  cm<sup>-1</sup> was observed in this band. As two primary reaction products CH<sub>2</sub>CH<sub>2</sub>F or FCH<sub>2</sub>CHF can be generated in the F + FCH<sub>2</sub>CH<sub>2</sub>F reaction studied in this work, assignment of the observed first photoelectron band should be made with the aid of computational calculations for the first vertical ionization energies. The vertical ionization energies computed in this work for CH<sub>2</sub>CH<sub>2</sub>F (X<sup>2</sup>A) and FCH<sub>2</sub>CHF (X<sup>2</sup>A) at MP2/6-311++G\*\* and B3LYP/6-311++G\*\* levels of theory were compared with the corresponding experimental value and led to the assignment of the observed first photoelectron band to the ionization of FCH<sub>2</sub>CHF (X<sup>2</sup>A) radical. Due to the vibronic nature of transitions observed in the experimental first photoelectron band, force constant calculations have been carried out at the same levels of theory for CH<sub>2</sub>CH<sub>2</sub>F (X<sup>2</sup>A) and FCH<sub>2</sub>CHF (X<sup>2</sup>A) and their singlet cationic states. The observed vibrational structure was then assigned to the excitation of C-F stretching mode in the ion.

# INTERACTION OF Ni(II) WITH DIMETHYLGLYOXIME AT THE PRESENCE OF PEROXYACIDS

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The well-known reaction of Ni(II) with dimethylglyoxime ( $H_2Dm$ ) in alkaline medium under the influence of such oxidants as persulphate and iodine is widely used for the photometric determination of nickel. The red product (RP) of this reaction is used for this purpose. However, the nature of this red compound has not been defined yet. Using of peroxyacids makes it possible to obtain additional data concerning the conditions and mechanism of generation of RP as well as to improve the metrological parameters of the method.

Data shown below refer to the use of diperoxysebacine acid  $(CH_2)_8CO_3H$  (DPSA) and peroxymonosulphuric acid  $H_2S_2O_5$  (PMSA). The rate of RP formation depends on pH, concentration of the constituents and order of their mixing. The optimum pH value lies in the pH range of 8-10 in pyrophosphate or borate buffer mixtures. The rate of RP formation slows down with the increase of pH value because of lowering of redox potential of the system of PMSA. The advantages of PMSA over DPSA were revealed: procedure of its synthesis is simpler: its diluted solutions ( $10^{-3}$ - $10^{-5}$  M) are more stable, time of generation of RP decreases from 10-15 to 3-5 minutes under optimum conditions.

The findings prove that peroxyacid oxidizes the reaction product; from 2 to 3 moles of PMSA are spent per 1 mole of RP. If the components are mixed uninterruptedly, the output of RP does not depend on the order of mixing. Value of  $(1.2-1.3) \times 10^4 \text{ mole}^{-1} \cdot \text{cm}^{-1} \cdot \text{l}$  is close to values, given for other oxidants. At the surplus of  $H_2Dm$  compared to nickel (6:1) 3 moles of PMSA are spent per 1 mole of RP, while at the surplus of PMSA (10:1) 3 moles of  $H_2Dm$  are spent per 1 mole of RP. The data obtained do not let us affirm what exactly oxidize in the RP – Ni(II) or  $H_2Dm$ . It is proved, that under conditions of formation, RP is not oxidized by PMSA.

The use of peroxyacids, including PMSA, makes it possible to improve photometric method of nickel determination – to increase selectivity, accuracy and reproducibility of measurements. Peroxyacids as oxidants are used for nickel determination in aluminium and copper alloys, natural waters, stomatological products.

# **OBJECTS OF THE ANALYSIS**

*Keynote lectures*

## SPECIATION ANALYSIS OF MATERIALS BASED ON INORGANIC COMPOUNDS OF LANTHANIDES

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Oxides ( $\text{Ln}_2\text{O}_3$ ), fluorides ( $\text{LnF}_3$ ), sulfides ( $\text{Ln}_2\text{S}_3$ ,  $\text{LnS}$ ), sulfofluorides ( $\text{LnSF}$ ) of lanthanides are bases of different functional materials. Analytical control of such materials must include non-destructive methods for the identification of compound's chemical forms and quantitative determination methods which does not require analytical standards. The main difficulties of this analysis by chemical methods are that it is necessary to transform weakly soluble samples in solution.

There's it is required to keep unchangeable chemical forms of material components, as well as lanthanide concentration ratio in different degree of oxidation. Therefore, the main conception of this work is to combine process of the sample decomposition and analytical reaction of the determined chemical form.

The sulfide ions in  $\text{Ln}_2\text{S}_3$ ,  $\text{LnSF}$  were determined after sample's treatment by  $\text{I}_2$  titrated solution in a weak-acid media. Excess iodine was titrated with  $\text{Na}_2\text{S}_2\text{O}_3$  solution. Fluoride ions in  $\text{LnF}_3$ ,  $\text{LnSF}$  were determined after sample's treatment by  $\text{H}_3\text{BO}_3$  titrated solution. After the removal of  $\text{BF}_3$  excess boric acid was converted into the stronger mannitoboric acid, which was titrated potentiometrically with  $\text{NaOH}$  solution.

$\text{Ln(II)}$  in  $\text{LnF}_3 \cdot \text{Ln(II)}$  were determined after samples dissolution in  $\text{H}_3\text{PO}_4$  in the presence of a titrated solution of  $\text{NH}_4\text{VO}_3$ , which excess was titrated with the  $\text{Fe(II)}$  salt. It was found that dissolution of the materials based on  $\text{CeF}_4 \cdot \text{CeF}_3$  in  $\text{H}_3\text{PO}_4$  does not change the oxidation state of cerium, thus phosphate complexes of  $\text{Ce(III, IV)}$  can be used for quantitative spectrophotometric determination of cerium valence forms. The contents of  $\text{Ln(II, III)}$  in  $\text{Ln}_2\text{S}_3 \cdot \text{LnS}$  may be counted from results of the determination of total sulfur (determined gravimetrically in  $\text{BaSO}_4$  form) and sum of the reducers –  $\text{S}^{2-}$  and  $\text{Ln(II)}$  (determined by iodometric method).

It was shown the effectivity of Diffuse Reflectance Spectroscopy (DRS) at UV, VIS and IR for non-destructive analysis of lanthanide compounds.  $\text{Ln}_2\text{S}_3$ ,  $\text{Ln}_2\text{O}_3$ ,  $\text{LnF}_3$  and  $\text{LnSF}$  may be identified. More than 1% of  $\text{Eu(II)}$  and  $\text{Yb(II)}$  in  $\text{LnF}_{3-x}$  may be detected and 1-30 %  $\text{Eu(II)}$  in  $\text{EuF}_{3-x}$  may be determined quantitatively.

## **FAST TRACE ANALYSIS OF EXPLOSIVE VAPORS. STATUS AND PROSPECTS**

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Fast detection of trace explosives in air is an urgent analytical problem, which solution will allow one efficiently to perform anti-terrorist measures. The difficulties that one runs into solving this problem are due to low vapor pressure of these compounds and the presence of interference compounds in air.

The present state technology makes it possible to detect explosives with a concentration of  $10^{-13}$ - $10^{-14}$  g/cm<sup>3</sup> in 30 s (with a gas chromatography) and 1÷3 s (with a drift spectrometry and its modification, mass-spectrometry).

The main steps of the trace explosives detection: sampling, concentration, including two stage concentration, sample injection, separation and detection are given in detail. To optimize the parameters of the above-mentioned steps of a fast high sensitive gas analysis, a system approach based on design models, starting with a vortex vapor sampling, is suggested

Fast concentration and sample injection are considered with the use of a theory of vibrational relaxation. A possibility to reduce a detection limit for trinitrotoluene to  $10^{-15}$  g/cm<sup>3</sup> in less than 1 min is shown. Such a detection limit can be obtained using selective ionization combined with ion drift spectrometry. The time of detection in this case is 1÷3 s. A detection technique based on fluorescent reinforcing polymers, when the target molecules strongly quench fluorescence, holds much promise for developing fast detectors.

# PHOSPHATE ANALYSES FOR ENVIRONMENTAL CHEMISTRY

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Three types of methods for phosphate analyses have been studied with the aims of monitoring the distribution and circulation of orthophosphate and observing the chemical forms of phosphorus compounds occurring in the natural water environment.

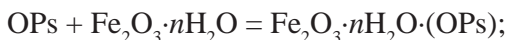
The first is the indirect spectrophotometry which is applicable to orthophosphate with concentrations of  $1 \times 10^{-8} \sim 1.2 \times 10^{-6}$  M. By applying it to lake water samples, were determined phosphorus fractions such as; P(I): orthophosphate-P; P(II): orthophosphate-P released from suspended substances by the action of 0.5 M HCl; P(III): filtrable inorganic- and/or organic-P; P(IV): unfiltrable-P being made into filtrable by 0.5 M HCl; P(V): unfiltrable-P incorporated in living organisms or bound firmly to suspended substances.

The second method is the flow-coulometry and can be applied to orthophosphates with concentrations of  $5 \times 10^{-6} \sim 1 \times 10^{-3}$  M contained in the interstitial water in sediments. The advantage of this method is that only small amounts of sample ( $\sim 100 \mu\text{l}$ ) are needed and the analytical results are entirely free from interference due to silicate ions.

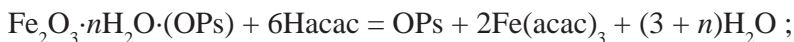
The last is ion-chromatography of organophosphorus compounds (OPs) coupled with their adsorption concentration using hydrous iron oxide (HIO,  $\text{Fe}_2\text{O}_3 \cdot n\text{H}_2\text{O}$ ).

The principle is given as follows:

Adsorption of OPs:



Release:



Here, Hacac denotes pentane-2,4-dion.

## ENZYMATIC METHODS IN ENVIRONMENTAL AND BIOLOGICAL ANALYSIS

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Enzymatic methods are promising for the application in environmental and biological analysis, owing to their very high sensitivity, selectivity, simplicity and rapidity. Toxic properties of many biologically active compounds are conditioned by their inhibitory action on the catalytic activity of enzymes responsible for the life processes (*in vivo*) of human beings and animals. Modeling such enzymatic processes *in vitro* and measuring their rate, which decreases proportionally to the enhancement of inhibitors concentration, provide the development of the methods for the determination of numerous inorganic and organic compounds – enzymes effectors. Besides, other effects of biologically active compounds, such as activation of the enzyme, liberative effect on the previously inhibited enzyme, and reactivation of apoenzymes, may be used.

It was stated that the catalytic activity of native and immobilized enzymes of oxidoreductases and hydrolases classes (peroxidases, alcohol dehydrogenases, alkaline and acid phosphatases) is significantly inhibited by different N-, P-, S-containing organic compounds, heavy metal ions (Hg(II), Pb(II), Sn(IV), Cd(II), Bi(III), Zn(II)), and anions (CN<sup>-</sup>, F<sup>-</sup>, WO<sub>4</sub><sup>2-</sup>, MoO<sub>4</sub><sup>2-</sup>). Various approaches to improve the analytical characteristics of the procedures were proposed. They are as follows: varying the enzyme substrates, using simultaneously two different inhibitors and different analytical signals for the determination of organic compounds of the same class, application of the preparations of the same enzyme isolated from diverse sources, and reactivation effect of the metal-ion that is a cofactor of the enzyme. The two last approaches were successfully used, in particular, for the sensitive and selective determination of Zn(II) and Mg(II) – cofactors of alkaline phosphatases.

The immobilization of the enzymes on various solid carriers gives perfect possibilities to develop not only sensitive and selective, but also rapid and simple test procedures for different compounds determination with visual detection of the analytical signal.

There are numerous examples of successful application of the developed procedures using native and immobilized enzymes in analysis of environmental (waters and soils of different types, air) and biological (blood serum, urine) samples.

# DETERMINATION OF TRACE ELEMENTS IN ALCOHOLIC DRINKS BY DIFFERENTIAL PULSE POLAROGRAPHY

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The determination of trace elements in alcoholic drinks is an important subject since they are widely consumed. Their composition depends on many factors related to the specific production area, to climate, soil and water used.

We determined the trace elements in red and white wine, raki and beer by using differential pulse polarography. For each drink a new method was proposed. Each sample was first wet digested by using  $\text{HClO}_4$ ,  $\text{HNO}_3$  and  $\text{HCl}$  acids. After evaporation of acids the sample was diluted to 10 ml and then 0.1 ml aliquots were taken and added into the polarographic cell containing a certain electrolyte. The polarogram is taken by scanning the potential in the negative direction at a scan rate of 2-5 mV/s from zero to about -1.5 V depending on pH value.

The electrolytes used were acetate buffer at pH values 2, 4 and 6 and the same electrolyte is used in the presence of EDTA at pH values of 2 and 6. Iron and copper contents could be most easily determined in EDTA medium at pH 6. The best medium for nickel was found to be as ammonia buffer pH 9.5:  $\mu\text{g/L}$ , it could be separated from zinc in this medium. The elements determined in white and red wine were Cu, Pb, Zn, Cd, Fe and Ni. The quantities found were for iron about 9000  $\mu\text{g/L}$ , for copper 290  $\mu\text{g/L}$ , Ni 80  $\mu\text{g/L}$ , lead 150  $\mu\text{g/L}$  and zinc 460  $\mu\text{g/L}$ . The validation was made by determining each element under different conditions.

Raki, a Turkish alcoholic drink was also analyzed by differential pulse polarography and copper, iron and zinc could be determined. For the arsenic content in beer a more sensitive method had to be applied. For this method a new catalytic method is established and the arsenic content was determined by using this new method.



# **CONTROLLING PRECISION OF ATOMIC-EMISSION MICROELEMENT ANALYSIS IN SOILS BASED ON APPLIED GEOCHEMISTRY CRITERIA**

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The results of reference samples analysis (GSS series, China) taken as the reference in the International Program of Global geochemical mapping and inter-laboratory comparison of results derived by different methods were applied for controlling precision of atomic emission (AEA) results on soils from cell N36E46 of the Global geochemical reference network.

Assessment of the quality of results involved the criteria proposed in the international programs of Global geochemical mapping and Proficiency testing in geoanalytical sciences GeoPT. Besides, we proposed the criterion considering heterogeneity of microelements distribution in natural study objects.

Inter-laboratory control for collecting samples of soils from cell N36E46 was performed, with AEA, XRF, ICP-MS employed, at the Institute of Geochemistry, Irkutsk, Russia and Kingston University, England.

The AEA results for Zn, Ag, Ge, Tl, B, Co, Cr, Ga, Ni, Sr, Sc, Ba in GSS series satisfy the criteria of quality proposed. This allows to believe that the values of microelements contents in soils under conditions of the methods applied for quantitative AEA are quite reliable.

*Oral presentations*

# APPLICATION OF DIFFERENT ANALYTICAL TECHNIQUES FOR Hg DETERMINATION IN ICE-CORE FROM BELUKHA GLACIER (ALTAI)

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The very low Hg concentration levels in ice core of remote glaciers require an ultra-sensitive analytical technique as well as a contamination-free sample preparation methodology. The potential of two analytical techniques for Hg determination – cold vapour inductively coupled plasma mass spectrometry (CV ICP-SFMS) and atomic fluorescence spectrometry (AFS) with gold amalgamation was studied.

ICP-SFMS (Thermo Finnigan, Element) with cold vapour generation was developed with a guard electrode and a gold amalgamation device using an Au-sorbent for sample pre-concentration to improve the sensitivity. Instrumental parameters of ICP-SFMS such as take-up time, heating temperature of Au-sorbent, additional gas flow, and sample gas flow were optimized. Detection limit calculated as 3 times the standard deviation of 10 blanks was 0,05 ng/l, RSD = 7-9 %.

As atomic fluorescence spectrometer a mercury analyzer “Mercur”, (Analytik-Jena, Germany) was used. In the amalgamation mode an increase of sensitivity by a factor of approximately 7-8 is obtained compared with direct introduction, resulting in a detection limit of 0,09 ng/l. This detection limit has been improved further by pre-concentration of larger volumes of samples and optimization of instrumental parameters. Detection limit 0,02 ng/l was achieved, RSD = 1-6 %.

Both methods yielded low detection limits suitable for Hg determination in ice and snow. However, ICP-SFMS has the disadvantages of being more time-consuming and more expensive. Moreover, further automatization of the amalgamation unit would be necessary to improve reproducibility. Thus, the AFS method was chosen as very sensitive, reliable and easy operated method for Hg determination in the ice core from the Siberian Altai. Hg concentrations were determined in the top 108 m of an ice core from Belukha glacier. The “pre-industrial” Hg level in ice is low and comparable with other remote areas. Nevertheless, short-time events (as volcanic eruption) were archived in ice-core. Hg concentrations in industrial time show mainly anthropogenic impact from regional sources. The paleo record reflects the history of atmospheric Hg contamination in the Altai region from 1760 until 2001.

# MONITORING RANCIDITY OF FARM MILK USING HEADSPACE SAMPLING

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Consumer acceptance of milk is strongly determined by its sensory characteristics. The development of off-flavor in milk as a result of lipolysis can reduce the quality of milk. The enzymatic release, by milk lipase, of free fatty acids (FFA) from triglycerides causes a flavor defect in milk described as 'rancid'. Triglycerides in milk contain both long chain and short chain fatty acids, which are released at random by milk lipase. The short chains FFA, like butyric acid, are responsible for the off-flavor.

In the Netherlands, milk from every farmer is tested twice a year for the extent of lipolysis, using the BDI method. However, the BDI method only detects long chain FFA, which does not induce off-flavor. On the other hand, headspace sampling does detect the short chain FFA. The aim of this study is to compare the BDI method to headspace sampling.

## Materials and methods

Raw milk was heated at 40°C and mixed in a blender for 1 min. This milk was added in different quantities (0-5 ml) to fresh raw milk to induce lipolysis. After 3 days, the milk was analyzed using the BDI method and headspace sampling.

For determining the BDI value, 30 mL of milk was boiled for 15 min with 8.9 mL of BDI reagent. 0.25 g of the separated fat was put in a titration tube with 5 mL BDI titration medium. Titration was performed with tetra-*n*-butyl ammonium hydroxide until the color of the medium changed.

Solid-phase microextraction (SPME) was used for headspace sampling. The FFA were extracted from the headspace with PA, Car/PDMS, and CW/DVB fibers. It was examined whether addition of salt (NaCl) and decreasing the pH by addition of sulphuric acid (H<sub>2</sub>SO<sub>4</sub>) increased the sensitivity. FFA were analyzed using gas chromatography coupled to mass spectrometry in selected ion monitoring.

## Results

Different options have been tested to increase the sensitivity of the SPME method. First, the PA fiber had a better sensitivity compared to the other fibers. Second, addition of 10% NaCl and lowering the pH to 1.5 increased the sensitivity with a factor of 10.

Whether the headspace sampling produces comparable results to the BDI method is subject of current research and the results of these test will be presented during the conference.

**VACUUM RADIATING DESORPTION AND INFRARED  
SPECTROMETRY (VRDIR) FOR CONTINUOUS MONITORING  
OF SUSPENDED PARTICULATE ORGANIC MATTERS  
IN ATMOSPHERE**

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Previous chemical speciation analysis of atmospheric suspended particulate matters reveals dominant volatile components and moisture tend to vary according to sampling time and temperature. However, current method of volatile organic carbon in particulate matter collect the sample on the quartz filter during 24 hours and measure by the thermal carbon analysis. This method tends to change according to temperature, humidity and pH during one day. So, 24 hours sampling method results in long-term artifact history that has changed during sampling time. Thermal carbon analysis has also a problem that carboxylic acid in particulate organic matter changes to elemental carbon during combustion and makes error to distinguish with real organic carbon value. Our proposing new method utilizes radiating light on the raw samples on the filter in vacuum chamber of which are hourly collected and measures infrared spectra to determine vaporized organic compounds.

# METHODOLOGICAL APPROACHES TO THE INVESTIGATION OF THE METAL SPECIATION IN THE NATURAL WATER

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Elemental speciation is one of the predominant trends of trace metal analysis. The greatest interest to the trace metal speciation in natural water is probably explained by their influence on the bioavailability of essential elements and availability and toxicity of toxic metals. Dissolved metals can exist in surface water as “free” (hydrated) ions as well as complexes with inorganic and organic ligands of both different chemical nature and molecular weight. It is impossible to determine the concentrations of individual metal species because they cannot be distinguished by many analytical techniques used in trace metal analysis. Therefore various forms of the metals need to be separated into several fractions related to their specific activity, such as charge, molecular weight, chemical, physical and biological properties etc. Hyphenated techniques are the most suitable for these purposes. Liquid and gas chromatography as well as non-chromatographic techniques (dialysis, ultrafiltration, extraction) are the most widely applied separation methods. ICP-MS, ICP-AES, ETAAS can be considered as the most sensitive detection techniques. The impossibility of determination of the individual metal species without preliminary division is the main disadvantage of these techniques. Detection of the most toxic metal form is one of the principal problems of analysis. Only few species-specific techniques allow the direct study of the metal speciation. They include stripping voltammetry, radiochemical methods, chemiluminescent (CL) analysis. These methods are suitable for the reliable determination of the concentration of “free” metal ions and some labile complexes. Moreover, the techniques above mentioned are characterized by a low detection limit and wide calibration ranges as well as reasonable cheapness. They do not require preliminary sample concentrating. The short time of analytical signal registration is a very important factor, as the equilibrium between the several metal forms in the water sample is not disturbed during the detection.

In this work ion-exchange and gel-permeation chromatography coupled with membrane filtration, photochemical oxidation of organic metal complexes and CL detection were applied to the study of the speciation of cobalt, copper, iron and vanadium in water from the Dnieper reservoirs and some rivers of Ukraine. The role of various groups of organic matters in the complexation of metals is established.

# THE GENERALIZED PARAMETERS IN SYSTEM OF THE ESTIMATION QUALITIES OF WATERS

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In a basis of modern methodology of an estimation of quality of water measurement of the generalized parameters lays. One of the most essential such parameters are oxidability and toxicity of components of waters.

It was determined  $\text{KMnO}_4$ -oxidability (COD- $\text{KMnO}_4$ ) of water of city reservoirs of Astrakhan during the autumn-winter period of 2004. It is revealed, that oxidability of natural waters does not exceed the values allowable for reservoirs fish-value.

By results of biotesting sewage dumped in a reservoir the payment for toxic dump pays off. More often in toxicological experiments as test-object are used *Daphnia*. Toxicity of water of city reservoirs of Astrakhan during the different periods 2004 by use *Daphnia magna* is investigated. Results of researches are shown in the table.

Definition of a degree of toxicity of water with *Daphnia magna* during 2004

No. of test	Place of sampling	Average size	
		2004, summer	2004, autumn-winter
1	r. Volga. 17 quay. River station	55 sharp action	29 close to sharp
2	r. Car. A dam.	25 close to sharp	47 close to sharp
3	r. Volga. Zaton. The bridge	38 close to sharp	52 sharp action
4	p. Volga. Stadium	18 close to sharp	14 close to sharp
5	The channel on May, 1. Bridge along Kirov st.	63 sharp action	64 sharp action

As follows from the received data, toxicity of water is high and is a little reduced during the autumn-winter period.

Further it is planned to use tests - organisms of various trophic levels to carry out systematic researches on comparison of results of an estimation of quality of natural waters to the help of the different generalized parameters.

# THE EFFECT OF PROTON-DONATING MODEIFIER ON THE SOLUBILITY ENHANCEMENT OF TRIS( $\beta$ -DIKETONATO) CHROMIUM(III) IN SUPERCRITICAL CARBON DIOXIDE

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We found previously that the solubility of tris(pentane-2,4-dionato) chromium(III) ( $\text{Cr}(\text{acac})_3$ ) in a supercritical carbon dioxide fluid ( $\text{SF-CO}_2$ ) was drastically enhanced upon the addition of 2,2,2-trifluoroethanol (TFE) with comparison of general modifiers such as methanol. In this work, the effect of various hydrogen-bond donors as modifier, such as, methanol, ethanol, TFE, 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP) and 3,5-bis(trifluoromethyl)phenol (BTMP), on the solubility of  $\text{Cr}(\text{acac})_3$  in  $\text{SF-CO}_2$  was studied by UV/VIS spectrophotometry. Experiments were done at 318 - 338 K and 10.1 – 20.3 MPa using the  $\text{SF-CO}_2$  extraction apparatus reported previously. The absorption spectra of  $\text{Cr}(\text{acac})_3$  in modified and non-modified  $\text{SF-CO}_2$  provided the same absorption maximum at 562 nm. Moreover, the molar absorptivities were found to be almost the same both in modified and non-modified  $\text{SF-CO}_2$ . The solubility of  $\text{Cr}(\text{acac})_3$  in modified and non-modified  $\text{SF-CO}_2$  was calculated from the absorbance at 562 nm. The IR spectrum of  $\text{Cr}(\text{acac})_3$ -TFE system in  $\text{SF-CO}_2$  showed that the remarkable solubility enhancement effect of TFE can be ascribed to the formation of an association complexes between  $\text{Cr}(\text{acac})_3$  and TFE through a hydrogen-bond in  $\text{SF-CO}_2$ . The compositions of the association complexes were ascertained as  $\text{Cr}(\text{acac})_3 \cdot \text{TFE}$  and  $\text{Cr}(\text{acac})_3 \cdot 2\text{TFE}$  based on the solubility equilibrium analysis. The value of the association constant between  $\text{Cr}(\text{acac})_3$  and TFE increased with an decrease in both  $\text{CO}_2$  pressure and temperature. The values of the formation constant of the association complex between  $\text{Cr}(\text{acac})_3$  and hydrogen-bond donors increased in the following order of ethanol < methanol < TFE < HFIP < BTMP. This order agreed with the reverse of the magnitude of the  $\text{p}K_a$  values of hydrogen-bond donors.



# PECULIARITIES OF FISH OTOLITHS EPMA AS A PROMISING METHOD TO MONITOR ENVIRONMENT

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The elemental composition of the fish otoliths is a potential source of the useful information to recreate environment history of the individual fish in some of the species. In-depth study of the chemical composition of the otolith center (formed early in fish life) and otolith edge (formed later in fish life) ensures chronological and environmental information stored in the otoliths [1]. This information may be achieved by X-ray electron probe microanalysis (EPMA). EPMA is the analytical method to determine the elemental composition of different otolith's parts, their sizes varying from ten up to some tens of microns.

In this paper, the technique for investigation fish otoliths using the microanalyzer Superprobe-733 (JEOL Ltd, Japan) has been elaborated.

The change of element's intensity in accordance with the beam power densities have been chosen as the criterion to select optimum conditions for analysis of the elements. The unstable state of biological samples during electron action is one of the significant difficulties to study the biological samples by EPMA. With this in mind, it is crucial to check up the otolith stability to local heating under the action of electron probe. The stability characteristics given by authors of paper [2] were calculated. These characteristics indicated that otoliths are resistant to the electron action during 30 seconds, if the beam power densities are below 2,8  $\mu\text{W}/\mu\text{m}^2$ . The metrological testing the elaborated technique has been carried out. The quality of all available results complies with the "applied geochemistry" category of performance (category 2).

This technique provided satisfactory results when utilized in analyzing otoliths of Baikal's omul, which can be used as indicators for evaluating the pollution level of the water, as well as revealing pollution mechanisms.

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# THE WASTE WATER TREATMENT - OIL REMOVAL BY FREEZE AND THAW (MICROWAVE) METHOD

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Demulsification is a process which signifies separation of oil and water from emulsion into two phases [1]. Typical demulsification techniques include thermal, electrical, chemical, acoustic, or mechanical methods [2]. Recently, a special method has been encountered in this group: freeze/thaw method (F/T), for water removal from water-in-oil emulsions [3]. In our paper emulsion samples have been separated with the combined use of F/T and microwave radiation (MWR). MWR destabilizes emulsions with the high temperature that reduces the continuous phase viscosity and breaks the outer film of the drops, thus allowing the coalescence; and MWR rearranges the electrical charge distribution of the water molecules while rotating them, and moving ions around the drops. Both effects of MWR result in breaking of the emulsion [4-7]. This demulsification combination has proved to be more effective than F/T method, alone. The object of investigation, in this paper, were emulsion samples prepared by mixing the metal-working-oil, FESOL 09, produced by FAM, Krusevac, Serbia, and deionized water. F/T method has been successfully applied for the removal of oil from emulsions in our previous work [6]. The efficiency of oil removal has been improved with the assistance of MWR, with the achieved oil removal above 90 %. F/T and MWR, are both non-destructive, physical methods, that don't demand addition of chemical agents for their application, which implies that there is no further waste water treatment which usually exists when chemicals are applied. The methods are in accordance with "green chemistry" demands.

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# DETERMINATION OF FERROCENE IN GASOLINE BY ATOMIC-ABSORPTION AND PHOTOCOLORIMETRIC METHODS

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Various knock-reducing metallized additives, including ferrocene, are added to petroleum to improve performance and reduce ecological impact. The use of metallized additives is governed by strict standards, including European standards, because a high content of heavy metals in fuel leads to the deterioration of engine operation and ecological properties of the fuel. As a result the quantity of combustion products emissions increases. An analysis of petrol with the aim of measuring the amount of metallized additives is necessary for checking for adulterated motor fuel. Because of this, enhancing the quality control methods for commercial fuels in order to determine the quantity of iron in them is very topical.

Atomic-absorption methods of measuring metal quantity based on atomization of the fuel itself or of its compounds using organic solvents in a combustion atomizer are described. The given methods are limited to use with petroleum with a high content of unsaturated hydrocarbon.

The modern specifications of the contents of heavy metals in fuel require application of selective, express and safe methods of their determination.

We developed a procedure for the atomic absorption measurement of the quantity of iron in petroleum. This includes its extraction from the organic phase into an aqueous phase which is then atomized directly into an acetylene-air flame. The influence of a number of acids and complexing agents on the iron extraction completeness is investigated. The developed technique is notable for its great reproducibility, expressibility, use of widely-available reagents and ecological compatibility. The method of iron extraction from petrol into the aqueous phase also underlies the photolorimetric methods of ferrocene determination. Optimal conditions and reagents with great potential for getting colored compounds for the selective photometric determination of iron in petroleum are chosen. Two kinds of methods are developed: an express extraction-photolorimetric method and a visual-colorimetric test-method. Accuracy of the developed methods is checked by the method of standard additions and the comparison with the results of the analysis carried out with the use of independent methods. The developed technique was applied for the analysis of fuels sold at filling stations in Donetsk.

# PHOTOMETRIC DETERMINATION OF ACIDIC IMPURITIES IN OILS AND ORGANIC LIQUIDS WITH THE USE OF THE ION PAIR OF TRINONYLOCTADECYLAMMONIUM AND BROMOTHYMOLO BLUE AS THE COLORED REAGENT

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The concentration of acid impurities is an important indication of the quality of petroleum products and the purity of organic solvents, plasticizers, mineral oils, food fats, and polymers. Methods are used to detect organic acids in such compounds have many disadvantages: the alkalimetry - low sensitivity, especially in the determination of weak acids, the extraction-photometric method is laborious, instrumental methods are expensive. In addition, most of methods are commonly unsuitable for direct analysis.

In this work we studied the interaction of the ion pair Bromothymol Blue (BTB-trinonyloctadecylammonium (TNODA)) with organic acids in toluene and its mixtures with different solvents and proposed the method for determination of carboxylic acids in solvents, oils, and other chemicals.

Bromothymol Blue (sulfophthalein dye) is a dibasic acid and can form ion pairs with a quaternary ammonium base at two groups: the sulfo group and the hydroxy group. It is known that in the systems of this kind the stability of ion pairs formed at the sulfo group is rather high, and they virtually are not decomposed by carboxylic and even alkylphosphoric acids. However, the attachment of the second quaternary ammonium base cation (at the phenol hydroxyl group) is characterized by the relatively small formation constant of the ion pair. As a result, in the presence of acids the disubstituted ion pair of trinonyloctadecyl-ammonium and Bromothymol Blue is partially decomposed and the monosubstituted ion pair is formed according to Eq.:



The spectra of these ion pairs are largely different, which forms the basis of the determination method for the spectrophotometric determination of acidic impurities.

This method is highly sensitive (detection limit achieves  $5 \cdot 10^{-7}$  M), reproducible and simple in implementation. The accuracy of the results was verified by the added—found and dilution methods.

*Poster presentations*

# PECULIARITIES OF DETERMINATION OF COMPOSITION OF THE SOLID SOLUTIONS OF THE BIVALENT METALS HYDRATED DIPHOSPHATES

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Questions of the analytic control of maintenance of the bivalent metals cations to their joint presence in materials of diverse fixing always were actual. A simultaneous presence in their composition of two cations with like descriptions makes analysis by sufficiently complicated process. Determination of composition still more complicates, if analyzed object is a solid solution, in which side by side with pair of cations (for example,  $Mg^{2+}$ - $Co^{2+}$ ,  $Mn^{2+}$ - $Co^{2+}$ ,  $Zn^{2+}$ - $Co^{2+}$ ) attends diphosphate anion. Their analysis demands for individual approach to working of methods using to each concrete cations pair.

In report discuss the methodical aspects determination of magnesium, manganese, cobalt, zinc to their joint presence in nitric, sulphuric, chloric salts, and peculiarity of the analysis using to solid solutions of the hydrated diphosphates.

Concentration limits of the diphosphate-ion, admissible to determination of magnesium and cobalt, manganese and cobalt, zinc and cobalt by spectrophotometric method with application of the 1-(2-pyridylazo)-resorcinol (PAR) are presented. Exceeding maintenance of the diphosphate-ion higher admissible supposes a preliminary its separation on the anionite in the  $H^+$ -form. The optimum conditions of cobalt determination and amount of the PAR, necessary for its full fastening are established on foundation of dependence of optical density of the cobalt complex with PAR from concentration  $Co^{2+}$  and pH (buffer solutions citrate-ammoniac and acetate-ammoniac).

In report separately discuss the peculiarities of determination of the anion composition of the solid solutions, that conditioned by ability of diphosphate anion to destruction in water solutions. In given concrete case by most acceptable method of control of the diphosphate anion in the hydrated solid solutions is a traditional method of the quantitative chromatography on the paper. Methodical ways which providing of minimum destruction of the diphosphate anion in the time of preparation of the model to analysis (translation in soluble condition) and during quantitative determination of the  $P_2O_7^{4-}$  anion are considered.

# DETERMINATION OF COMPLETE COMPOSITION OF NON-STABLE GAS CONDENSATE BY GAS CHROMATOGRAPHY

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Gas condensate is the second product of importance yielded at gas condensate fields. Unstable gas condensate (UGC) is mostly consists of liquid and lighter hydrocarbons. In addition, UGC may contain significant amounts of high-boiling hydrocarbons (up to  $C_{44}$ ), hydrogen sulphide (up to 25 % m/m) and mercaptans, inorganic gases ( $N_2$ ,  $H_2$ , He,  $CO_2$ ), methanol and some other components. Then, UGC is an unstable product being under pressure of 1-10 MPa. That is why a problem of the determination of complete composition of UGC is quite complicated. Main method used in its solution is gas chromatography.

The actual Russian standards allow presentation of hydrocarbon components of UGC as individual compounds only for  $C_1$ - $C_6$  hydrocarbons. The rest is described as pseudo-compound  $C_{7+}$ , although its content may reach 60 % m/m. Apparently, the detailed determination of composition of hydrocarbons  $C_{7+}$  in UGC allows essentially to raise quality of both its processing and its record. The best method for the determination of heavy hydrocarbons is capillary gas chromatography. Typical approach is based on preliminary separation of UGC samples to gaseous and liquid phases.

In VNIIGAZ a complex of methods is developed allowing the determination of complete composition of UPG samples. The high-boiling hydrocarbons may be presented as groups ( $C_n$ ) or as component-fraction composition. For the determination of high concentrations of hydrogen sulphide gas chromatography with thermo-conductometric detector is used, and for the determination of low concentrations of  $H_2S$  and individual light mercaptans ( $C_1$ - $C_4$ ) flame-photometric detector is applied. Methanol in UGC samples is determined by vapour-phase gas chromatography.

The approach developed will be used for working up of a new generation of the corresponding standards. The same approach may be also adapted for analysis of some other products of gas industry, such as liquefied gases, natural gas, etc.

# DIRECT ANALYSIS OF UNSTABLE GAS CONDENSATE USING HIGH-PRESSURE SUPPLY OF THE SAMPLES INTO A GAS CHROMATOGRAPH

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Unstable gas condensate (UGC) is a large-tonnage raw material for producing of liquefied gases, motor fuels and other products. It is characterized with very complicated composition being under pressure up to 10 MPa. That is why analysis of UGC samples is rather complicated task.

There are two main approaches to its solution. Traditional approach is based on preliminary separation of UGC samples to gaseous and liquid phases and their subsequent analyses [1]. This approach is well-developed and it allows obtaining quite precise results being used properly. However, this method is relatively complicated. Multi-stage procedure is a source of potential errors, then, it makes the analyses quite time consuming. More progressive approach is based on the direct analysis of the pressurized UGC samples. In both cases the determination of heavy hydrocarbons (up to  $C_{44}$ ) is made by capillary gas chromatography.

Both these approaches may be realized using laboratory gas chromatographs produced by Joint-Stock Company SKB Chromatek (Russia). Application of a specially designed injector for the pressurized sample supply to the chromatograph Crystal 5000.1 allows reducing time of the determination of full hydrocarbon range of the sample from 6-8 h to about 1 h. In addition, significant simplification of the procedure improves precision and accuracy of the data obtained. In the nearest future this device will be equipped with the facilities allowing direct determination of inorganic gases (including hydrogen sulphide).

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## HEAVY METAL FRACTIONATION IN ROOF RUN-OFF IN ILE-IFE, NIGERIA

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Runoff was collected from three different roofing materials that are commonly used for roofing in Ile-Ife, Nigeria. The samples were collected in four geographical locations in the town. The run offs were analysed for pH, Temp, TDS, Cl<sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, PO<sub>4</sub><sup>3-</sup>, NO<sub>3</sub><sup>-</sup>, EC and some heavy metals both as regards total, dissolved and particulate fraction. The quantity of these parameters varies with different roofing materials. In terms of dissolved metals, Fe is the most predominant metal with mean values ( $0.59 \pm 0.29$ ,  $0.89 \pm 0.14$ , and  $1.04 \pm 0.27$  mg l<sup>-1</sup>) for asbestos, ceramic tiles and metal sheets respectively. The tendency of the roofing materials to leach dissolved metals is arranged as follows: Zn and Cr (metal sheet > asbestos > ceramic); Fe (metal sheet > Ceramic > asbestos), Cd (asbestos > metal sheet > ceramic) and Pb (asbestos > ceramic > metal sheet). In terms of particulate metals, the concentration of Cd and Pb are higher in the asbestos than other roofing stuffs. The sequence of their predominance in asbestos is as follows: Pb ( $0.83 \pm 0.55$  mg l<sup>-1</sup>) > Cd ( $0.29 \pm 0.07$  mg l<sup>-1</sup>). In all the roofs, both particulate and dissolved metals except Zn exceed WHO permissible limits for drinking water. The high levels of the metals obtained in this study may likely result in consumer complaints since some of the metals are not only carcinogenic but are also liable of impacting bad taste in water. Direct discharges of the runoff could have toxic effects on natural waters and their local infiltration would rapidly lead to soil contamination. Result of spiking experiments with the run off samples showed good recoveries for all the metals analyzed. Blank determinations were made for background corrections.

## DETERMINATION OF ORGANIC COMPOUNDS BY RADICAL INDICATOR REACTIONS IN KINETIC METHODS OF ANALYSIS

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The determination of organic compounds by their direct catalytic effect on indicator reaction rates is a relatively unexplored area promising valuable analytical characteristics, as we have recently shown in the determination of traces of unsymmetrical dimethylhydrazine (UDMH) by the oxidation of 3,3',5,5'-tetramethylbenzidine (TMB) by atmospheric oxygen initiated with persulfate [1].

We have studied the effect of some inorganic ions and ~30 organic compounds in radical chain processes: the polymerization of vinylpyridine (VP) or methyl methacrylate (MMA) initiated by tetraethyl-ethylenediamine-persulfate system and in the oxidation of TMB by O<sub>2</sub> initiated photochemically or by persulfate. Theoretically, the analyte effect on a reaction rate may be governed by the following: (1) formation rate of a radical particle of the analyte and (2) reaction rate of this radical with the chain carriers (or initiating particles) of the indicator reaction. These interactions can result in either acceleration or retardation of final product formation by which the indicator reaction rate is measured. Practically, the set of compounds changing the reaction rates depends on the nature of the indicator reaction *per se* and by the nature of the initiating system. In polymerization, the nature of monomer has a great effect: VP polymerization is influenced mostly by electron acceptors through their effect on the rate, while that of MMA is affected by electron donor compounds through their influence on the lag period. Some systems demonstrate interesting selectivity, e.g. signals are obtained from primary C<sub>1</sub>-C<sub>3</sub> amines in the presence of all secondary and tertiary C<sub>1</sub>-C<sub>3</sub> amines and all C<sub>4</sub> amines (TMB – O<sub>2</sub> with photoinitiation); di- and trinitrophenols are detectable in the presence of phenol and nitrophenol (VP polymerization), etc.

Effects of compounds observable at lower concentrations are probably connected with the effect on the initiation/termination stages (transition metals in TMB–O<sub>2</sub> reaction with photoinitiation, UDMH in the same reaction with chemical initiation), while the compounds influencing only at higher concentrations may affect chain propagation stages.

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# SPECTROPHOTOMETRY APPLICATIONS FOR ORGANIC ELEMENTAL MICROANALYSIS

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Elemental organic microanalysis is one of the main methods for purity verification of organic and organoelement compounds and polymers.

The spectrophotometric (SPh) determination of heteroelements in organoelement compounds (OEC) and materials is the most universal, accurate and widely spread. The possibilities of the method for determination of such establishing heteroelements as F, B, P, Si and some metals are comprehensively investigated in the laboratory of microanalysis at the INEOS RAS. The more rational variants of OEC mineralization were supposed. There are three main variants for mineralization of organic matrix before the SPh determination of heteroelements. They are oxygen flask combustion by Shoemaker, wet acid digestion by Kjeldall and melting with KOH in nickel bomb. Frequently for fluorinated organic substances the oxygen flow combustion in presence of granulated MgO by Pregl-Korschun with following pyrohydrolysis of  $MgF_2$  is specially performed.

SPh determination of silicon and phosphorus in form of Si-Mo and P-Mo heteropolyacids are used successfully for series determination of these heteroelements in OEC and polymers (polysiloxanes, polyphosphazenes, etc.).

SPh boron determination in form of complex with Azomethine-H is the reliable microanalytical method for boronorganic compounds, carboranes, metallacarboranes, etc. Before boron determination the samples should be melted with KOH at 900°C.

The differential variant of SPh (DSPh) is the most accurate for SPh fluorine determination in highly fluorinated compounds and polymers. The DSPh determination of fluorine is based on the optical density reducing of the colored Th(IV)-Arsenazo(I) complex due to the presence of fluoride ions. There are two types of mineralization before the DSPh variant – special digestion in oxygen flow by Pregl-Korschun or in oxygen flask by Shoemaker.

The most universal method for sample destruction before SPh metal determination (Fe, Mo, Al and etc.) is the sulfur acid digestion at high temperature by Kjeldall. It can be enforced by microwave decomposition in the microwave oven.

SPh ultramicrodetermination methods were developed for P, B, Si from sample weights in 1-2 mg.

All these microanalytical methods are in the everyday use at the analytical laboratory of INEOS RAS.

# MATHEMATICAL MODELING OF THE PROCESS TAKEN PLACE IN THE “SOLID SUPPORT – SOLUTION”, TYPE INDICATOR PIPES

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One of perspective development trends of methods of heavy metals contents reification in natural waters is the creation of selective and express test-method with a possibility of detection at a level and above than maximum allowable concentrations (MAC) of metals - toxiferous.

In this aspect the special attention is caused by indicator pipes (IP) of a type „solid support - solution toxiferous<sup>2</sup>, devices distinguished by a simple working in a dynamic behaviour. Cr(VI) is one of the most widespread and broad scale contaminants of waters of different categories with rather low MAC = 0,05 mg/l. At the working out of IP for definition of the Cr(VI) contents at level of MAC and higher, we have chosen Cr(VI) complex with 1,5-diphenylcarbazine (DPC) and sorbent sulfo cation exchange resin KU-2-8. The visually - color scale permitting semiquantitative Cr(VI) definition in interval as a sorbent of concentrations 0,025÷0,300 mg/l has been offered. In works [1, 2] the results on stability of a complex on a surface KU-2-8, as well as the data describing kinetic and weight exchange taking place in a layer of cation exchange resin KU-2-8 at sorption of a complex Cr(VI)·DPC are presented. In this work the series of parameters effecting noticeably on processes taking place in IP for a heterogeneous system, in “KU-2-8 - solution Cr(VI)·DPC” using the method of mathematical modelling is reviewed. For the description of the dynamic processes, taking place in a layer of cation exchange resin KU-2-8 in internal diffusion and external diffusion areas the mathematical model has been accounting longitudinal diffusion of a complex on an altitude of a layer. This model allows to established effect of some sorption process parameters on its dynamics without realization of fissile experiment. By calculations and experimentally it has been established, that in a complex solution passing range velocity from 2 up to 18 ml/min on a surface KU-2-8 sequentially mono- and poly-layers are formed of a complex, and when the rate of volume flow increases only the monolayer is formed. The obtained results confirm the adequacy of obtained model and can be utilized at practical working out of IP for definition of metals - toxicants in waters of the different nature.

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# GAS CHROMATOGRAPHY/MASS SPECTROMETRY DETECTION OF XENOBIOTICS IN ENVIRONMENTAL OBJECTS

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Intensive application of pesticides and polymers in agriculture and industry cause the increase of number of toxic organic substances, which circulate in an environment, and constantly complicates their disclosure, identification and quantitative detection.

Polychlorinated dibenzo-*p*-dioxins (PCDD) are the highly toxic and highly stable impurities of some pesticides and industrial chemicals, for example, chlorphenols and their derivatives (chlorphenoxiacetic acids, their salts and ethers) and polychlorinated biphenyls (PCB). Most danger is presented by tetra- and pentachlorosubstituted isomers and, especially, 2,3,7,8-*p*-dioxin (TCDD). Presently the PCDD detection in different objects of environment is impossible without the use of combined gas chromatography – mass-spectrometry, which allow carrying out reliable identification of picograms ( $10^{-12}$  g) and femtograms ( $10^{-15}$  g) quantities of these substances. It is necessary to notice that reliability of identification, for example, TCDD by these methods largely depends on presence in the analyzed sample of other stable organochlorine substances, such as organochlorine insecticides and products of their decomposition – DDT, DDE, DDD, PCB, the fragments of molecules of which can influence on the nature of TCDD mass-spectrum.

Triazole derivatives (diniconazole-M, epoxiconazole, fluhinconazole etc.) are widely used in agricultural practice as fungicides. The low application rates of these formulations require specific conditions for identification of residual quantities in different objects.

Method 1613 of US Environmental Protection Agency (US EPA) was used for the PCDD detection in the objects of environment (water, soil etc.). PCDD detection was done with the help of Polaris Q gas chromatograph/mass spectrometer on mass-spectrum of electronic impact in the MS-MS mode. Division of isomer PCDD was carried out on a capillary column from the sintered quartz DB-5 MS (60 m × 0,25 mm, thickness of tape 0,25 μm). The same device was used for detection of fungicides formulations active ingredients in soil.

The results of analysis of samples from Desnyansky and Dniper water-supply stations water are given in the report concerning the contents of PCDD and soil samples concerning the contents of triazoles.

## ACCELERATED DETERMINATION OF METALS IN SOILS

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The increase of technogenic load at soils puts before the analysts a problem of improvement the existing techniques of determination of heavy metals; they are the main contaminants which are capable to migrate on a soils profile and to fall in plants and a hydrosphere. The perfecting of existing in agrochemistry techniques of heavy metals extraction in selective solvents is possible by the introducing of additional physical effect, for example, ultrasonic (US). Mincing and dispersion of assay take place under the influence of ultrasonic, that make for increase of a reactionary surface and extraction rate of heavy metals in a solvent.

The optimum conditions of heavy metals extraction from ordinary chernozem in different solvents are selected both at determination of the mobile forms of elements, and at an estimation of their gross contents. It is established, that the stage of elements extraction in the greater measure depends on time of action and intensity of ultrasonic, nature of selected solvents and determined elements. It is shown, that for all type of soils the time of low frequency ultrasonic action does not exceed 10 minutes, and the intensity ranges in an interval of 3-4 W/cm<sup>2</sup>.

The accelerated techniques with the satisfactory metrology characteristics of heavy metals extraction from soils of different type with use of ultrasonic at the stage of sample preparation are designed, they have allowed to reduce time of extracts obtaining in 6 times and time of gross decomposing in 3 times. It is established, that the heavy metals in ordinary chernozem basically are represented by compounds, well solvable in weak acids and buffered solutions. The part of exchange cations of heavy metals makes 10-12 %, acid soluble - 40-50 (80) %. 40-60 % of heavy metals compounds are solved in mixtures of strong acids. The water-soluble forms of heavy metals practically are not represented.

Thus, it is shown, that use of ultrasonic at the stage of sample preparation or different type soils allows considerably to reduce time of extracts obtaining for determination of soil forms of heavy metals and realization of full decomposing for an estimation of the gross contents.

# FEASIBILITY TO APPLY THE PROCEDURE OF NONDESTRUCTIVE X-RAY FLUORESCENCE ANALYSIS OF PLANTS FOR MILK POWDER EXAMINATION

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Lack of standard references materials (SRMs) of milk and dairy products in the State Register complicates the chemical analysis of milk powder. This is particularly vital at the stage of selecting standard samples for calibration plotting. Their biochemical composition and properties should be adequate to the objects analyzed. For this purpose the effectiveness of nondestructive x-ray fluorescence procedure of Na, Mg, Al, Si, P, S, Cl, K, Ca, Mn, Fe, Sr and Zn determination in plants [1] was estimated when analyzing milk powder by XRF. The calibration was plotted with SRMs of plants. Cellulose, the organic basis of plants, is similar in the ratio between the matrix elements (carbon, hydrogen and oxygen) to the low-fat milk matrix, mainly presented by lactose. However the fat content in dry milk achieves 30-50 %. In this case the proportion of oxygen in the matrix decreases two-fold.

The error values characterizing the effect of dry milk organic basis composition on the accuracy of XRF results were estimated by theoretical intensities. The dry milk matrix was simulated by: (1) lactose assuming complete absence of fat fraction in milk; (2) 90 % lactose and 10 % oleic acid simulating low-fat milk; (3) 70 % lactose and 30 % oleic acid, as well as 50 % lactose and 50 % oleic acid, when simulating high-fat milk. The error values, characterizing the discrepancy between the calculated intensities, when cellulose is selected as the dry milk matrix, and, when the matrix is presented by above compositions, were below 1 % and 3-9 % for low-fat and high-fat milk, respectively. Available data provide the conclusion that the procedure of nondestructive x-ray fluorescence analysis of plants is applicable for analyzing dry low-fat milk samples without refining distinctions of organic component of these objects. In analyzing high-fat milk it should be considered, that the value of overall error would grow according to the fat content. The content of the above elements in 40 dry milk samples was defined by the procedure discussed in the paper.

1. E.V. Chuparina, T.N.Gunicheva. Nondestructive X-ray fluorescence determination of some elements in plant materials // J. Anal. Chem. 2003. V. 58, No. 9. p. 960-966.

## IDENTIFICATION AND QUANTIFICATION OF SEVERAL PESTICIDES IN LAB ATMOSPHERE

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The pesticide mixture sample from the air of the GC lab in which raw materials and pesticide products are analyzed was collected for three consecutive months. The sample to be analyzed was made using the extraction of the filter taken from the air purifier.

Observing the amount and variety of pesticides analyzed by GC chromatography we decided to observe 14 of the most represented pesticides: Prometryn, Deltamethrin, Fenitrothion, Tebuconazole, Buprofezin, Malathion, Myclobutanyl, Atrazine, Acetochlor, Bifenthrin, Alachlor, Pendimethalin, Dichlormid and Trifluralin.

To analyze pesticides from the sample, several GC techniques were used: GC with FID and EC detectors and GC/MS with external standards. Pesticides are mostly analyzed using split/splitless technique where higher amount of injected solution exits the gas chromatograph without decomposing; therefore by quantification of the several pesticides in the filter, we found out how harmful is exposing analysts to pesticide compounds during the GC analysis.

Since numerous pesticides are cumulatively deposited in the living organisms and have harmful effects on them, the results of this work can contribute in increasing the protection of the analysts, especially those in the domain of pesticide analysis.

1. The Pesticide Manual, Twelfth Edition, BCPC 2000
2. Compilation of EPA's Sampling and Analysis Methods, SE, CRC, 1996.
3. Official Methods of Analysis of AOAC International, 16<sup>th</sup> Edition



## **ADVANTAGES AND DISADVANTAGES OF MOLYBDENUM DETERMINATION BY NAA**

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Molybdenum because of its unique chemical versatility and unusually high bio-availability has been incorporated widely into biological systems. It is the only second-row transition metal that is essential for most of living organisms and belongs to elements (along with Cu, Cd, Hg, Pb and Cr) potentially hazardous to humans.

Molybdenum is classified among the elements for which the state of art of analysis is still unsatisfactory. The modest number of referenced materials available with certified value for Mo seems to confirm this.

Neutron Activation Analysis (NAA) is one of the analytical methods recommended for low level Mo determination in biological materials.

In this work some important factors affecting the uncertainty of results of Mo determination by radiochemical NAA in the materials of biological origin have been discussed.

The concentration of uranium in the analyzed sample, as well as the effectiveness of digestion of the examined materials and the effect of caning material needs to be considered.

Bi-functional radio-analytical scheme, based on exchange and extraction column chromatography, which provides the reliable information on molybdenum and uranium contents in biological materials has been elaborated. The contribution of uranium fission reaction has been strictly monitored. The uncertainty of the results of Mo determination by the presented method is very low.

It has been proved lately that the NAA method of Mo determination meets the requirements of primary ratio methods of measurements.

# NEW METHOD FOR DETERMINATION OF DRY RESIDUE IN NATURAL WATER BY MEANS OF DIRECTED CRYSTALLIZATION

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Total water salinity (TWS) is the most important water quality index in the ecological monitoring, and also in the verification of falsification of medical and drinking waters. The content of dissolved organic, inorganic compounds, colloids and suspensions in water is called as total salinity. As a rule, TWS in the form of dry residue is estimated by means of standard gravimetric procedure after evaporation of water. This method takes 1-2 working days and demands great volumes of analyzed sample (0.5 - 1 L).

As alternate method, we offer a new one of determination of TWS by means of directed crystallization (DC), which is known as an efficient method of group analytical concentrating of impurities from water solutions. This method differs by the opportunity of automation, small duration (3 hours), simplicity of modification and the small volume of analyzed sample (15 ml). DC of water samples was carried out by means of Bridgeman-Stokbarger method in glass cylindrical containers, starting from the seed. It was revealed, that the bottom of a generated ice ingot is transparent, and there is an opaque field on top. It is shown, that the extent of this opaque field correlates with the content of the inorganic salts dissolved in the water and can serve as the analytical signal in the analysis. Solutions keeping equal parts of total mass of the basic ingredients of natural water ( $\text{NaCl}$ ,  $\text{Na}_2\text{SO}_4$ ,  $\text{NaHCO}_3$ ) with their integral concentration from 0,05 up to 4 g/L were used for graduation of the method.

It is shown that metrological characteristics of the suggested methods are commensurable. Dissolved gas is pushed away by front of crystallization, takes the air and does not influence on the obtained results during the analysis of the water. Process is carried out at the lower temperature ( $-15^\circ\text{C}$ ), expelling chemical transformations of ingredients. The procedure was tested on different samples of natural and drinking water of the Kharkov region.

The offered method can be recommended for changing of more laborious and prolonged standard procedures of definition of total water salinity, which are used now.

# **BROMATE AND DISINFECTION BY-PRODUCTS IN THE WATER SUPPLY OF METRO MANILA, PHILIPPINES**

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This paper presents a study of bromate and organic disinfection by-products (DBPs) in the drinking water supply in Metro Manila. DBPs are unintended by-products of the chlorination of the water supply. Bromate may occur in water as a probable contaminant of the technical grade hypochlorite used in the water treatment. In the period of October 2002 to June 2003, bromate and DBPs were measured in tap water samples from different areas in Metropolitan Manila. A microextraction followed by gas chromatography with electron capture detection was used for the determination of DBPs that included the trihalomethanes (THMs), haloacetonitriles (HANs), haloketones (HKs), chloropicrin, and haloacetic acids (HAAs). The analysis of HAAs required derivatization using acidified methanol. Chloroform, bromodichloromethane, dichloroacetonitrile, trichloroacetone, and monochloroacetic were the organic compounds quantified in some of the treated water samples. Bromate was determined by fuchsin reaction and spectrophotometry. Bromate concentrations were between 17 and 411  $\mu\text{g/L}$  in all water samples. Our results indicate that the levels of bromate and DBPs exceeded the US EPA National Drinking Water Standards and the WHO Drinking Water Guidelines.

## USE OF SEMI PERMEABLE MEMBRANE DEVICES (SPMDs) TO INDOOR AIR MONITORING OF PYRETHROID INSECTICIDES

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An easy, rapid and environmentally friendly methodology was developed for the extraction of pyrethroid insecticide residues from semi permeable membrane devices (SPMD), based in a microwave-assisted extraction, in front of a dialysis method nowadays widely employed. Several solvent such as hexane, toluene, acetonitrile, cyclohexane and ethyl acetate were tested as microwave-assisted extraction solvent. Mixtures of hexane and toluene with acetone were also assayed and provide better results than single solvents.

The proposed procedure are detailed next: each SPMD was microwave-assisted extracted twice with 30 mL hexane:acetone, and irradiated with 250 W power output, until 90°C in 10 minutes, being this temperature held for another 10 minutes. Clean-up of extract was performed by acetonitrile-hexane partitioning coupled by a solid-phase extraction with a combined cartridge of 2 g basic-alumina (deactivated with 5% water) and 0.5 g C<sub>18</sub>.

Gas chromatography mass-mass acquisition was used for the pyrethroid determination. Pyrethroids investigated were Allethrin, Prallethrin, Tetramethrin, Bifenthrin, Phenothrin, λ-Cyhalothrin, Permethrin, Cyfluthrin, Cypermethrin, Flucythrinate, Esfenvalerate, Fluvalinate and Deltamethrin. Piperonyl butoxide, main synergist compound for pyrethroid compounds, was also studied.

Limits of detection values ranging from 0.2 to 0.8 ng/SPMD and repeatability from 2.0 % to 8.3 % were achieved. Pyrethroid recoveries for spiked SPMD (100 ng each pyrethroid) were from (57 ± 5) to (101 ± 4) % for microwave-assisted extraction, versus from (34 ± 3) to (91 ± 3) % for dialysis reference method. A substantially reduction of solvent amount and analysis time were achieved.

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# UPTAKE AND BIOAVAILABILITY OF PERSISTENT ORGANIC POLLUTANTS BY PLANTS GROWN IN CONTAMINATED SOIL

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This study assesses the uptake of persistent organic pollutants ( $\alpha$ -Endosulfan,  $\beta$ -Endosulfan and Endosulfan sulphate) from lettuce. The lettuce plants were grown on compost that had previously been contaminated at 10 and 50  $\mu\text{g/g}$ .

The soil was slurry spiked by adding the appropriate amount of each Endosulfan compound in acetone in an approximate ratio of 1:2, w/v soil:solvent. The solvent was left to evaporate at ambient temperature for 24 hours.

Lettuce plants were grown under artificial day-light for 12 hours a day. The uptake of POPs was assessed by measuring the amount of Endosulfan compounds in roots and leaves from lettuce plants after 10, 20 and 33 days. In addition, control plants grown in uncontaminated soil were monitored and analysed.

The influence of soil ageing on the recovery of POPs from spiked soil samples was also assessed. Spiked lettuce samples were subjected to *in vitro* gastrointestinal extraction to assess the bioavailability of Endosulfan compounds. All samples (soil and lettuce) were extracted using pressurised fluid extraction and analysed using gas chromatography with mass selective detection.

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# SPECTROPHOTOMETRIC DETERMINATION OF Ce(III) AND Ce(IV) IN FUNCTIONAL MATERIALS

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Cerium is one of the most widely used activators, which improve the working characteristics of many scintillators. Determination of the valence state of cerium in single crystals of alkaline and rare-earth borates allows to establish the nature of activator centers for purposeful influence on the scintillation efficiency of the matrix.

Due to high oxidation ability of Ce(IV), special attention is to be paid to retaining its valence state unchanged in the dissolution process of the analyzed samples which contain microquantities of the determined component.

Investigated is the influence of the purity degree and concentration of sulfuric acid used for samples dissolution, on the analysis precision. Chosen are optimum conditions of sample preparation for the analysis excluding loss of Ce(IV) due to its interaction with organic impurities-reducers present in sulfuric acid. The photometric technique for Ce(IV) 0.002 – 0.1 % determination in alkaline and rare-earth borates is worked out. The technique based on *o*-tolidine oxidation by Ce(IV). The relative standard deviation is 0.02 – 0.1.

To determine of Ce(IV) in acid soluble single crystals, a simple and sensitive method is proposed. The method is based on the reaction of tropeoline 00 oxidation by cerium(IV) in sulfuric acid solution with subsequent measurement of the light absorption decrease of the solution. The influence of the reagent concentration on the analysis precision is studied. The procedure for Ce(IV) determination in ammonium dihydrophosphate doped by cerium is elaborated. The minimal determined concentration of cerium equal to 0.04  $\mu\text{g/ml}$  is lower than that of analogous methods by a factor of several dozens. The relative standard deviation does not exceed 0.1.

The total cerium content in the single crystal samples on the basis of rare-earth elements is determined by photometry after Ce(III) oxidation by ammonium persulfate. The Ce(III) content is calculated from the difference. Comparison of the determination results of the total cerium content obtained by photometric and atomic emission methods for  $\text{Li}_6\text{Gd}(\text{BO}_3)_3:\text{Ce}$  demonstrated the elaborated procedure precision and systematic error absence.

**RAPID PHOTOMETRIC METHODS FOR WATER ANALYSIS IN FIELD. EXTRACTION-FREE RAPID PROCEDURES FOR THE DETERMINATION OF TRACES OF REGULATED METALS WITH 1-(2-PYRIDYLAZO)-NAPHTOL-2**

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Development of extraction-free photometric procedures for the determination of traces of metals for which hygienic and environmental regulations have been established is an urgent problem. For solution of this problem we used as an organic reagent 1-(2-pyridylazo)-naphthol-2 (PAN) which forms intensely coloured complex compounds with many metals and is frequently used for their extraction-photometric determination; however these procedures did not find wide application in water analysis due to lack of selectivity and necessity of using organic solvents.

We examined a possibility of carrying out complex formation in aqueous PAN-Me system in presence of surfactants of different nature – cationic, anionic, non-ionic. Conditions have been studied of obtaining complexes of Zn, Ni, Co with PAN in water-micellar solutions of non-ionic surfactants (OP-10, OS-20, Triton X-100), optimum concentrations of reacting compounds as well as their mixing order were determined, possibility was verified of using different buffer solutions and masking agents. Conditions of selective determination of Zn, Ni, Co in presence of each other have been found as well as in presence of other metals – Cu, Cd, Pb, Fe, Mn, Al, for this purpose EDTA, sodium sulfide and sulfite were used as masking agents. Using data obtained extraction-free photometric procedures for the determination of Zn, Ni and Co in water have been worked out with lower limit of determination 0.01-0.02 mg/dm<sup>3</sup>. These procedures compared to unified ones are more simple in performance, and in the case of Ni and Co determination – more sensitive. Carrying out reactions in water-micellar medium permits to exclude organic solvent extraction stage which increases rapidity and environmental safety of analysis. Procedures have been checked by determination of standard additions of metal salts in real water samples and applied for analysis of natural surface and ground water. Developed procedures of Zn, Ni and Co determination have been introduced into technical supply of portable laboratory for water analysis “Aqua-Test”.

# MONITORIZATION OF $\text{Ca}(\text{OH})_2$ CONTENT IN ANHYDRITE, SUBPRODUCT OF HF PRODUCTION PROCESS, BY FT-IR SPECTROSCOPY USING PLS CALIBRATION METHOD

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Nowadays, environmental concern is an important aspect that governments take into account more and more. So, industrial waste recycling is a way to improve resources, economy and environmental issues. In this sense anhydrite, an industrial waste, has different applications such as: building material and road construction.

Anhydrite is formed as a result of the HF production process, when fluorspar mineral ( $\text{CaF}_2$ ) reacts with  $\text{H}_2\text{SO}_4$  (cc). However, before using this subproduct, anhydrite must be neutralized with CaO resulting in a maximum amount of 1.5 % CaO. The neutralization reaction generates water, and then a part of CaO is hydrated.

Determination of the CaO excess is carried out using chemical analyses which are time and reactive consuming. Nevertheless, Fourier transform infrared (FT-IR) spectroscopic analysis of this kind of material shows a common vibration band at  $3640\text{ cm}^{-1}$ , which belongs to O-H group, due to  $\text{Ca}(\text{OH})_2$  generated during the neutralization reaction.

The aim of this research consists on the development of an analytical methodology to quantify  $\text{Ca}(\text{OH})_2$  content in neutralized anhydrite samples, using FT-IR spectroscopy and partial least squares quantitative analysis technique.

A previous study was carried out to optimize resolution and scan spectroscopic variables in order to improve the FT-IR signal. The baseline method was used to quantify the O-H group band.

The results obtained by lineal regression (LR) and by parcial least square regression (PLS) methods have been compared to quantify the O-H signal in anhydrite samples. The PLS quality is characterized by a correlation coefficient of 0.9942 (cross-validation) using four factors and a root mean square error of calibration (RMSEC) of 0.058. The correlation coefficient of LR method obtained was 0.9753.

PLS method applied to spectral data provides excellent quantitative analytical results. It offers more accurate and robust prediction compared with the results obtained by LR method. Therefore, the  $\text{Ca}(\text{OH})_2$  determination by FTIR using a PLS model calibration has demonstrated to be an adequate tool, despite the disadvantages of quantitative analysis using FTIR spectroscopic technique.



# SPECTROPHOTOMETRIC DETERMINATION OF RARE EARTH ELEMENTS IN MONOCRYSTALS AND STARTING LEAD MOLYBDATE RAW MATERIAL

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Lead molybdate monocrystals find wide application as scintillators, laser systems of acusto-optical deflegmators and modulators. Present impurities-activators in molybdate as Nd, Pr etc cause the appearance in doped crystal regions of selective absorption and spontaneous luminescence. For the quality characterization of lead molybdate crystals doped by rare earth elements it is necessary besides the stoichiometry to monitor the activator content. Even minor deviation of rare earth additive in monocrystal from the given value substantially change its optical, scintillation and other useful properties. To analyze minor samples of lead molybdate it is necessary to determine microgram quantity of rare earth element. The most simple and sufficiently accurate is photometric method with using of colour reagents. For 0,05-3% rare earth elements was chosen arsenazo III as a of good studied and frequently used reagent. However this reagent is not selective for rare earth elements and their determination in presence of molybdenum and lead macroquantities provides preliminary macrocomponent separation. Separation methods that is based on precipitation, rare earth extraction etc are enough laborious and prolonged. For the system that is under study to rise Nd determination selectivity is promising utilization of EDTA as complex forming agent. The elaboration of photometric determination for rare earth, for example Nd, in the presence of molybdenum and lead milligram quantities is a matter of interest.

As the result of the performed investigations was offered to make direct photometric determination of Nd microgram quantities in the presence of 500-fold and 1100-fold quantities of Mo and Pb correspondingly. The rare earth determination procedure involves sample dissolution in HCl, molybdenum reduction to Mo (V) by hydrazine and lead and Mo (V) masking by EDTA. The maximal colour development of Nd-arsenazo III complex was obtained at pH 2,7-2,8. The optimal condition of Nd determination that was established permit to estimate Nd without separation in solution after sample decomposition. Relative standard deviations at determination of 5-20  $\mu\text{g}$  of Nd from 0,1 g  $\text{PbMoO}_4$  are 0,1-0,03. The received data allow to use the offered procedure for solving of wide circle of analytical problems.

# RESULTS OF STUDYING HOT PRESSING ADAPTABILITY FOR NONDESTRUCTIVE X-RAY FLUORESCENCE ANALYSIS OF PLANTS

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For the purposes of environment monitoring the priority of nondestructive procedures for analysis of plants remains the same. Under nondestructive XRF determination of Na, Mg, Al, Si, P, S, Cl, K, Ca, Mn, Fe, Sr in plants [1] a pellet is pressed from mixture of 7,2 g sample and 0,8 g H<sub>3</sub>BO<sub>3</sub>. However solving many geochemical tasks is based on the samples with mass no exceeding 2 g. Pressing 3 g of plant fodder powders at 120-160° C during 2-3 min, pressure of 60-120 MP, proposed by [2], permitted to prepare durable pellets without binder. The results of studying hot pressing adaptability for preparation of plant pellets with the mass, never exceeding 2 g, are discussed.

Powders of artichoke tubers, grass mixture, birch leaves and cellulose obtained with treating raw plant material by different technologies were used. Estimating was fulfilled for Cl, K, Ca, Cr, Mn, Fe, Ni, Cu, Zn, Rb, Sr, Zr. The intensities of analytical lines were measured by spectrometer S4 PIONEER. The obtained results demonstrate that hot pressing is suitable to prepare plant materials for XRF analysis. This procedure is simple, fast in performance, free from using reagents; necessary temperatures are low and easily realizable in practice. However, its spreading on the other types of biological materials must start with prior studying the element behavior and factors affecting exactness of XRF results.

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# PHYSICAL-CHEMICAL METHODS OF INVESTIGATION IN ANALYSIS OF POLYMER-SILICA NANOSORBENTS

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Nanostructures synthesis and treatment are corrected to various material types (organic, inorganic, and biological), which are used in different spheres of science, medicine and technologies. These processes have the special importance, because the possibility of materials practical use depends just of them. Molecular design allows decreasing the questions, connected with regulation of shape, size, structure and morphology as well to investigate the questions of molecules, supermolecular formations nanoobjects and nanostructural materials connection with various properties.

The hybrid nanocomposite polymer-silica materials on the basis of oligomer alkoxy silane (polyethoxysilane (PES) obtained from tetraethoxysilane) with polycaproyamide, polyacrylonitrile, chitosan and zirconyl oxychloride were investigated.

The IR-spectrum of initial polycaproyamide and polyacrylonitrile, sample taking for modification of porous microspherical silica gel, contain clear characteristic bands amide groups at  $1650\text{ cm}^{-1}$  and  $1545\text{ cm}^{-1}$  and cyan (CN) groups at  $2245\text{ cm}^{-1}$ . The sharp bands at  $3325\text{ cm}^{-1}$  agree corresponds to amid group stretching connected by hydrogen lines with other groups. In all spectra of sample porous microspherical silica gel modified by polycaproyamide the band at  $930$  and  $691\text{ cm}^{-1}$  does not decrease of intensity of the bands  $960\text{ cm}^{-1}$  is seen. It testifies about violation of regularity, which lends to amorphoisation of polycaproyamide in the surface layer of sorbents of partiniles. From the indicated spectra it is visible, that microcapsulating of a porous microspherical silica gel by polycaproyamide leads to hydrogen bands between CO and NH groups, because the form of a band valence NH groups stretching is changed.

It has been shown by IR-spectroscopic investigations which evidence on the appearance of new absorption bands after chitosan introducing, elementary analyses data. ( $\text{N}_2$  occurrence in the samples, which quantity depends on chitosan nature and isolation conditions) It leads to significant increase of sorption capacity and specific surface of sorbents, which contain chitosan from silk wren chrysalises. Where as these parameters decrease for sorbents with chitosan from crabs. Evidently it is connected to more dense structure of the last one. It has been shown, that yield of sorbent on the base of PES and chitosan obtained by sol-gel method has depended significantly on such factors as components ratio, temperature, catalyst quantity etc.

Analysis of microscopical data shows that all samples synthesized have the particles of spherical form. On the electron microscopical level on the sorbent surface the nanostructure in the form of fine elements ( $100\text{--}500\text{ nm}$ ). For hybrid sorbents synthesis these elements are smaller and more homogeneous due to more effective conditions of synthesis (mixing of PES and  $\text{ZrOCl}_2$  solutions, treatment of prepared MSS in  $\text{ZrOCl}_2$  solution).

Information on the morphology of the nanohybrid sorbents also was revealed with SEM analysis. Dispersed spherical polymer-silica particles with a diameter of  $0.3\text{--}5\text{ }\mu\text{m}$  were observed. Every particle, in one's turn, is a porous material with size of pores to  $200\text{ nm}$  and spherical particles from  $100\text{ nm}$  to  $500\text{ nm}$ . Therefore, the obtained samples were demonstrated to form a nanometer – scale porous structure.

# SEMIVOLATILE HALOGENATED SUBSTANCES IN DRINKING WATER AFTER CHLORINATION. FACTORS AFFECTING THE COMPOSITION AND CONTENTS OF THESE BY-PRODUCTS IN WATER

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A great variety of the chlorinated and brominated semivolatile organic compounds (Cl-,Br-SVOC) refers to the by-products of the water disinfection with chlorine. As precursors of these by-products can be both the humic materials which are found in the water source, as in an event of the haloacetic acids (HAA), and the developmental contaminants typical for the particular region. Analysis of the contaminants content in drinking water of the surface water treatment plant and infiltration treatment plant (using water from the wells at depth 12-28 m) in Ufa after their extraction by methylene chloride (pH 2) by cromato-mass-spectrometry has allowed to identify more than 40 Cl-,Br-SVOC. All of them were indicated form in microconcentration and derive from the developmental contaminants of the water sources. The mid-annual concentrations of Cl-,Br-SVOC in drinking water of the surface water treatment plant and infiltration one accounted for 0,014 mg/dm<sup>3</sup> and 0,008 mg/dm<sup>3</sup>, respectively. The contents of the total organic chlorine (TOCl) and total organic bromine (TOBr) in analytes, determined by gas chromatography with atomic-emission detection, correlate with the chlorine doze used for the water disinfection. Practically at the constant chlorine demand of the water before it's chlorination the TOCl and TOBr content varies insignificantly. These parameters ratio depends on the quality of the parent chlorine used as a disinfection agent.

Determination of the HAA in drinking water by liquid-liquid extraction, derivatization was made according to U.S.EPA method 552.2. Monochloro-, dichloro-, trichloroacetic, monobromo-, chlorobromo-, diclorobromoacetic- and dibromochloroacetic acids were identified in drinking water of the surface water treatment plant. The sum content of those correlates with the turbidity of the parent water, oxidability by permanganat and with the doze of chlorine used as a chlorination agent. At turbidity from 1 up to 2 mg/dm<sup>3</sup> the sum content of the HAA in drinking water of the surface water treatment plant does not exceed 0,05 mg/dm<sup>3</sup> that is lower than tolerable data of the U.S.EPA for the sum of six HAA in water. The HAA contents in drinking water of the infiltration treatment plant does not exceed 0,01 mg/dm<sup>3</sup>.

# THE DETERMINATION OF RARE EARTH ELEMENTS IN GEOLOGICAL SAMPLES BY X-RAY FLUORESCENCE FOLLOWING ION-EXCHANGE

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The rare earth elements are characterized by a remarkable similarity of their physical as well as their chemical properties. These similarities make the determination of REE, especially at trace levels, a very challenging task. But the increasing interest in their geological, industrial and environmental roles, has enhanced the need for rapid, sensitive and accurate methods for their determination. Classical methods of analysis such as gravimetry, compleximetry, and colorimetry have all been used for the determination of REE(I-3). Since these methods are typically non-selective and time consuming, they are generally used only for total REE determination. More selective and rapid techniques like neutron activation analysis, atomic spectroscopic techniques, mass spectrometry and X-ray fluorescence spectrometry are currently the methods being used (4-9). Even though all of these methods are capable of determining individual REE, they all require a separation or a pre-concentration step due to matrix and interelement interferences.

The X-ray determination of REE in geological samples is normally complicated by the relatively low concentrations of the REE, their complex X-ray spectra, the high concentration of matrix elements and the lack of reference standards with certified values for REE. A rapid and sensitive ion exchange and X-ray fluorescence procedure for the determination of trace quantities of rare earths is described. The REE in two U.S.G.S. standards, two inhouse synthetic mixtures and three new Japanese standards have been determined and corrections for inter-rare earth element interferences are made.

The REE values obtained for the U.S.G.S. standards by this method compare well with the literature values obtained by NAA, MS and other methods. Linear calibration curves in the range of about 0 to 200 µg/g are obtained and detection limits in the range of 0.06 to 0.04 µg/g are achieved.

# DETERMINATION OF THE RESIDUAL CONTENTS OF CATIONIC FLOCCULANTS IN WATERS

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Cationic flocculants are widely used in clearing oil-water, waste, natural and drinking water. At the same time they are moderately toxic substances which have cumulative properties. For the majority of flocculants, produced and used in Ukraine, limit admission concentration is  $0,1 \div 0,4 \text{ mg/dm}^3$  for drinking water and  $0,01 \text{ mg/dm}^3$  and less – for natural waters.

The study of colour reactions of flocculants with organic reagents of various classes revealed that they can be used for determination of residual amount of flocculants in various types of waters. Best spectrophotometric characteristics were demonstrated of flocculants with the sulphophthalein reagents and dioxyazocompounds.

It was suggested to determine the content of flocculant K-580 (copolymer acrylamide and threemethyl ammonium ethyl acrylate chloride) in drinking water with the help of reagent 2-(2'-hydroxy-3'-sulpho-5'-nitrobenzenazo)- $\epsilon$ -acid – sulphonitrazo  $\epsilon$  ( $\lambda_R = 520 \text{ nm}$ ,  $\lambda_{as} = 600 \text{ nm}$ ,  $\Delta\lambda = 80 \text{ nm}$ ,  $\epsilon' = 2,3 \cdot 10^4$ , pH value of 4,0 to 7,6, interval of determined concentration  $0,05 - 1,5 \text{ mg/dm}^3$ ). The components of drinking water on the LAC level are not mixed, including the  $\text{Al}^{3+}$  compounds, which are part of the structure of coagulants used for purifying water.

The content of Magnafloc 368 (Zetag 7568, Fixacol 131, VPK-402) low-molecular ( $M < 1 \text{ mln}$ ) copolymer dimethyl amine and allyl chloride (polydadmac) in waste water of city purifying stations was determined by 2-(2'-hydroxy-3',5'-dinitrobenzenazo)- $\epsilon$ -acid – picramin  $\epsilon$  (pH value of 2,0 to 7,62,  $\lambda_R = 510 \text{ nm}$ ,  $\lambda_{as} = 590 \text{ nm}$ ,  $\Delta\lambda = 80 \text{ nm}$ ,  $\epsilon' = 2,23 \cdot 10^4$ , interval of determined concentrations  $0,1 - 2,5 \text{ mg/dm}^3$ ). The advantage of this reagent is the interaction in acid environments, which do not require the additional stabilization of associates. The determination is not prevented by the basic components of water: 1000-multiple quantities alkali and alkali-earth metals, ions  $\text{Al}^{3+}$  and  $\text{Fe}^{3+}$  at a level LAC; non-ionic surfactants, spirits, phenols, soap, proteins compounds, and also basic anions in quantities typical for waste water. Some transition metals and cationic surfactants prevent determination.

## COMPARISON OF TECHNIQUES OF METALS DEFINITION IN AEROSOLS

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Standardized techniques atomic absorption (AAA) and photometric (FMA) of the analysis and designed by us a technique X-Ray fluorescence of the analysis (XRF) for metals definition in air of cities and the working areas of plants to production of non-ferrous metals are applied. The samples of aerosols were collected on cellulose (AFA-HA) and perchlorovinyl (AFA-VP and FPP) filters (Russia). The techniques AAA and FMA include a stage of an acid-temperature ashing of a loaded filter or selective extraction of defined elements from filter by approaching dissolvent. At XRF loaded filters were specimens.

The results of definition Ni and Zn, obtained with the help of the indicated techniques, are well agreed, while for Cr, Fe, Co, Cu, Pb the ratio  $C_j^{XRF} / C_j^{AAA}$  varies in 1,1-10 times depending on a element. By a technique FMA the Cr (VI) in sample containing 30  $\mu\text{g}$  of element on the data XRF, is not detected.

For exposure of reasons of observable discrepancy of results of the analysis simulated experiment with application synthetic reference samples of aerosols [1]. The models have demonstrated absence of significant systematic errors in results XRF. While results AAA and FMA depend on sort of chemical combination of an elements, method of an ashing of a material and mass of silicic acid remaining after an ashing of samples. The investigations performed have shown that silicic acid adsorbs up to 40 % (rel.) ions of metals. The coefficient of a variation  $V_c$ , describing effect of the indicated factors on results of the analysis, varies (%) for Mn and Fe from 5 up to 20, for Cu - from 10 up to 40, for Pb - from 10 up to 70, for Co the ambassador of a dry ashing of samples - exceeds 50. At definition Cr by a method AAA the value  $V_c$  reaches 70 %, if element presences an atmosphere in the form of  $\text{Cr}_2\text{O}_3$ . At photometric definition Cr (VI) the value  $V_c$  is equal 40%, when the element is present at aerosols in the form of chromates of heavy metals.

1. Patent of Russia No. 2239170. The method of prepared reference samples of atmospheric aerosols loaded on a filter / Korzhova E.N., Kuznethzova O.V., Smagunova A.N., Kozlov V.A.

# DETERMINATION OF ARSENIC (As) IN NATURAL AND WASTE WATER USING HIDRIDE GENERATION ATOMIC FLUORESCENCE SPECTROMETRY

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Contamination of waters with arsenic occurs as a result of a number of industrial activities such as treatment of industrial wastes, fertilizers, pesticides production, mining, metal smelting etc. and natural processes (e.g. weathering of minerals, volcanic and biological activities).

Arsenic is both toxic and carcinogenic element. It is necessary to have a fast, reliable and accurate method for determination of arsenic in water. The hydride-generation atomic fluorescence spectrometry (HG AFS) is one of the simple and sensitive techniques for the determination of this element in various types of waters.

Atomic Fluorescence System - Millennium Excalibur PSA 10.055 -was used in our work. This system consists of the autosampler, the integrated continuous flow vapour generator and the atomic fluorescence spectrometer with the boosted discharge hollow cathode lamp and a control computer.

Inorganic arsenic normally occurs in two oxidation states: As(V) and As(III). Arsenic (V) gives a significantly lower response than arsenic (III). For pre-reduction As(V) to the As(III) concentrated hydrochloric acid and potassium iodide/ascorbic acid reagents were used. As organoarsenic compounds do not react with sodium tetrahydroborate, they were decomposed with a mixture of  $\text{HNO}_3$  and  $\text{H}_2\text{O}_2$  on a hot plate.

Acidified sample solutions were treated with sodium tetrahydroborate to generate the arsine. The hydride and excess hydrogen were purged out of the generation vessel using a stream of argon directed into a chemically generated hydrogen diffusion flame. The hydrides were atomized and resulting atoms were detected by atomic fluorescence spectrometry at 193.7 nm. Optimized instrumental conditions were as follows: lamp currents primary – 27.5 mA, boost – 35 mA; flows 4-5  $\text{ml min}^{-1}$  for sodium tetrahydroborate and 8-10  $\text{ml min}^{-1}$  for sample and blank solutions; the argon was applied as carrier gas and air as dryer gas with flow rates of 300  $\text{ml min}^{-1}$  and 2.5  $\text{l min}^{-1}$  correspondingly.

The method is characterized by a linear calibration range from 0.5  $\mu\text{gl}^{-1}$  to 100  $\mu\text{gl}^{-1}$ , a detection limit of 0.2  $\mu\text{gl}^{-1}$ .



# PRECONCENTRATION AND DETERMINATION OF THALLIUM TRACES IN WATER BY STRIPPING VOLTAMMETRY

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The method of stripping voltammetry (SV) is one of the most perspective methods in concentration range of thallium(I) determination of  $10^{-9}$ – $10^{-7}$  M. Achievement of high sensitivity of thallium(I) determination needs carrying out its additional concentration and separation from other metals which are close by electrochemical properties. For these purposes it is offered to use a method of coprecipitation with collector. The combination of SV and a method of coprecipitation on a collector have shown that minimum detectable concentration can be decreased by 2-3 orders of magnitude.

Stripping voltammetry procedure has been developed for determination of thallium(I) traces in aqueous medium on a mercury film electrode with application of thallium preconcentration by coprecipitation with manganese (IV) hydroxide. More than 90% of thallium present in water sample is uptaken by a deposit depending on conditions of preparation of precipitant. Direct determination of thallium was carried out by stripping voltammetry in AC mode with anodic polarization of potential in 0,06 M ascorbic acid in presence of  $5 \cdot 10^{-5}$  M of mercury(II) on PU–1 polarograph.

For determination of thallium content at a level of 0,1–0,01  $\mu\text{g/l}$  pretreatment of water samples has been proposed by solutions of  $\text{MnSO}_4$  and  $\text{K}_2\text{S}_2\text{O}_8$  at fixed pH and contact time resulting in oxidation of thallium(I) to thallium(III), manganese(II) to manganese(IV) as well as in destruction of organic matter of water. Simultaneous oxidation of ions of thallium and manganese up to the highest oxidation states provides coprecipitation of hydroxides of Tl(III) and Mn(IV) at subsequent heating.

Thus excess of Mn(IV) hydroxide represents itself as a collector of thallium which practically completely passes into a deposit, and interfering metal ions (Cu, Cd, Pb, Ni, etc.) remain in a solution and are separated providing high selectivity of thallium determination. Effect of some factors on the value of analytical signal of thallium has been investigated at the stages of water pretreatment. Based on of these data the unified technique for thallium determination has been developed and tested on natural waters. The method proposed allows to determine content of thallium in waters which is 10 times lower than it is required by maximum allowable concentration limits.

# METHODS OF CONTROLLING THE QUALITY OF FOOD PRODUCTS FORTIFICATED BY IODINE AND SELENIUM

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Optimization of nourishment for the population of Ukraine is a key factor in improving the health of the nation. Therapeutic and preventive significance of the fortified food products depends on keeping to the scientifically substantiated regulated levels of fortification. Taking into consideration the above-mentioned, a sanitary and chemical control of the quality of the fortified products seems to be of great importance.

The researchers of ECOHYNTOX jointly with the colleagues of the Research Industrial Enterprise “Burevestnik” (St. Petersburg) have developed, validated, and introduced into practice the methods of inverse voltampermetric estimation of iodine and selenium in drinking water using AVA-2 apparatus.

Characteristic of the above methods:

	Iodine in drinking water	Iodine in food products	Selenium in drinking water
Methods of preparing tests	–	Dry liming with $K_2CO_3$ at 500 °C	Wet mineralization by $HNO_3+HClO_4$
Potential of analytical peak	-250 to -300 mV	-250 to -300 mV	850 to 950 mV
Background electrolyte	10 ml 0.05M potassium tetraoxalate + 0.02 g ascorbic acid	10 ml 0.05M potassium tetraoxalate + 0.02 g ascorbic acid	10 ml 0.025 M $H_3PO_4$
Linearity	2-25 $\mu\text{g}/\text{dm}^3$	2-25 $\mu\text{g}/\text{dm}^3$ (mineralization)	5-50 $\mu\text{g}/\text{dm}^3$
Limit of quatitativity estimation	0.004 $\text{mg}/\text{dm}^3$	0.02 $\text{mg}/\text{dm}^3$	0.005 $\text{mg}/\text{dm}^3$

Thus the above methods allow to realize a sanitary and chemical control of the quality of the products which have been fortified by iodine and selenium.

# DETERMINATION OF MERCURY (Hg) IN NATURAL AND WASTE WATERS BY MEANS OF THE MILLENNIUM MERLIN ATOMIC FLUORESCENCE SPECTROFOTOMETER

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Mercury is widespread in the environment, originating both from natural (natural gassing of the Earth's crust, leaching from rocks) and industrial sources (e.g. production of caustic soda and chlorine, electrical industry, biocides, etc.).

Mercury generally is found in low and trace concentrations. So there is need to determine Hg in ranges corresponding to various types of water samples. Detection levels of Hg can be improved by the use of vapour generation technique. This technique allows to separate the analyte from the sample matrix and so to overcome the matrix interference. The fluorescence technique, with its high sensitivity and linearity, in combination with vapour generation, provides for a possibility to detect Hg in parts per trillion per liter regions.

In this work, atomic fluorescence spectrometry (AFS) with vapor generation is used for Hg determination in different types of waters (drinking, surface, underground, industrial waste).

An aliquot of acidified sample is digested using chemically generated bromine, able to breakdown all commonly occurring organo-mercury species to mercury (II). Elemental mercury vapour was generated from the decomposed sample by reduction with tin (II) chloride, and was purged from solution by the argon carrier stream. Influences of experimental conditions such as type of acids and oxidants ( $\text{HCl}/\text{H}_2\text{O}_2$ ,  $\text{H}_2\text{SO}_4/\text{K}_2\text{Cr}_2\text{O}_7$ ,  $\text{HNO}_3/\text{K}_2\text{S}_2\text{O}_8$ , and  $\text{HCl}/\text{Br}^-/\text{BrO}_3^-$ ), concentrations of reagents, flow rates of the sample, reductant and hydrochloric acid were investigated.

The mercury vapour was detected by atomic fluorescence spectrometer Millennium Merlin PSA 10.025.

The linear dynamic range of this method is  $0.1 \mu\text{g l}^{-1}$  to  $100 \mu\text{g l}^{-1}$ . The method detection limit (MDL) depends on selected operating conditions and a calibration range. It is important to use high purity reagents in all determinations.

This method can be used to determine Hg in waters used for fish farming, at levels half of maximum acceptable concentration ( $0.2 \mu\text{g l}^{-1}$ ).

## ACCELERATED DETERMINATION OF 2,4-DICHLOROPHENOXYACETIC ACID

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2,4-Dichlorophenoxyacetic acid (2,4-D) is a selective effect herbicide of widely applied for annihilation of bichromatic weeds in sowings of gramineous cultures.

A series of techniques of determination 2,4-D is known. However, there is an actual problem of development of express and semiquantitative methods of determination, which would allow to monitor fastly the content of this herbicide, both in lab and in field conditions.

The extractive and photometric procedure of 2,4-D determination in aqueous solutions with crystal violet (CV) is developed. Determination method is based on interaction dye cation with formation of hydrophobic and ionic associate, which is extracted well by toluene. The colour intensity of toluene layer proportional to concentration of coloured cations and 2,4-D-anions respectively.

The influence of temperature, solution's pH and other parameters in formation of ionic associate is investigated. As a result, optimal conditions of determination are established: pH 4,0; volume of acetate buffer – 0,5 ml; volume of 0,1% aqueous solution of CV – 0,3 ml; extraction time – 3 minutes. The ratio of aqueous and organic phases is 1:1. Photometric measurement of toluene layer is carried out at  $\lambda_{\text{ef.}} = 606,0$  nm. The accuracy of procedures checked by the method of additives.

The method allows to determine the 2,4-D in range of working concentrations from 3,8 to 20,0  $\mu\text{g/ml}$ , the sensivity of method is  $10^{-6}$  g/ml, the reproducibility is 3%.

The colour test-scale for the semiquantitative determination of 2,4-D in working liquids is worked out on the basis of extractive and photometric method.

There are a number of the optimal conditions for sorption pointed below: volume of extract – 4 ml; ratio of aqueous and organic phases is 1:1; cyllindric foampolyurethan (marc – T 25-3,8) with diameter 8 mm, height – 4,5 mm, mass – 0.007 g. Time of full sorption is 20 min. Completeness of sorption is determined by spectrophotometric method.

So, extractive and photometric determination of 2,4-D with CV and also the test-scale for its semiquantitative determination with separation from instrumental basis are proposed.

## EXPRESS METHOD OF AN ESTIMATION OF QUALITY OF COGNACS

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At identification of cognacs and cognac alcohols on authenticity use the following characteristic attributes: presence in them significant concentration of (15-150 mg/l) bytanol, the high level of acids - acetic, propionic and oil; the high contents of polyphenolic bonds.

All known methods of identification of authenticity products of cognac demand presence of such difficult and expensive devices as gasohromatographs, weights - spectrometers; application crystallization, extractions, etc. methods of division increases time of carrying out of the analysis.

The purpose of our work - to find more simple, reliable and fast method the determination of quality and falsification of cognacs.

It is known, that there is a connection between quality of cognac and optical density of its diluted solution at length of a wave of 275-280 nm. The above the optical density - is better quality of cognac. However, studying of spectra of absorption of various marks of cognacs and substances which add at falsification of cognacs (an extract of the tea, burnt sugar, vanillin more often, etc.) has shown, that these substances also have maxima light absorption with range of the wave lengths of 275-285 nm. Therefore it is necessary to have precise parameter differentiating an original cog-nac and falsificate.

Biological activity (BA) was chosen as such parameter. The BA determined using a system and a technique for a class of natural polyphenolic bonds: nicotinamide adenine dinucleotide restored ( $\text{NAD}\cdot\text{H}_2$ ) - ferricyanide ( $\text{K}_3\text{Fe}(\text{CN})_6$ ) in a phosphates buffer solution.

BA expected under the relation of speed of oxidation  $\text{NAD}\cdot\text{H}_2$  in control experience and in investigated samples of cognacs diluted 1: 50 at wave the length in 325 nm. Speed of oxidation was determined on reduction of optical density of solutions ( $\Delta A$ ) for 2 minutes. Determination of BA in more than 50 samples of cognacs has shown the full correlation of its size with term of their quotation, and very small BA in the forged cognacs. Spectrophotometry research of quality of cognacs on their biological activity shows, that BA can be one of the basic parameters for the characteristic of cognacs and determination of their falsification.

# ISOLATION OF URANIUM AND THORIUM FROM NATURAL SAMPLES

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Uranium and thorium are the first members of natural radioactive chain which makes their determination in natural materials interesting from geochemical and radioecological aspect. They are quantitatively determined as elements by spectrophotometric method and/or their radioisotopes by alpha spectrometry. It is necessary to develop inexpensive, rapid and sensitive methods for the routine researches because of continuous monitoring of the radioactivity level.

Development of a new method for the isolation of uranium and thorium from liquid samples and subsequent spectrophotometric determination will be described in this paper. It is possible to isolate uranium and thorium from drinking and seawater using extraction chromatography or ion exchange. Uranium and thorium can be strongly bound on the extraction chromatographic resins (TRU and/or UTEVA) from 3 mol dm<sup>-3</sup> HNO<sub>3</sub> (chemical recovery is 100%). From alcoholic solutions of nitric acid thorium can be strongly bound on the anion exchanger Amberlite CG-400 (NO<sub>3</sub><sup>-</sup> form). Uranium is much more weakly bound on the anion exchanger which enables its separation from thorium. After the separation uranium and thorium are determined by spectrophotometric method with arsenazo III and thordin respectively. Developed method enables selection of the optimal mode of isolation for the given purposes.

# STUDY OF CONDITIONS FOR DETERMINATION OF TIAMETOXAM METHYL BY THE METHOD OF THIN LAYER CHROMATOGRAPHY

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The fungicides are among the chemicals of wide use as plant diseases control agents in intensive agriculture. At the same time these pesticides could have toxic effects, when accumulated in man and animals. Because of general society concern about fungicides use, they should be monitored in waters, soils and crops.

We studied conditions for the determination of tiametoxam (TM), the active component of the fungicide "Actara" (Syngenta, Switzerland) by the method of thin layer chromatography with use of the Perkin-Elmer liquid chromatograph combined with spectrophotometric detector. The 250 mm-long and 4.6 mm in diameter steel column filled with "Silasorb C<sub>18</sub>" was used.

The mixture of acetonitrile/water (1:1, v/v) was selected as most effective mobile phase. The optimum conditions for chromatography were: the velocity of mobile phase utilization – 0,6 ml/min, the wave length in spectrophotometric detector – 254 nm. The linear dependence of the height of peak in chromathography from the TM concentration was observed in the range of 1-12.0 µg/mL.

The conditions of TM extraction from water were studied. The best extraction of TM from water was in acidic medium (pH 2-3) by chloroform. The method of the CM determination in sewage waters is developed as result of the study.

# GAS CHROMATOGRAPHY DETERMINATION FOR SMALL QUANTITIES OF WATER IN ORGANIC SOLVENTS

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Determination of water of different materials is one of the important tasks of the analytical chemistry. For water determination in organic solvents physical-chemical methods use side by side with the classic titration method by Karl Fisher. In particular, gas chromatography (GC), distinguished its universality and selectivity, is used. However, GC usually used for determination of relatively large quantity of water.

Conditions for the determination of small quantity of water in methanol and iso-propanol are investigated in this work. It is shown that using of deep dried carrier gas, optimizing of evaporator and column temperatures, nature of sorbent, evaluating and taking into account a sensitivity coefficient of detector are important things for high sensitive GC analysis. For major quantity of water in methanol and iso-propanol the sensitivity coefficient of the detector is steady and closed to 1, that corresponds to one obtained by other authors. However for minor quantity of water (less than 0.5 mass. %) the coefficient increases abrupt. The comparison of the results obtained by GC in optimal conditions with the results obtained by Karl Fisher titration method for the same samples showed absence of significant systematic errors.

Suggested method characterized by relative standard deviation of 0.02-0.1 allows determination of water in organic solvents until 0.008 mass.%. Concentrations under mentioned above can not be detected by direct GC due to residual humidity of sorbent and parts of chromatographic equipment.



## **DETERMINATION OF PYRETHROIDS IN AIR BY GAS CHROMATOGRAPHY**

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New disinsectional means (DM) on the basis of synthetic pyrethroids: deltamethrin, permethrin, prallethrin, tetramethrin, transfluthrin, d-fenothrin, cyfenothrin, cyfluthrin, cypermethrin, esbiothrin are intensively applied in medical disinsection and in common life. Taking into account an opportunity of inhalation receipt of active ingredients into human organism during DM application, dynamics of their contents was investigated in air of apartment during and after application.

For carrying out of given researches method of synthetic pyrethroids determination in air has been developed. Chromatographic behaviour is investigated and optimum conditions of the synthetic pyrethroids' analysis with application of capillary column with stationary phase DB-5 and electron-capture detector are selected.

Dependences of retention time, limit of detection with nature and structure of analyzed substances were investigated. Chemically pyrethroids are derivatives of cyclopropanecarbonic acid. Researches have shown, that pyrethroids' retention times depends on nature of assistants and increase with introduction into molecule of complex radicals (phenoxybenzyl-) or polar assistants (Cl-, Br-, CN-groups).

In connection with a variety of disinsectants' formulations (aerosols, foams, electric fumigators) on basis of pyrethroids the income of the given substances into air during application is possible as aerosols and as vapors, especially in case of electric fumigators' application.

The opportunity of application of filters, solid sorbents and absorbing solutions has been investigated for synthetic pyrethroids' concentrating from air. Silicagel KSK and polysorb are provided quantitative sorbption and desorbption pyrethroids. In case of aerosol formulations application of paper filters is possible.

Influence of speed and duration of aspiration on concentrating from air of pesticides as aerosol and vapors are investigated. Optimum conditions of concentrating on solid sorbents and paper filters are speed of 5 l/min during 20 minutes.

As result of the carried out investigations the method of GC detection of pyrethroids in air is developed, providing limits of quantitative determination from 0.0005 up to 0.005 mg/m<sup>3</sup>.

## ANALYSIS OF COMPOSITION OF JOJOBA OIL BY GS-MS AND LC-MS METHODS

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Jojoba oil produced by pressing from the seeds of the jojoba tree (*Simmondsia chinensis*, *Euphorbiaceae*), now cultivated in Israel. Jojoba oil is very resistant to oxidation and is largely used in cosmetic application. Industries use sulfated or hydrogenated oil as lubricant, polishes and coatings. Jojoba oil is formed quite exclusively of alcohol esterified with long-chain fatty acids and contains long-chain wax esters also. The acids, converted into the methyl or ethyl esters were analyzed by GS-MS (6980N with MS detector 5893 Agilent technologies) with capillary column HP5 MS. It is established, that fatty acid of jojoba oil contains of 14 to 24 carbon atoms. Usually, they are unsaturated fatty acids with one double bond (62.5% of gadoleic acid, 21.4% of erucic acid and 9.8% of oleic acid, suitable). The determination of long-chain wax esters was carrying out by direct injection of sample to chromatographs injector. It was shown, that allocation of esters change from C36 to C46 with maximum of C42 (52%). The study of mass-spectra of long-chain alcohol's and fatty acids esters, obtained with electron impact ionization, shown the absence of characteristics fragments for determination of length of fatty acids and alcohol's radicals. The analysis of esters was carrying out by LC-MS (Bruker 3000 plus Agilent technologies) with APCI (atmospheric pressure chemical ionization) source. In the process of ionization occur having break of double bond in an acid radical and is formed the ion  $[R1-CH_2]^+$ . The presence of this ion allow to define in APCI system for each ether the length of chain and unsaturation of acids radical. Combination of knowledge of molecular weight of ether and R-acids allow to define R-alcohol.

# ANALYSIS OF PEROXIDE GROUPS IN POLYMERS BY CHROMATOGRAPHY AND THERMOGRAVIMETRY

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One of the possible ways to increase the stability of dispersive polymer systems and to create new composite is modification of phase interface of polymers and oligomers containing different functional groups and also containing peroxide groups. Modification of phase interface is realized by bonding to it different polymer chains containing different functional groups. Chemical bonds are created in radical reactions of chain transfer and recombination initiated by peroxide groups. In order to investigate the process of modification made by polymers containing different functional groups and also containing peroxide groups is important to determine the quantity of peroxide groups. In this report we describe how to measure the quantity of prime – tertiary peroxide groups in copolymer Octene – co-Maleic Anhydride) – co-*tert*-Butylperoxymethylmaleate (Oct-MA-TBPMM) using chromatography and thermogravimetry.

Content of prime – tertiary peroxide groups was measured by the quantity of products of complete decay, which were measured by chromatography. It is known that the main contents in products of the complete decay of Oct-MA-TBPMM samples are acetone and 2,2-dimethylpropanol, which arise in reactions of chain fragmentation of *tert*-butylperoxy radical or in reaction of chain transfer of this radical. In this case the sum of acetone and 2,2-dimethylpropanol molecules is equal to the quantity of peroxide groups in polymer. As an internal standard we used chloroform.

We improved the results of chromatography by thermogravimetric and differential – thermal analysis of Oct-MA-TBPMM samples in flow of nitrogen using derivatograph Q-1500 of “Paulic – Paulic – Erdey” system. We measured the quantity of peroxide groups by intensive loss of weight in temperature 359-411 K interval. Measured values were similar to those of chromatography and also to the values we calculated theoretically according to the scheme of decay we proposed.

## DETERMINATION OF SULFATE IN MINERAL WATER USING SULFATE-SELECTIVE ELECTRODE

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Methods of sulfate determination used in common practice suffer from essential disadvantages (time consumption, laboriousness, low sensitivity, etc.). For this reason, creation of sulfate-selective electrode suitable for direct potentiometric determination of this ion, has been attempted for a long time. Nowadays, nearly a dozen of sulfate-selective electrodes based on charged or neutral carriers of different structure have been described. However, no known receptors for sulfate ions are available commercially.

Low sulfate selectivity of the ion-selective electrodes (ISE) based on lipophilic quaternary ammonium salts (QAS) is usually explained by unfavorable ratio of sulfate hydration and solvation energies. We have been shown that another reason does exist as well; namely, low efficiency of sulfate-QAS cation interaction caused by steric hindrance for simultaneous approach of two QAS cations, containing four long-chain hydrocarbon substituents, to sulfate ion.

It was found that utilization of QAS with increased steric accessibility of exchange center, containing nitrogen atom with three methyl substituents and one superlipophilic substituent, – tris(2,3,4-dodecyloxy)benzyl, – leads to dramatic, up to 7 orders, increase of ISE's selectivity towards sulfate in the presence of single-charged anions. Incorporation of hexyl 4-trifluoroacetylbenzoate into membrane leads to additional substantial increase – up to 4 orders – in sulfate selectivity.

Practically complete elimination of interference both of anions (chloride, carbonate) and cations (calcium, manganese) is achieved by diluting the sample 50-100 times and adjusting pH to  $3,5 \pm 0,1$  with concentrated phosphoric acid. After that, the sulfate concentration can be determined by one of the commonly used methods, e.g. standard additions, calibration plot or limiting solutions method. Investigation of mineral water series with a variable degree of mineralization (1,5–4,5 g/L) by these procedures has given satisfactory reproducibility and good correspondence with independent methods of nephelometry and gravimetry. Relative error of sulfate determination in mineral waters does not exceed 10%.

## THE OXYGEN STECHIOMETRY DETERMINATION IN OXIDE CERAMIC

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Zelenko M.A., Manchenko O.F.

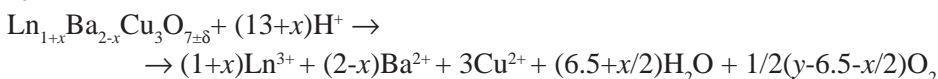
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One of the important and difficult problems in studying the composition/properties dependence of complex oxide materials is oxygen stochiometry determination.

One of the most simple and reliable methods is iodometric analysis.

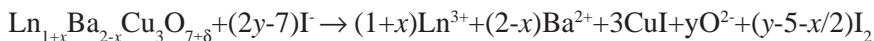
1) Ln123 compounds analysis is realized by two stages.

On the first stage the total contents of cuprum in the  $\text{N}\ddot{\text{u}}^{2+}$  form is determined by reaction:



For that, the mixture of HCl and KI solutions is added to calculated quantity of analyzing compound. The solution is mixed on magnetic stirring rod during fixed time. The generated iodine is titrated by  $\text{Na}_2\text{S}_2\text{O}_3$  solution.

On the second stage the total contents of cuprum in different forms  $\text{Cu}^+$  and  $\text{Cu}^{2+}$  or  $\text{Cu}^{2+}$  and  $\text{Cu}^{3+}$  is determined.



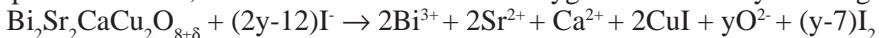
Based on experimental data, the oxygen index (y) is calculated by formula:

$$y = 6.5 + x/2 + 1.5 \cdot (V_{\text{II}} - V_1) / V_1,$$

where  $V_{\text{II}}$ ,  $V_1$  – the volumes of  $\text{Na}_2\text{S}_2\text{O}_3$  solution reacted with analyzing compound on the first and second stages respectively.

The difference of  $\text{Na}_2\text{S}_2\text{O}_3$  volumes ( $V_{\text{II}} - V_1$ ) is equivalent to  $\text{Cu}^{3+}$  contents and mobile oxygen contents in the samples.

2) For Bi-based HTS compounds, as well as for nickel-based and cobalt-based compounds of REE, the determination of active oxygen is realized by one stage.



In this case the excess of aside solution and potassium iodide solution are added to analyzing compound with continuous stirring. The generated iodine is titrated by  $\text{Na}_2\text{S}_2\text{O}_3$  solution. The calculation of oxygen index (y) is carrying out by formula:

$$y = 0.001 \cdot N \cdot V \cdot \Sigma nM^{n+} + 14m/2m - 0.016 \cdot N \cdot V,$$

where N – normality of  $\text{Na}_2\text{S}_2\text{O}_3$  solution, V – volume of  $\text{Na}_2\text{S}_2\text{O}_3$  solution, which was used up for titration of analyzing compound, n – a number of metal atoms,  $M^{n+}$  – the atomic mass of metal.

The error of oxygen contents determination by using method of iodometric titration is around  $\pm 0.02$  on formula unit.

# RETROSPECTIVE ASSESSMENT OF EMISSION POINTS FOR ALTAI REGION AIR POLLUTION ON THE BASIS OF THE LAYER-BY-LAYER ANALYSIS OF THE ICE CORE FROM BELUKHA GLACIER

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High elevated cold glaciers situated in mid-latitude regions are well suited as archives for past environmental changes and to document the impact of humans on the environment. Such glaciers are especially attractive for study of polluting species with short atmospheric lifetimes, which are non-uniformly distributed in the atmosphere and showing highest concentrations closest to the emission sources (e.g. soot particles, mineral dust, heavy metals or sulfate).

The main purpose of our study is to carry out the inventory of emission sources (natural and anthropogenic) in South-West Siberia and East Kazakhstan and compare this result with results of Belukha ice core analysis for assessment the regional contribution in Altai region air pollution. Long ice core (140 m) was recovered from Mt. Belukha glacier (49°48'26" N, 86°34'43" E, 4062 m a.s.l.) in Mountain Altai (Altai Republic) in summer 2001. Layer-by-layer chemistry composition of upper 86 m, covering the last two centuries, is represented by biogenetic emissions (ammonium, formate), aeolian dust (calcium, magnesium, chloride, sodium) and anthropogenic species (sulfate, nitrate, ammonium, heavy metals).

In contrast to Europe rising nitrate concentration in Belukha ice core since 1960 reflects the influence of power stations and agriculture and the decrease in the 1990s tracks the downscaling of the political and economic systems. A nitrate peak of short duration in 1908 is thought to be the atmospheric signature from the Tunguska event on June 30, 1908. Sharp increasing of calcium and magnesium concentrations in 1960-1980 is the sequent of catastrophic scale of soil wind erosion caused by Tzelina project realization in steppe Altai and East Kazakhstan. There is the good correlation of chronological features of Altai industry (serfdom repeal in 1861, crisis caused by slump in metal's prices in the 1870s, the policy of granting concessions in 1905-1914, and etc.) and ex-sulfate ( $[\text{SO}_4^{2-}] - 0.21[\text{Ca}^{2+}]$ ,  $\mu\text{eq/L}$ ) concentration in layers of Belukha ice core.

## ELEMENT DISTRIBUTION IN TISSUES OF BAIKAL SPONGES

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The sponges of the family *Lubomirskiidae* endemic to Lake Baikal are an important constituent of the littoral zoobenthos and play a significant role in the self-purification of water. Their sessile life-style and habitats preferred by the majority of them, being located at small depths, promote their utilization as objects for water ecosystem status control. This work was aimed at studying the dependence of concentration of biogenic elements and microelements on the age of branchy sponge *Lubomirskia baicalensis*, as well as the composition of some parts of this sponge: skeleton (spicules and spongin), cells and symbiont organisms.

Sponge cells, unicellular green algae of zoochlorella (*Chlorella*) and bacteria were isolated with manipulator “3D Hydraulic Micromanipulator”, Marishige, from precipitate which was obtained after sedimentation of homogenized squeezing of sponge in glucose solution of variable concentration and centrifugation of suspension. Spicules representing biogenic silica were isolated from organic matter with sodium hypochloride, while silicon was removed from spongin with hydrofluoric acid. The age changes were detected from well-washed sponges.

The complex of the following destructive and nondestructive analytical methods was used for studying the composition of sponges: inductively coupled plasma mass-spectrometry (ICP-MS), X-ray fluorescence (XRF), electron probe microanalysis (EPMA), and atomic absorption spectrometry (AAS). Techniques of sample preparation were developed for each method and their metrological characteristics were defined. Relative standard deviations for all the elements did not exceed 0.25 within detection limit. The accuracy of techniques elaborated was checked with the method of additions and control methods of analysis.

The accumulation of biogenic elements (P, S, and Ca) and a number of microelements (Sc, Ni, Fe, Cu, Zn, Mo, Cd, Y, La, Ce, and Pb) was observed with age in tissues of sponges. Such elements as Mg, P, Cl, and Cu are concentrated in zoochlorella. Silicon is accumulated in sponge spicules. Cl was observed in sponging.

# **RESULTS OF EVALUATING NONDESTRUCTIVE X-RAY FLUORESCENCE ANALYSIS OF DRIED MILK SAMPLES OF LIMITED MASS**

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Variety of biochemical composition and physical features of milk, as well as compound forms of mineral components foreordain necessity to develop the analytical procedures, in which initial sample state suffers minimum change. Absence of dried milk reference standards (RSMs) is an obstacle to use nondestructive XRF for solving the given analytical task. In this communication results of nondestructive x-ray fluorescence determination of Na, Mg, Al, Si, P, S, Cl, K, Ca, Cr, Mn, Fe, Ni, Cu, Zn, Rb, Sr, Zr in dried milk powders of limited mass (less than 2 g), obtained with using plant RSMs to calibrate, are discussed.

“Hot” pressing was used to prepare pellets of 2g mass. The study showed that pressure and temperature, being suitable for pressing dried milk powders, are responsive to content of milk fat, which proves «gluing effect» when hot pressing. The conditions of pellet preparation, as well as effects, action of which are caused by milk bioorganic variability were recognized. Composition of non-fat milk and milk with 99.9% of fat were used as the limited bioorganic compositions of milk. Matrices of non-fat milk and fat milk were simulated by lactose, content of which in dried non-fat milk is no less than 50%, and fatty acids, belonging to triglycerides of milk fat, correspondingly.

The presented results allow an understanding of the effect of inadequacy organic matrix of plant reference standards and dried milk on XRF result exactness. In the absence of similar RSMs calibrations, obtained with the help of plant RSMs, may be used for analysis of only non-fat milk powders. Correction on fat content will allow a spreading these calibrations on analysis of milk powders with any fat contents.



## NEW FLUORESCENCE QUENCHING METHOD FOR DETERMINATION OF COPPER (II) IN WATER

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Copper is a one of important trace element required for many biochemical and physiological functions, but excess quantity of this metal in water and food may have undesirable consequences. In accordance with Russian sanitary standard, general concentration of copper in drinking, fresh, domestic waters and in treated effluent hasn't to be more than 1 mg/l.

Fluorescence quenching methods with aromatic complexing reagents are often recommended for copper (II) determination in water.

In present work a fluorescent properties of of N,N-di(2-carboxyethyl)-3,4-xylidine (**H<sub>2</sub>R**) and determination of copper (II) by its quenching effect on the fluorescence of **H<sub>2</sub>R** are reported. The excitation and fluorescence wavelengths of **H<sub>2</sub>R** were 215 and 360 nm respectively; the optimal pH value for copper (II) determination is 6.0. The range of determined copper(II) concentration in water solutions is 0.03 – 3.0 mg/l.

The interfering effects from other ions in water were investigated. When molar concentration of studied ions not N-fold higher than that of the Cu(II) no interference was found; N = 1000 for Ca<sup>2+</sup>, Mg<sup>2+</sup>, K<sup>+</sup>, Na<sup>+</sup>, NH<sub>4</sub><sup>+</sup>; N = 200 for Ni<sup>2+</sup>, Co<sup>2+</sup>; N = 50 for Cd<sup>2+</sup>; N = 10 for Al<sup>3+</sup>, Cr<sup>3+</sup>; N = 1 for Fe<sup>2+</sup>; N = 0.5 for Fe<sup>3+</sup>.

In according to proposed procedure the drinking water samples with spiked copper (II) standard solution and the copper-smelting plant wastewater samples have been analyzed. The found results were verified by atomic absorption spectrometry. The developed method (standard addition version) was found suitable for determination of Cu (II) in drinking water and industrial wastewater.

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## DETERMINATION OF MACRO- AND MICROELEMENTS IN BIOLOGICAL SAMPLES BY ATOMIC SPECTRAL METHODS

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It is well known that the lack as well as excess of chemical elements in human organism leads to serious problems in health disorder. The knowledge concerning an elemental status of the human organism is very informative from the point of the right medicine diagnose. Therefore a lot of doctors use this information in their practice.

In frames of the present work the problems of elemental analysis of human bio-substrates (blood serum, hair and bones) are discussed. Sample pre-treatment procedures using ash and mineral acids digestion were developed. The main sources of systematic errors were studied and their elimination ways were suggested.

As a result a new approaches in DCP-arc atomic–emission spectrometry were applied for Ca, Mg, Cu, Zn, Fe and P determination in blood serum and Ca, Mg, Cu, Zn, Fe, P, Mn, Pb, Cd, Sn, Sr et al. - in human and animals hair with relative standard deviation (RSD) about 10-20 %. The accuracy control has been realized by a comparison of data produced with the results of independent methods (atomic-absorption spectrometry and inverse voltammetry).

For the bones the preference has been given to atomic-absorption spectrometry with flame and graphite furnace atomization because of a strong effect of calcium and phosphorous on the analytical signals of microelements under determination in DCP-arc AES. It has been shown that In the presence of lanthanum chloride no interference effects were observed in flame AAS for Ca, Mg and Sr. ETA AAS has been used to determine Mn and Li in bones. RSD for FAAS determination of Ca, Mg, Sr were 3-6 %, as for Li and Mn - 10-12%.

These techniques were successfully applied for the assessment of normal elemental status in medical investigations.

# DETERMINATION OF CONCENTRATION OF ORGANOCHLORINE INSECTICIDES IN DRINKING WATER OF SERBIA

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Determination of the content of organochlorine insecticides in the drinking water is primary for establishing the level of contamination of the water ecosystem and for human health protection.

In this study the concentration of organochlorine insecticides in the drinking water was determined at different sites in Serbia (Vranje, Kraljevo, Novi Pazar, Raska and Usce).

After adequate analytical preparation according to standard EPA method 608 samples were analysed gas chromatographically on a gas chromatograph 8500 Perkin Elmer, in glass and capillary columns using a capture electron detector and mass spectrometry, temperature program.

The concentration of the residues of isomers of HCH, DDT, Lindane, Aldrine, Dieldrine, Heptachlorine and Heptachloroepoxide and Endosulphanes in investigated samples are within norms of currently applied Standards while concentration of organochlorine insecticides are greatly below the MAC in range of  $0.00-23.53 \cdot 10^{-2} \text{ mg/dm}^3$ .

The obtained results of our analyses reveal that investigated drinking waters of Serbia are suitable for consumption.

## **SAMPLE STORAGE AND ARSENIC DETERMINATION IN NATURAL WATERS**

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Arsenic can be found in the atmosphere, soils, rocks, natural waters and organisms. Arsenic can be present in nature mainly as inorganic species, arsenite and arsenate, and as methylated species. Presence of arsenic in the environment, even at low levels, has negative effects on people and animal health. The range of its concentrations found in environment is large (in natural waters from less than 0,5 to more than 5000 µg/L). Arsenic can occur in several oxidation states +5, +3, 0 and -3 and is found in inorganic and organic forms. Total arsenic, arsinic acid and dimethylarsinic acid were selectively determined in natural waters by hydride generation / AAS, using sodium tetrahydroborate as reductant but in different reduction media. River water samples from the north region of SCG were analysed and showed arsenate as the principal arsenical form.

# ENERGY IN HARMONY WITH ENVIRONMENT: MONITORING AND REDUCTION OF NO<sub>x</sub>, SO<sub>2</sub> AND CO IN THERMAL POWER PLANTS

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One of the primary concerns of all power plants is to ensure high electricity production and reduce hazardous and waste substances. In that way green electricity could be produced. It is essential to monitor the presence and movement of impurities in various measuring sites in air, water and soil [1]. The presence of hazardous species in these eco-systems, even at low-mg/l levels, has negative effects for nature and human beings [2, 3].

The aim of this work is to analyse processes for determination and removal (or reducing) greenhouse gases (GHG: NO<sub>x</sub>, SO<sub>2</sub> and CO) from air and make the comparative study of GHG emission and with production of electricity. Among various analytical methods „green analytical techniques” were analysed and tested for GHG determination.

It is concluded that GHG emission reduction could be estimated and calculated as follows:

$$\Delta\text{GHG} = (e_{\text{base}} - e_{\text{prop}}) E_{\text{prop}} (1 - \lambda_{\text{prop}}) (1 - e_{\text{cr}}),$$

where  $e_{\text{base}}$  is the base case GHG emission factor,  $e_{\text{prop}}$  is the proposed case GHG emission factor,  $E_{\text{prop}}$  is the proposed case annual electricity produced,  $\lambda_{\text{prop}}$  is the fraction of electricity lost in transmission and distribution for the proposed case, and  $e_{\text{cr}}$  the GHG emission reduction credit transaction fee.

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# APPLICATION OF SURFACE ELECTROCHEMICAL PASSIVATION OF LEAD-ANTIMONY ALLOY FOR A SIMPLE AND RAPID ELECTROCHEMICAL DETERMINATION OF ANTIMONY CONTENT OF ITS ALLOYS

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Antimony is widely used for production different types of lead alloy for different applications. One of the most applications of lead- antimony alloys are for grids production of lead-acid battery. Antimony improves the castability and the subsequent handling of the grid alloy. In addition, these alloys are extremely strong and creep-resistant and can be cast into rigid, dimensionally stable grids that are capable of resisting the stresses of charge/discharge reactions. On the other hand, these alloys are extremely used as suitable electrode in electroplating and copper electrowinning plants. Antimony concentration is very effect on the quality of Pb/Sb alloy applications, hence simple, rapid and selective determination of Sb is very important.

A simple, rapid and selective electrochemical method is proposed as a novel and powerful analytical technique for the solid phase determination of less than 4% antimony in lead-antimony alloys without any separation and chemical pretreatment. The proposed method is based on the surface antimony oxidation of Pb/Sb alloy to Sb(III) at the thin oxide layer of PbSO<sub>4</sub>/PbO that is formed by oxidation of Pb and using linear sweep voltammetric (LSV) technique. Determination was carried out in concentrate H<sub>2</sub>SO<sub>4</sub> solution. The influence of reagent concentration and variable parameters was studied. The method has detection limit of 0.056% and maximum relative standard deviation of 4.26%. This method was applied for the determination of Sb in lead/acid battery grids satisfactory.

# OPTIMIZATION OF THE METHOD FOR TUNGSTEN DETERMINATION IN STEELS AND ALLOYS BY INDUCTIVELY COUPLED PLASMA ATOMIC EMISSION SPECTROMETRY

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The simple analytical procedure of tungsten determination in high alloy steel and nickel base alloys by atomic emission spectrometry with inductively coupled plasma (AES-ICP) was developed. Proposed technique includes the dissolution of 0.1-0.5 g of material in mixed acids (25 ml HCl, 3 ml HNO<sub>3</sub>, 5 ml HF), complexation of tungsten by 9 % solution of oxalic acid and measurement of tungsten emission intensity ( $\lambda = 207.911$  nm).

A simple calibration curve based on distilled water is suitable for tungsten determination (linearity range is 1-50 mg/dm<sup>3</sup> of W), no interference from Fe, Co, Cr, Ni was found. The accuracy of the method is confirmed by analysis of certified reference materials of high alloy steels and nickel based alloys (in range of 0.3 to 15 % W). The analyzed values are agreeing well with the certified values.

Results of the tungsten determination in Russian reference materials of steels and alloys by the proposed AES-ICP procedure ( $n = 16$ )

Material	Certified value, % weight	Found value*, % weight
CRM 1640-88 (steel)	0.34 ± 0.01	0.33 ± 0.01
CRM 1220-93 (steel)	1.15 ± 0.01	1.16 ± 0.02
CRM 716-93 (steel)	4.55 ± 0.02	4.51 ± 0.04
CRM 1587-93 (steel)	9.60 ± 0.03	9.64 ± 0.07
CRM 1609-85 (nickel base alloy)	5.50 ± 0.04	5.56 ± 0.08
CRM 1631-86 (nickel base alloy)	13.47 ± 0.07	13.58 ± 0.14

$$*\text{Mean} \pm \frac{2\sigma}{\sqrt{n}}$$

The possibility of simultaneous AES-ICP determination of Ti, V, Mo and Nb in solution after complexation with good accuracy and precision was established.

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## ANALYSIS OF THE ESSENTIAL OIL OF *NEPETA SINTENISII* BORNM. FROM IRAN

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*Nepeta* (Lamiaceae) is a genus of perennial or annual herbs found in Asia, Europe and North Africa. About 250 species of *Nepeta* are reported of which, 67 species are present in Iran. Some species of this genus are important medicinal plants and their extracts have been used for medicinal purposes. Aerial parts of *Nepeta sintenisii* Bornm. was subjected to hydrodistillation and the chemical composition of isolated essential oil has been analyzed by GC/MS method for first time. Identification of components of the volatile oil was based on retention indices relative to *n*-alkanes and computer matching with the Wiley275.L library, as well as by comparison of the fragmentation patterns of the mass spectra with those reported in the literature.

Aerial parts of *N. sintenisii* yielded 0.3% of a clear yellowish oil. Forty constituents (96.5% of the total oil) were identified. The main components were 4 $\alpha$ ,7 $\alpha$ ,7 $\beta$ -nepetalactone (23.4%), elemol (16.1%), E- $\beta$ -farnesene (9.5%), 1,8-cineole (8.2%), *cis*-sabinene hydrate (6.5%),  $\beta$ -bisabolene (4.2%), germacrene-D (3.5%),  $\beta$ -sesquiphellandrene (2.8%),  $\beta$ -bourbonene (1.5%) and  $\alpha$ -epi-cadinol (1.3%). According to available data, *Nepeta* species can be divided into two groups of nepetalactone-containing and nepetalactone-free species. The results of this study indicate that the compositions of volatile oil of *N. sintenisii* are similar to the other *Nepeta* genus and this plant could be classified in the group which 4 $\alpha$ ,7 $\alpha$ ,7 $\beta$ -nepetalactone is the major component of their oils.



# DYNAMIC LEACHING OF ENVIRONMENTALLY RELEVANT FORMS OF HEAVY METALS FROM SOILS

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Accumulation of heavy metals (HM) in different compartments of the biosphere, and their possible mobilization under changing environmental conditions induce a perturbation of the ecosystem and adverse health effects. Fast and correct estimating the environmentally relevant forms of HM in soils, sediments, and sewage sludge is an urgent need for environmental monitoring and assessment.

It should be noted that the toxicity of HM depends strongly on their chemical forms and type of binding, e.g. with mineral components of soils. Batch sequential extraction procedures (SEP) are usually employed to access the potential risk HM for biota. These procedures are based on leaching HM, bound to defined soils phases, under the sequential action of more or less selective reagents. A lot of different leaching schemes have been proposed. According to the three-step SEP adopted by Standards, Measurements and Testing Program of the European Commission (former BCR Program) exchangeable/acid soluble, reducible, and oxidizable fractions are separated. However, in many cases more detailed information on potential mobility and bioavailability of HM is needed.

In this work a novel five-step leaching scheme for HM has been developed addressing exchangeable, acid soluble (carbonate), easily reducible (bound to Mn oxides), easily oxidizable (bound to humic and fulvic acids), and moderately reducible (bound to amorphous Fe oxides) fractions extractable by 0.05 M  $\text{Ca}(\text{NO}_3)_2$ , 0.43 M  $\text{CH}_3\text{COOH}$ , 0.1 M  $\text{NH}_2\text{OH}\cdot\text{HCl}$  (non-acidified), 0.1 M  $\text{K}_4\text{P}_2\text{O}_7$  (pH 11), and 0.1 M  $(\text{NH}_4)_2\text{C}_2\text{O}_4$  (pH 3), respectively. The sequence of extractants was chosen according to recent studies on the selectivity of leachants toward dissolved phases of soils.

The new scheme was applied to the flow-through (dynamic) fractionation of Zn, Cu, and Pb in soils using rotating coiled columns. The efficiency of leaching reagents and distribution of different HM forms in investigated samples were considered.

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# METHODICAL ELABORATION OF X-RAY FLUORESCENCE SILICATE ANALYSIS

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X-ray fluorescence (XRF) analysis is successfully used to determine chemical composition of various geological and ecological materials. It is known that XRF analysis has a high productivity, acceptable accuracy of results, developed theory and industrial analytical equipment sets. Therefore the complex methods of XRF analysis have to be constituent part of basis data used in ecological and geochemical investigations

This analytical complex is created and is successfully used in Geological Department of Kyiv Taras Shevchenko National University. It is used to perform the quantitative determination of main components in silicate rocks, grounds, silts and others geological and ecological units. The serials multichannels x-ray spectrometers are used, which are provided by fixed channels with wave dispersion. The mass parts of determined components (or elements) are calculated by  $\alpha$ -correction method or by simplified fundamental parameter method (FPM) with effective wavelength of primary excite spectrum. The system of equations for calculates mass parts of determined components are solved by simple iteration method. The samples for measuring x-ray fluorescence intensity of elemental analytical lines are prepared by fine grinding and pelletising obtained powders in the form of round fluorescence spectrum irradiators.

The methodical elaboration is included for estimation of random and systematic errors by using of single factor dispersion analysis. For this aim the set of reference samples is used. X-ray analyses of reference samples are performed with followed calculation of mass parts of components and comparison of results with real chemical compositions. Metrological characteristics of x-ray fluorescence silicate analysis are established both for  $\alpha$ -correction method and simplified fundamental parameter method. It is established, that systematic error of simplified FPM is less than  $\alpha$ -correction method, if the correction of zero approximation for simplified FPM is used by preliminary established correlation between theoretical and experimental set data.

The method of XRF silicate analysis has a State certificate of Ukraine. Established errors of XRF silicate analysis data are allow using its results in broad problem fields of geochemical and ecological investigations.

# EVALUATION OF POLYCHLORINATED BIPHENYLS AND ORGANOCHLORINE PESTICIDES CONTENT IN FISH TISSUE OF DNIEPER RIVER BASIN BY GC/MS

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Polychlorinated biphenyls (PCBs) and organochlorine pesticides (OCPs) are toxic compounds of anthropogenous origin, able to accumulate in tissues of alive organisms and to cause different diseases. These compounds are the most dangerous for aquatic ecosystems as they easily adsorb in sludge and are included in food chains of biota. Humans consume PCBs and OCPs mostly with fish.

PCBs and OCPs were identified and their concentrations determined by GC/MS in 14 samples of muscle tissue of fishes (pikes and pike-perches), caught in the Dnieper river and its tributaries. To obtain a representative data, the tissues of 3 fishes were united in 1 sample for each from 14 places of sampling. Homogenized muscle tissue (10.00 g) was mixed with anhydrous copper sulfate and extracted in Soxhlet apparatus for 24 h with dichloromethane, or accelerated solvent extraction was used at the temperature 80 °C and step gradient of solvents: diethyl ether, dichloromethane, and mixture of benzene/methanol (9/1). Extracts of muscle tissue of fishes were evaporated and redissolved in hexane. Then a sulfuric acid cleanup was performed. The samples, cleaned in this manner, were additionally purified using one of the two methods: oleum treatment or micropreparative isolation of fraction, containing PCBs and OCPs, on the reverse phase HPLC column (C<sub>18</sub>). For the purpose of target compound losses evaluation during sample preparation procedure, samples were spiked with 200 ng per sample of 2,3,3',4,4',5-hexachlorobiphenyl (internal standard). Method blanks were carried out for each batch of samples. The samples were concentrated to 100 µl and analyzed on the gas chromatograph HP 5890 equipped with HP 5972 MSD in SIM mode. The instrument was calibrated using mixtures: Aroclor 1221, 1242, 1254 and 16 OCPs. In all analyzed samples concentrations of DDT and its isomers, DDE, DDD, and PCBs (tri-, tetra-, penta-, hexa-, hepta-, octachloroisomers) were determined. Method detection limit for total PCBs content was 100 µg/kg (wet tissue) and for OCPs – 20 µg/kg. Recoveries for accelerated solvent extraction ranged from 75 to 115 % as compared to Soxhlet extraction.

## CHARACTERIZATION OF *MORINGA OLEIFERA* SEED OIL CULTIVATED IN DIFFERENT REGIONS OF PUNJAB, PAKISTAN

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The present study reports the characterization of *M.oleifera* seed oil cultivated in different regions of Punjab, Pakistan. The hexane-extracted oil content of *M.oleifera* seeds harvested from Jhang (Chenab Nagar), Layyah and Rahim Yar Khan (Sadiqabad) was ranged from 30.36-38.37%. Results of physical and chemicals parameters of the extracted oil were as follows: iodine value, 65.86-70.50; refractive index (40°C), 1.4570-1.4582; density (24°C), 0.9002-0.9061 mg/mL; saponification value, 181.1-183.7; unsaponifiable matter, 0.84-0.97%; acidity (as oleic acid) 0.28-0.35%. The induction periods (Rancimat 20L/h, 120 °C) of the crude oils were 8.33-9.63 h. Specific extinctions at 232 and 270 nm were 1.68-1.98 and 0.75-1.02 respectively. Tocopherols ( $\alpha$ ,  $\gamma$  and  $\delta$ ) in the oils as determined by HPLC were up to 97.85-100.78, 79.98-86.88 and 57.75-62.81 mg/kg respectively. The oils were found to contain high level of oleic acid (up to 75.55%) followed by palmitic, stearic, behenic and arachidic acid (up to 9.26, 3.30, 5.46 and 2.39%) respectively. Results of various parameters of *M.oleifera* seed oils indigenous to Punjab province of Pakistan compared with those of *M.oleifera* indigenous to Sindh, India and some other conventional oils, predicted a high-quality edible potential of this valuable oil seed crop.

# DETERMINATION OF HEAVY METALS IN ATMOSPHERIC PARTICLES (PM 10 & PM 2.5) BY ELECTROTHERMAL ATOMIC ABSORPTION SPECTROMETRY

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The sources of heavy metals in the urban atmosphere are sub-divided into two groups; 1) natural sources, and 2) anthropogenic sources [1, 2]. The major sources responsible for releasing heavy metals into urban atmosphere are man-made processes include; metallurgical processes, power plants, garbage incineration, and combustion of fossil fuels in automobile engines [3]. The toxic effects of heavy metals are now well recognized and determination of their concentrations is of great interest in air pollution studies because of both the size of population at risk and also the continuous nature of exposure [4].

In this work, atmospheric particles (PM 10 and PM 2.5) were collected by a dichotomos air sampler. Several leaching procedures were investigated for decomposition of heavy metals. The digests were pre-concentrated with sodium diethyldithiocarbamate. The determinations were carried out on a Varian Model AA-220 atomic absorption spectrometer. The instrument was equipped with a GTA-110 graphite furnace system. Table 1 shows the concentrations of heavy metals associated with PM 10 and PM 2.5 particles.

Table 1. Concentrations of heavy metals in PM 10 and PM 2.5 atmospheric particles (ng/m<sup>3</sup>)

Sample	PM 10				Sample	PM 2.5			
	Pb	Cd	Cr	Zn		Pb	Cd	Cr	Zn
1	178	3.9	18	329	1	91	2.1	9	172
2	189	4.2	19	328	2	96	2.2	10	179
3	182	4.0	19	340	3	94	2.1	10	189

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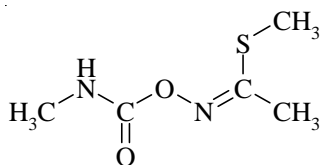
# PHOTOCHEMICAL BEHAVIOR OF THE INSECTICIDE METHOMYL IN ORGANIC SOLVENTS

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Insecticide methomyl is a very toxic pesticide and is highly soluble in water (57.9 g/l). It has a low sorption affinity to soil and can cause groundwater and surface water contamination in agricultural areas. Solubilities of methomyl in different solvents are: in methanol 1000 g/l, in acetone 730 g/l, in ethanol 420 g/l, in isopropanol 220 g/l, in toluene 30 g/l.



Structure of methomyl

This study describes the direct photochemical degradation of the methomyl presents at low concentration in different organic solvents. Also the kinetic behavior of photolytic reaction of methomyl with solvents has been studied.

Photolytic reactions were studied using Shimadzu UV-Visible spectrophotometer with Spectrum and Quantitative Mode. The pH measurements were performed by TOA Electronics pH meter at 20 °C.

Under the conditions it was found that the methomyl was effectively decomposed in different organic solvents and reaction's rate depends on type of solvents.

**ELEMENT PROFILE OF TABACO PLANTS AFTER THE  
TREATMENT WITH HETEROPOLY COMPOUNDS  
WITH ANTIVIRAL ACTIVITY INVESTIGATED  
BY EDXRF SPECTROMETRY**

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The group of experiments designed on *Nicotiana tabacum*, var. *Samsun* and *Nicotiana glutinosa* systematically infected by *Tobacco mosaic tobamovirus* (TMV) and *Cucumber mosaic Cucumovirus* (CMV), proved the antiviral activity of heteropoly compounds of Keggin type, such as 12-tungstophosphoric acid (WPA) and its compounds. A very low fitotoxicity opens the possibility for further investigations on using those compounds against the plant viruses that could be of a big economic interest.

As the side effect during the experiments, there found a better plants' growth in the group treated with WPA in comparison with the control group, especially the plants treated with magnesium WPA salt. That effect could not be explained by the phosphorus doping, due to extremely low concentration of phosphorus in WPA solutions using for spraying during the experiments. So, the effects of WPA and its compounds (its magnesium salt and compounds with Gly and Ala) on element profile of tobacco plants, tried to be connected. For such purpose, after the appropriate procedure of collecting, separating and storage, the EDXRF spectrometry of the leaves, trunks and summitas was performed. Radioisotope excitation source <sup>109</sup>Cd was used, the tablets weighted 100 mg of dried plant material and the measurement time was 2000 s. The contents of K, Ca, Fe, Cu, Zn, Na and Sr were determined in the control plant group, as well as in the tobacco plants groups after the once, twice and thrice spraying with ten days between the two treatments. A special attention was paid on the element profile of summitas (the top of the plant) witch was not directly spraying during the experiments, and its content of Zn, important element for the plant growth.

## **SUGGESTED METHOD FOR THE RATIONAL ANALYSIS OF THE NON-METALLIC MATERIALS**

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A recognizable development has been achieved in the field of chemical and instrumental analysis, it may be more easier these days to run complete chemical analysis for large number of samples of non-metallic materials, with high accuracy, in few hours or even minutes, where this before few years may require weeks or months, but on the hand this development fail to give the desired answer for most of researchers (material engineers, geologists, chemists,.. etc) - where all of them need to know the quantitative mineralogical composition of the raw material, since most of the available techniques can offer the qualitative composition rather than quantitative,

This paper proposes a new methodology for the rational analysis of the non-metallic materials that may lead at the end to the real mineralogical composition based on elemental analysis.



# DETERMINATION OF FREE CHLORINE AND CHLORAMINES WITH ETHYL DERIVATIVE OF MICHLER'S THIOKETONE

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One of the most widespread methods of water disinfection is its chlorination. As chlorination products are toxic, their content is to be controlled. Among them free chlorine and inorganic chloramines are predominant in water. Maximum contaminant limit for free chlorine is 0.3 – 0.5 mg/L, for chloramines – 0.8 – 1.2 mg/L.

Photometric methods are simple and rapid for the determination of components of active chlorine. But photometric reagents not always are enough sensitive and reliable.

We proposed new photometric reagent 4,4'-bis(diethylamino)-thiobenzophenone (ethyl derivative of Michler's thioketone, EMT) for the determination of free chlorine and chloramines in drinking water.

Interaction of EMT with chlorine and monochloramine has been studied. Electronic spectra of EMT and of its product of oxidation by chlorine and monochloramines have been obtained.  $\lambda_{\max}$  = 470 nm for EMT, 400 nm and 670 nm – for monochloramine. Effect of different variables on chlorine and chloramine determination has been investigated. Optimum conditions of determination: pH 3-7, ethanol 40-50%. Stability of oxidation product is 20 min.

Oxidation product has been isolated out of chloroform solution. Based on IR spectra and literacy data assumption has been made that oxidation of EMT leads to transformation of thionic group into disulphide tetraethylamino-thiobaenzophenone.

Interference of different inorganic ions has been examined. Selectivity coefficient are 1000-5000 for major water constituents ( $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{SO}_4^{2-}$ ,  $\text{Cl}^-$ ,  $\text{HCO}_3^-$ ). At pH 4 100-fold excess of  $\text{ClO}_4^-$ ,  $\text{BrO}_3^-$ ,  $\text{IO}_3^-$ , 10-fold excess of  $\text{IO}_4^-$ , 5-fold excess of  $\text{Cr}_2\text{O}_7^{2-}$  do not interfere with the determination. Working range for free chlorine is 0.1 – 1.0 mg/L. Detection limit calculated as background signal plus its triple standard deviation is equal to 0.04 mg/L, lowest limit of chlorine determination is 0.1 mg/L of final solution. Working range for monochloramine is 0.05 - 0.7 mg/l.

Tap water has been analyzed by the method proposed. Total content of chlorine and chloramines in water makes up  $0.12 \pm 0.02$  mg/L which is less than maximum contaminant level. Standard deviation does not exceed 0.15.

# **SEPARATION AND PRE-CONCENTRATION**

*Keynote lectures*

# **FRACTIONATION OF TRACE METALS AND METALLOIDS IN ENVIRONMENTAL SOLIDS: BATCH AND DYNAMIC METHODS**

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The impact of anthropogenic metal/metalloid ions on the soil environments cannot be evaluated by measuring merely the total concentration of individual species, because the mobility, bioavailability and, consequently, toxicity strongly depend on their chemical forms and type of binding with the sample matrix. Thus, procedures for distinguishing different solid-phase associations of trace elements (TE) are required. An approach that has been found to be preferable is the fractionation of TE into *operationally defined* forms under the sequential action of different leaching reagents. Selective reagents used in sequential extraction procedures (SEP) are intended to simulate conditions whereby TE associated with certain components of soil, sediment, or sludge can be released. Different sequences of leaching reagents are evidently required for the fractionation of trace metals and elements existing mostly in anionic forms (As, Se).

Despite the recent efforts for settling operational conditions for metal and metalloid fractionation, conventional batch sequential extraction schemes lack automation and are rather time consuming and laborious. Two additional main problems are the phase overlapping and possible re-adsorption of released elements.

Alternative methodologies are based on dynamic (non-equilibrium) approaches. Particulate samples are retained or fixed in a column or a stirred chamber whereas different aqueous solutions of acids, salts and complexing reagents are continuously pumped through. In such a way the leaching solution being in contact with the solid phase is constantly renewed. Dynamic procedures enable the extraction time required for the separation of each fraction to be significantly reduced. Investigating the elution curves makes it possible to study the kinetics of trace and major elements release, to test efficacy of extractants and to assess the maximum pool size of target fractions. When packed microcolumns or rotating coiled columns are employed, elements in the effluent can be determined on-line.

In routine analysis batch extraction appears to be still the method of choice. However, developing alternative flow-through schemes for comprehensive studies on the fractionation and mobility of TE in environmental solids looks rather promising.

# ANALYTICAL USE FOR LIQUID MEMBRANE EXTRACTION

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In this presentation principles and applications of liquid membrane extraction techniques for sampling and sample pretreatment in environmental analytical chemistry will be described.

The techniques of membrane extraction permit an efficient and modern application of classical liquid-liquid extraction (LLE) chemistry to instrumental and automated operation. Various shortcomings of LLE are overcome by membrane extraction techniques as they use none or very little organic solvents, high enrichment factors can be obtained and there are no problems with emulsions. A three phase SLM system (aq/org/aq), where analytes are extracted from the aqueous sample into an organic liquid, immobilized in a porous hydrophobic membrane support, and further to a second aqueous phase, is suitable for the extraction of polar compounds (acidic or basic, charged, metals, etc.) and it is compatible with reversed phase HPLC. A two-phase system (aq/org) where analytes are extracted into an organic solvent separated from the aqueous sample by a hydrophobic porous membrane is more suitable for hydrophobic analytes and is compatible with gas chromatography.

Membrane extraction can easily be set up in flow systems and can be connected in an automated way on-line to various analytical instruments. Also, offline cheap hollow-fiber systems are available. High degrees of clean up and enrichment are obtained, which is very important for reliable and sensitive chemical analysis. Recent applications of automated determination of PCB and phenols will be presented.

Membrane extraction can also be a basis for environmental field sampling and for determination of freely available fractions of both metal ions and organic compounds. Procedures and devices for this are developed, as will be described in the presentation.

## MICROWAVE-ASSISTED SAMPLE PREPARATION AND PRECONCENTRATION

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The use of microwave irradiation as an energy source for chemical reactions and processes has been extensively investigated during recent years and has found wide application in various fields of chemistry and technology. The following presentation focuses on the scope and potential of microwaves in chemical analysis.

Theoretical and applied aspects of microwave heating, as well as the advantages of its application are discussed for the individual analytical processes and also for the sample preparation procedures. Special attention is paid to the various preconcentration techniques, in part, sorption and extraction. Improvement of microwave-assisted sorption preconcentration is shown on the example of separation of noble metals from matrix components by complexing sorbents. Advantages of microwave-assisted extraction and principles of choice of appropriate solvent are considered for the extraction of organic contaminants from solutions and solid samples by alcohols and room-temperature ionic liquids (RTILs).

The performance of microwave-assisted decomposition of most difficult samples of organic and inorganic natures in combination with the microwave-assisted sorption preconcentration is illustrated by sample preparation of carbon-containing matrices followed by atomic spectroscopy determination of noble metals. Microwave-assisted extraction of most dangerous contaminants, in particular, pesticides and polycyclic aromatic hydrocarbons, from soils have been developed and successfully used in combination with polarization fluoroimmunoassay (FPIA) and fluorescence detection.

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## **NOVEL MATERIALS FOR CATALYSIS AND ANALYSIS DERIVED FROM RENEWABLE RESOURCES**

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The development of novel materials for applications such as catalysis has been a very important area of work, with several classes of materials being developed and applied (for example, zeolites and their mesoporous analogues, hydrotalcites, hydroxyapatites, clays).

Recently, however, we have embarked on a programme aimed at developing biodegradable and renewable support materials based on the very abundant sources of biomass such as starch, chitosan and cellulose, in addition to the inorganic materials mentioned above.

The presentation will focus on our work in functionalising these materials and modifying their physical properties to generate a range of materials with properties suitable for catalysis, and in some cases analytical applications.

For example, the amino groups of the chitosan material can be functionalised to give supported metal catalysts; starch can be expanded to give a very high surface area material and subsequently functionalised to give a range of materials with various properties. We have demonstrated their potential in catalysis and begun to look at them as stationary phases for chromatography with some success. Separations are good and often require considerably less solvent than more traditional silica based stationary phases.

# THE POTENTIAL OF USING ROTATING COILED COLUMNS IN ANALYTICAL CHEMISTRY

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Application of rotating coiled columns has become attractive for preparative-scale separations of various substances from different samples (natural products, food and environmental samples) due to advantages over traditional liquid-liquid extraction methods and other chromatographic techniques. The studies mainly made during the last fifteen years have shown that using rotating coiled columns is also promising for analytical chemistry, particularly for the extraction, separation and pre-concentration of substances to be determined (analytes) before their on-line or off-line analysis by different determination techniques.

Numerous two-phase solvent systems with a broad spectrum of polarity or containing different extracting reagents, applicable to the separation of organic, bioorganic and inorganic substances, are examined. The developed and potential procedures are valuable for analysis of plant and other natural products, for food and environmental analysis, for the analysis of geological and high-purity materials. Combinations of rotating coiled columns with various determination methods (fluorimetry, UV-visible spectroscopy, mass spectrometry, inductively coupled plasma atomic emission and atomic absorption spectrometry, etc) are discussed.

## SILICA-ANCHORED ANALYTICAL REAGENTS AND COMPLEXING LIGANDS

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At the present time silica carriers have been widely used for transfer of many organic ligands and some important analytical reagents to a heterogeneous state. Advantages of use of such silica-supported preparations for detection, separation, and preconcentration of ions and molecules manifest themselves in mechanical, microbiological, chemical, radiation and thermal stability, rigidity of skeleton, not changing structure during varying of pH, ionic strength and type solvent.

This presentation is intended to analyze the experience acquired in developing efficient and versatile enough methods for activation of surfaces of functional organosilicas, carrying amino-, vinyl-, mercapto- and silicon hydride groups in modifying layer, and in their use for immobilization of oxygen, nitrogen-, and sulfur-containing complexing ligands, some analytical reagents. Main physicochemical properties of the such mineral complexing sorbents are analyzed, and the prospects of its practical application for extraction, preconcentration and chromatographic separation of metal ions are discussed.

Application of the Mannich reaction is of doubtless interest for binding of heterocyclic compounds which fall in the important complexing reagents class. Conditions of a single-stage method of chemical attachment of 8-hydroxyquinoline, 1-(2-pyridylazo)-2-naphthol, 4-(2-pyridylazo)resorcinol to the surface of inorganic carrier through the use of the aminomethylation reaction and adsorption properties of the chemically modified silica gels obtained towards ions of toxic metals have been studied.

In recent years the solid-phase hydrosilylation reaction was successfully employed for synthesis of hydrolytically stable surface chemical compounds with Si-C bonds. Of special interest is application of this method for attachment of functional olefins, in particular of acrolein and some chiral ligands. Such matrices can be used for subsequent immobilization of a wide range of amine-containing organic reagents and in chiral chromatography.



*Oral presentations*

# ON-LINE CONCENTRATION TECHNIQUES IN MICELLE ELECTROKINETIC CHROMATOGRAPHY (MEKC) IN DETERMINATION OF THE QUANTITY OF NEUTRAL BIO-ACTIVE SUBSTANCES

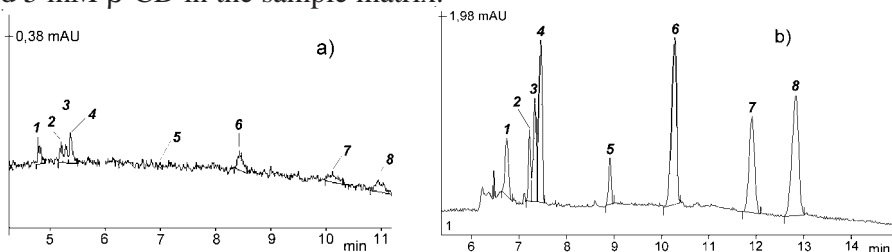
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One of the important problems in the diagnosis of different disease in their early stages is the determination of bio-active substances in biological fluids. We are currently interested in applying capillary electrophoresis (CE) as technique for the rapid and highly efficient separation of corticosteroids in serum and urine. Steroids can analyze by MEKC.

The levels of steroids in real samples are sub-micromolar. CE suffers from poor UV-sensitivity. Therefore it requires a special sample preparation. On-line sample preconcentration (stacking, sweeping, etc.) represents an effective way to enhance concentration sensitivity in CE. We have compared the sensitivity enhancement of five on-line preconcentration techniques, namely normal stacking, stacking with reversed migration micelles, stacking with high conductivity matrix, enhanced sample injection - reversed migration micelles and sweeping for model mixture of steroids by CE. Sweeping has provided 100-fold increases in detection sensitivity for steroids (50 ng/ml), which is greater than any other examined technique. Fig.1 depicts optimum focusing by sweeping using a combination of 10 mM SDS, 4,5M urea in buffer and 5 mM  $\beta$ -CD in the sample matrix.



**Figure 1.** Optimization of sweeping procedure on the steroids mixture. Electropherogram for a mixture containing 2,5 mg/ml (1) progesterone, (2)11-dexoxyprogesterone, (3)17-hydroxyprogesterone, (4)11-dexoxycortico-sterone, (5)corticosterone, (6)11-dehydrocorticosterone, (7)cortisone, (8)cortisole. Sample matrix, electrophoresis buffer (without SDS) with the same conductivity and with addition 5 mM  $\beta$ -CD. Separation voltage: -25 kV. Buffer, 25 mM  $H_3PO_4$  (pH = 2,5), 10 mM SDS, 4,5 M urea. Injection: (a) 60 mbar-s, (b) 3000 mbar-s.

We have developed the method of the determination of steroids in biological fluids (serum and urine) by MEKC with on-line concentration (sweeping) with detection limit for about 3 ng/ml (S/N=3).

# THE COMBINED CHEMICAL AND PHYSICAL INFLUENCES IN SAMPLE PREPARATION

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Sample preparation is a limited stage of the analytical process taking about 90 % time of practically any method of element analysis for determination of both basic substances and admixtures. The intensification of sample preparation stage is one of the important problems in analytical practice. For the decision of this problem we offer use of the combined chemical and physical influences on a number of processes of a sample preparation stage (decomposition, concentrating, separating etc.).

The acoustic and electromagnetic fields are the most perspective of physical influences. We selected application ultrasonic (US) and microwave (HF and SHF) radiations, and the stages of analytical process include the combined influence: at ultrasonic action on process the electromagnetic field is imposed, at plasmochemical action the process is accompanied by electrochemical reactions etc.

Physical influence is employed on the different stage of sample preparation:

- to accelerate the sample dissolution (US, SHF, plasma);
- to destroy organic and other compounds (US, SHF, plasma, IR, radiolysis, photolysis);
- to intensify the process of substances separation (US, SHF);
- to accelerate the stage of mineralization (US, IR, SHF);
- to transfer of the determined elements into specific condition (plasma, US);
- to stabilize analytical forms (US, SHF).

The nearness of character of the physical fields action on substances has been established. Use of the wide spectrum of frequencies, intensities and time of physical action had allowed to receive the maximum analytical effect. In many cases not only intensification of mass transfer but also a change of solution structure, hydration of ions, their reaction capability, rupture of polymer bounds, and formation of free radicals take place.

Compatibility physical influence with tool chemical methods of sample preparation and the stage of determination based on any principle of an analytical signal generation, the opportunity of automation of a sample preparation stage, control, modeling of conditions of analytical process opens prospects for their use in the analysis of food-stuffs, environment objects, geological samples, etc.

## **SAMPLE PREPARATION FOR X-RAY ANALYSIS OF LIQUID MEDIA**

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X-Ray fluorescence (XRF) analysis favorably differs from other instrumental techniques by rapidity, automation ability, selectivity, accuracy. Quality of specimen obtained from sample to be analyzed has influence to the accuracy.

The review of different methods for making specimens from analyzed liquids (aqueous and organic ones) is carried out. Characteristics of the specimens are considered. The direct XRF analysis of liquid samples is the most simple but the least suitable. However solid specimens are more preferable for XRF analysis. Sometimes frozen liquids, low-temperature melting extract agents, which turn into specimens during their congelation, are used for this purpose. Most often liquid samples are evaporated on a filter or another substrate. It's shown that the quasi-solid specimens on the base of gel forming agent (gelatine or agar) obtained by means of easy temperature treatment of these liquids, as well as polymer glass on the base of sucrose and polymer films are the best kind of specimens for the analysis of liquid media. Organic solutions can be turn into organogels using gelatine and a surfactant.

There are noted the most convenient, simple and chip methods, which ensure the high quality of specimens and can be easily combined with different techniques for analytical pre-concentration of impurities. In particularly, it is proposed to make specimens in the form of gel, film or glass in the case of XRF analysis of concentrates obtained by low-temperature crystallization of aqueous solutions. One can prepare film or organogel specimens from organic concentrates obtained by means of extraction of impurities by organic solvent. Techniques for XRF analysis of drinking, natural and wastewater using considered specimens are adduced.

## **APPLICATION OF NANOTECHNOLOGY FOR PREPARATION OF STATIONARY PHASE FOR CHROMATOGRAPHY**

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For the fabrication of organic-inorganic hybrid (nanocomposite) materials with interpenetrating polymeric network structures the most promising process entails the use of sol-gel techniques. The main advantage of this method, which typically entails the in-situ, co-reaction of organic polymers with tetraethoxysilanes or other inorganic precursors, is the possibility to use a range of inorganic and polymeric species with different structures and the resultant possibility to obtain nanohybrid materials with regulated and complex properties. One such family of materials, which will form the basis of this investigation, are polymer-silica nanocomposite sorption materials. Such materials have potential widespread application in areas such as chromatography, coatings, entero- and haemosorption.

The development of a simple and effective approach to development of new organo-inorganic nanohybrid materials in accordance with the requirements and demands of modern industrial technologies necessitates fundamental investigations in this area, in particular to obtain an in depth understanding of the factors determining the structure and properties of the resultant materials, in order that these can be engineered by control of suitable process parameters. These hybrid materials, possessing nanostructure are interesting to use of them as chromatographic stationary phases for HPLC and HPTLC.

In the present report the opportunity of use of the sol-gel process for preparation of supports for chromatography is considered by three ways:

- a) preparation of nanohybrid supports by simultaneously going reactions of polymerization of the organic monomers - acrylonitrile and hydrolytic polycondensation of alkoxysilanes;
- b) synthesis of nanohybrid supports by hydrolytic polycondensation of alkoxysilanes in polymer solution (polycaproamide or chitosan);
- c) synthesis of hydrolytic stable microspherical zirconia-silica gel hybrid support by including zirconium oxychloride in process of hydrolytic polycondensation of polyethoxysiloxane oligomer prepared by hydrolysis and condensation of tetraethoxysilane.

# **ANALYTICAL APPLICATION OF SILICAS WITH COVALENT AND ION-EXCHANGE BONDING OF IMMOBILIZED ORGANIC COMPOUNDS FOR SELECTIVE PRE-CONCENTRATION AND DETERMINATION OF PHENOLIC POLLUTANTS**

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Phenols hold an important place among organic pollutants, which need to be constantly monitored in waters and in places of military activities. Sampling of phenol matrix is conducted with solid phase extractions (SPE) with further HPLC or GC analysis. Application of the known SPE usually is ineffective as it doesn't give the possibility to provide full extraction of the analyt (microcontents) in the matrix media. Therefore SPE application needs further progress in their selectivity.

In the stated work we propose a rate of modified silicas for extraction of activated and deactivated phenols. Two methods were proposed for extraction of the activated phenols. The first approach is based on heterogeneous azo-coupling reaction of phenols with aryldiazonium salts bonded on the silica surface. For this purpose *p*-aminoacetophenone and *m*-aminophenylarsonic acid were used. First reagent was covalently bonded on the silica, while second was bonded by the ion-exchange on the silica with covalently grafted quaternary ammonium salt. These diazo-couplers were transferred into aryldiazonium salts, which were stabilized with potassium tetrafluoroborate and were azo-coupled with phenols in aquas media. The second approach is based on a direct interaction of phenols with 4-nitrophenyldiazonium tetrafluoroborate in aquas media and its further extraction by modified with polyoxyethylene isooctylphenol silica in the presence of cationic surfactant. In both of the described methods formation of immobilized azocompounds as a result of SPE reaction with phenol leads to a drastic change in the sorbent's color. Visual-testing and photometric methods were developed for detection of phenols in water.

For the selective pre-concentration of deactivated phenols a new silica-based material with the grafted 2,3,5-triphenyltetrazole was proposed. This method is based on the formation of molecular charge-transfer complexes of 2,3,5-triphenyltetrazole ( $\pi$ -acceptor) with picric acid ( $\pi$ -donor) in the phase of the sorbent. Proposed SPE is suitable for HPLC analysis of nitrophenols after their desorption by acetonitrile. Test-system for visual monitoring of polynitrophenols under their maximum concentration limits was developed using the proposed adsorbent.

# SORBENTS FOR CONCENTRATION OF Pd(II): NATURAL AND ACIDIC MODIFIED TRANSCARPATHIAN CLINOPTILOLITE

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Clinoptilolite is microporous crystalline solid with well-defined structure, which have great potential for a number of applications in various fields, such as adsorption, separation, ion-exchange and catalysis.

In our work palladium (II) sorption on natural and acidic modified with 12.0 M HCl clinoptilolite has been investigated. Optimum palladium(II) sorption under the static conditions on grains of the diameter: a) 0.355-0.500 mm – natural clinoptilolite; b) 0.200-0.315 mm – H-clinoptilolite at pH=4.50 from nitrate solutions and pH=10.0 from ammonia solutions have been achieved. Sorption properties of sorbent H-form dried out at 150-160°C are similar to the natural form dried out at 70-80°C. The time of the sorption equilibrium establishment on natural clinoptilolite (6 hours) is considerably larger than on H-clinoptilolite (1 hour). It was established that selectivity of the Pd(II) separation by different forms of clinoptilolite in the presence of inorganic salts with  $C > 2.0$  M considerably gets worse. It was found out that the presence of the 5-multiple excesses of Ag(I), Ir(IV), Ni(II), Pb(II), commensurable amounts of Os(IV) and Ru(IV) do not prevent palladium (II) sorption on natural clinoptilolite in an ammonia medium, and also the presence of the 10-multiple excesses of Os(IV), Ni(II), 5-multiple excesses of Fe(III), commensurable amounts of Ru(IV) do not prevent sorption in a nitrate medium on M-clinoptilolite. The sorption capacity of natural and H-clinoptilolite (treatment by 12.0 M HCl) towards to Pd(II) from nitrate (pH=4,2) solutions: 977 and 3440  $\mu\text{g/g}$  accordingly; and from ammonia (pH=10,0) solutions: 2404 and 11420  $\mu\text{g/g}$  have been determined respectively. The effective row of ion exchangeable cations under the acidic modification of clinoptilolite by 12.0 M HCl is built:  $\text{K}^+ > \text{Na}^+ > \text{Mg}^{2+} > \text{Fe}^{3+} > \text{Ca}^{2+} > \text{Mn}^{2+}$ . During acidic modification considerable dealumination of zeolite takes place, which is the principal reason of increasing of H-form sorbent sorption, because  $\text{H}^+$  has low ion exchangeable efficiency. The effective rows of ion exchangeable cations under palladium (II) sorption by natural clinoptilolite have been obtained:  $\text{Na}^+ > \text{Ca}^{2+} > \text{Mg}^{2+} > \text{Fe}^{2+} > \text{Al}^{3+} > \text{K}^+$  (pH=4.2) and  $\text{Ca}^{2+} > \text{K}^+ > \text{Na}^+ > \text{Mg}^{2+} > \text{Al}^{3+}$  (pH=10.0) and by H-clinoptilolite:  $\text{Na}^+ > \text{Ca}^{2+} > \text{H}^+ > \text{Mg}^{2+} > \text{K}^+ > \text{Al}^{3+}$  (pH=4.2) and  $\text{Ca}^{2+} > \text{K}^+ > \text{Mg}^{2+} > \text{Na}^+ > \text{Al}^{3+}$  (pH=10.0). Pd(II) desorption from the sorbents has been studied. HCl and NaCl are the most effective desorbents of both sorbent forms. The Pd(II) concentration by natural clinoptilolite in wastes of jeweller production have been carried out with further its determination by pulse voltammetry using a linearly varying potential. The elaborated method is implemented at the Lviv state jeweller plant.

# ABOUT EXTRACTION AND STABILITY OF HEXAVALENT CHROMIUM IN SOILS AND FERTILIZERS

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Some soils and fertilizers may contain huge amounts of chromium, particularly basic slags, or oxidic waste materials. Application of Cr(VI)-containing basic slags and basic slag potashes led to concerns about Cr(VI) intoxications in arable soils. Within this paper, possible systematic errors in the extraction of Cr(VI) from solids are outlined. Extraction from the solid may result in losses from reduction, particularly with organic compounds or divalent iron. 1M ammonium nitrate has been defined to extract the “soluble” chromate (DIN 19730), 0,5M phosphate buffer has been defined to extract the “exchangeable” chromate, and hot carbonate solution should yield total chromate. Whereas the ammonium nitrate extract of mineral fertilizers largely took the pH of the substrates, it got significantly acidified in real soil samples due to cation exchange. Soil extract were colourless, but at pH 4, stability of added chromate was <20% due to reduction with co-extracted organic substances during the 2 hours standard shaking time. In extracts within the range pH 5,5-6,9, the median recovery was 57%. When 0,5M phosphate buffer of pH 7,2 was used, most extracts were slightly more alkaline than the standard soil pH determined in 0,1M CaCl<sub>2</sub>. These extracts were faintly brown. The median of the recovery of chromate added to soil extracts was 67 % (range 60-100 %) due to photometry (Cr(VI)), and 86% due to ICP (total Cr). The pink color had to be corrected for the brown background. The alkaline extracts were intensely brown. After neutralization and cleanup with isolate cartridges, the resultant solution could be submitted to the reaction with diphenylcarbazide reagent, as an alternative to standard ion chromatographic separation and on-line post column derivatization. The recovery in these alkaline extracts was just 56-74%. All extracts were also run at the ICP-OES to monitor co-extracted Ca-Cd-Cu-Fe-Mn-S-Zn. The cleanup with isolate cartridges removed major parts of Mn, Cu, Ca and S. Fe, Zn, and Cd were below the blanks of the buffer. Co-extracted ions will not influence the spectrophotometric determination of chromate.

Fertilization with basic slags of about 5 mg/kg Cr(VI), which is above the threshold for waste deposition sites (2 mg/kg), did not results in detectable Cr(VI) in soils.



# EXTRACTATION AND CONCENTRATION OF DIFFERENT-CHARGED COMPLEXES OF SOME PLATINUM METALS WITH ORGANIC BASES AND WATER SOLUBLE EXTRACTANTS

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In order to find effective extractive system for withdrawal and separation of platinum metals in wastes distribution of different-charged chloride, thiocyanate complexes of rhodium(III), ruthenium(III), palladium(II) with liquid anion exchangers and water soluble extractants have been investigated. In concentrated hydrochloric acid solutions rhodium(III), ruthenium(III) exist in the state of highly charged acidocomplexes (HCA)  $[\text{RhCl}_6]^{3-}$ ,  $[\text{RuCl}_6]^{3-}$ . In thiocyanate solutions different charged complexes of the following structure  $[\text{Me}(\text{SCN})_n]^{(3-n)+}$ , where  $n=1-6$ , are formed.

Relationships connecting structure and properties of primary alkylamines of normal structure  $\text{C}_{12}-\text{C}_{18}$  in chloroform and other solvents with their ability to extract Rh(III) and Ru(III) HCA from chloride solutions have been studied. The out-sphere mechanism of extraction and composition of extracted associates has been ascertained by UV-VIS-, IR-, and  $^1\text{H-NMR}$  spectroscopy, saturation method, and analysis of organic phase. Tertiary alkylamines i.e. tri-*n*-octylamine, tribenzylamine do not extract Ru(III) and Rh(III) HCA. The decrease of radical volume of tertiary alkylamines by changing of two alkyl radicals to methyl make it possible to diminish steric effects and to use tertiary alkylamines with different radicals such as dimethyl-*n*-dodecylamine which has not been used previously for the extraction of Rh(III), Ru(III) HCA with localized charge.

Stratifying water systems for selective extraction of thiocyanate complexes of platinum metals have been proposed. The extraction degree of ruthenium(III) by ethyl and isopropyl alcohols, acetone, polyethylene glycol in optimum conditions amounts to 95-100%. By the help of electronic methods, IR-spectroscopy, equilibrium shift the extractive mechanism has been proposed and structures of extractable compounds, which contain single and double-charged acidocomplexes  $[\text{Rh}(\text{SCN})_4]^-$ ,  $[\text{Ru}(\text{SCN})_4]$ ,  $[\text{Ru}(\text{SCN})_5]^{2-}$  have been determined. Constants of extraction for associates investigated have been calculated.

The method of extraction of Ru(III) from thiocyanate solutions by water soluble extractants in the presence of ammonium sulfate as salting out agent followed by photometric determination of it in extract has been elaborated.

Method of Rh(III) - Ru(III) separation and isolation them from rare and nonferrous metals based on formation of different charged complexes with varied stability has been proposed. Possibility of separation of Ru(III), Rh(III), Pd(II), Pt(II) by water-soluble extractants from concentrated thiocyanate solutions has been displayed. Accelerated procedures of extraction-photometric determination of Rh(III), Ru(III) in solutions and waste products, which are characterized by high selectivity, availability, usage of non-toxic extractants have been worked out.

## **MEASURING SURFACE PARAMETERS VIA $^{19}\text{F}$ NMR OF ADSORBED ORGANOFLUORINE PROBE MOLECULES**

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A molecule adsorbed onto amorphous surfaces may be subject to a set of interactions as complex as those in a solution, yet these forces are difficult to observe or measure directly. Fluorine-containing molecules are ideal for study by NMR because of the high sensitivity of the chemical shift. The change in  $^{19}\text{F}$  NMR chemical shift on adsorption of an organofluorine compound from the gas phase to a surface provides useful information on local specific and non-specific bonding environments. Interactions of over 30 probe molecules have now been studied with a number of surfaces including inorganic oxides (silica, alumina) and carbonaceous materials. A number of parameters based on  $^{19}\text{F}$  chemical shift measurements are proposed, which describe and quantify the ability of the surface to become involved in, for example, hydrogen bonding and electrostatic interactions. Some thought is also given to the suitability of this approach for the measurement of porosity and specific surface areas.

# THE CONCENTRATION AND ANALYSIS OF TRACES OF NOBLE METALS USING SILICA GELS WITH GRAFTED SULFUR-CONTAINING COMPOUNDS

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In the most cases the determination of noble metals is impossible without their preliminary concentration. At present the sorption concentration has an indisputable preference. Chemically modified silica gels (CMSG) with organic compounds grafted to silicon dioxide surface attract great attention among sorbents used for these purposes. Silica gels with grafted sulfur-containing compounds are of particular interest for metal concentration due to their high selectivity of complexation reactions in relation to noble metals.

The second important class of sorbents on CMSG basis for noble metal concentration are anion-exchangers, that is predetermined by their presence as acidocomplexes in hydrochloric acid solutions.

The third one is a new class of sorbents, which we created, containing on the surface groups combining sulfur-containing (complexing) and anion-exchanging groups in the structure. The mechanism of interaction of ions of platinum metals and their tin chloride complexes with N-(2,6-dimethyl-4-methyltriphenylphosphonium chloride)-N-propylthiourea groups covalently bounded to a silica gel surface is examined in the report. It is established using diffusion reflection spectroscopy and luminescence, that the sorption occurs immediately by complex-forming mechanism for kinetic labile platinum (II) and palladium (II) complexes. For kinetic inert complexes of platinum metals the sorption takes place due to anion-exchanging interactions of platinum metal acidocomplexes with triphenylphosphonium groups with the subsequent long-term regrouping resulting in formation of surface complexes with thiourea groups.

The conducted researches of complexing processes of noble metals on a sulfur-containing CMSG surface formed the basis for development of sorption-photometric, sorption-luminescent, sorption-atomic-absorption, sorption-atomic-emission and sorption-nuclear-physic techniques of the analysis of noble metals in rocks, technological objects and environmental objects. Techniques of separation and determination of noble metals in various oxidation levels have been proposed in some cases.

# POLYURETHANE FOAM MODIFIED WITH HETEROPOLYACIDS ARE THE NEW SORBENTS FOR ONECHARGED CATIONS OF HEAVY METALS

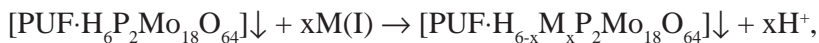
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The application of ammonium molybdophosphate and other insoluble in water salts of heteropolyacids for preconcentration of heavy metals of first group elements Cs(I), Ag(I), Cu(I) and also Tl(I), Hg(I) (M(I)) is described. The shortcomings of ammonium molybdophosphate as ionexchanger are:

- a) small crystals;
- b) the dependence of ion exchanged properties from the way of its receive;
- c) M(I) eluted with the large volume of concentrated solution of ammonium nitrate; that is need the repeat the sorption of M(I) for example on zirconium phosphate.

We achieved, that by contact of polyurethane foam with water solution of molybdophosphate, contain by pH 1-2,5 mixture of saturated  $[\text{PMo}_{12}\text{O}_{40}]^{3-}$  ( $\delta$  NMR  $^{31}\text{P} = -3.20$  p.p.m. apply to 85 %  $\text{H}_3\text{PO}_4$ ) and unsaturated monovacant  $[\text{H}_x\text{PMo}_{11}\text{O}_{39}]^{(7-x)-}$  ( $x=0\div 4$ ) ( $\delta$  NMR  $^{31}\text{P} = -0,96$  p.p.m.) heteropolycomplexes Keggin structure, equilibrium discharge in the direction produced of saturated heteropolycomplex of Dowson structure and on the surface of polyurethan foam formed 18-molybdo-2-phosphate acid ( $^{31}\text{P} = -2,40$  p.p.m. in ether extract). The formed surfaces heteropolycomplex is stable for action 1 M solution of strong acids and basics and have ion exchanged properties in static and dynamic conditions to relation to macro and micro amount of M(I):



where PUF is a matrix of polyurethane foam,  $x \leq 3$ .

The formation of more replaced compounds in studied conditions is not have place. Maximal yield on surface polyurethane foam of salts is observed by pH 2-6. By  $\text{pH} < 2$  the equilibrium ionic exchanges was displaced left and by  $\text{pH} < 0,5$  the sorbent practical completely was regenerated. It was studied the influence of the weight of sorbent, the nature of cations of light alkali and alkali earth metals and any other factors on the coefficient concentration of M(I).

*Poster presentations*

# COMPARATIVE SORPTION OF GOLD(III), PLATINUM(IV) AND PALLADIUM(II) ON VARIOUS ORGANOPOLYMERIC SORBENTS

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Sorption concentration of noble metals with organopolymeric complexing sorbents is widely used in practice of analytical chemistry. The great number of sorbents with various complexing or anion-exchanging groups is applied for these purposes. Sorbents with mixed complexing or anion-exchanging functions are used in some cases.

We have conducted the comparative study of gold (III), platinum (IV) and palladium (II) acidocomplexes sorption on macroporous granular sorbents on the basis of polystyrene with functional groups of methyleneamine, 3-methylpyrasolyl, N,N-dimethylaminomethylene, dimethylmethylene- $\beta$ -oxyethylamine and with functional 6-(3-methylpyridine) groups on polyvinylpyridine basis as well as fibrous polystyrene sorbent with pyrazolyl groups.

Gold (III) and palladium (II) are sorbed quantitatively on all studied sorbents, except for methyleneamine, from solutions 0,2-2 M HCl. The degree of platinum (IV) complex extraction substantially depends not only on the nature of sorbent functional groups, but also on geometrical parameters of the matrix. This factor influences gold (III) and palladium (II) sorption to a lesser extent.

The sorbent of fibrous structure has the best kinetic characteristics in relation to noble metals, for which reaching sorption balance does not exceed 20 minutes. The rate of sorption balance establishment depends on the form of nitrogen in functional groups of sorbents used and decreases in a line: tertiary nitrogen (linear group) > tertiary nitrogen (heterocycle) > quaternary nitrogen.

The capacity of studied organopolymeric sorbents depends on metal nature (Pd (II) > Au (III) > Pt (IV)) as well as on the composition and structure of sorbent matrix (polyvinylpyridine macroporous > polystyrene macroporous > polystyrene fibrous).

It can be concluded from the conducted researches, that it is advisable to use a fibrous sorbent with pyrazolyl groups and polystyrene macroporous sorbent with dimethylmethylene- $\beta$ -oxyethylamine groups for gold (III), platinum (IV) and palladium (II) group concentration and their subsequent desorption.

# CONCENTRATING OF THE MICRO-ADMIXTURES FROM AQUA SOLUTIONS OF THE NON-IONIC SURFACTANTS BY COOLING

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Micellar extraction with non-ionic surfactants (NS) at cloud point temperature is a high effective and ecologically safe method for micro-components preconcentrating, which has been developed intensively recent years. High concentrating coefficients, selectivity and simplicity of combination with a number of analytical procedures allow using the micellar extraction for elaborating high-sensitive and convenient hybrid methods. Nevertheless, the necessity of heating of the solutions limits the procedure's capabilities especially at preconcentrating of high charged metal ions. At the same time, the variety of temperature phase transformations in surfactants solutions allows the creation suitable for concentrating purposes liquid phases at cooling too. These phases formation can be stimulated by electrolytes or some organic compounds additions. Thus, the conditions of the phase formation in the cooled solutions of the nonionic surfactant OP-7 in the presence of KCl, HCl and phenols were studied.

It was shown that cooling of OP-7 water solutions in the 1-2% concentration range did not result in new phase formation. Additions of KCl and HCl in the wide concentration interval were found to be useless too. However addition even of a small amounts of phenol (0,5-1%) caused the new solid phase formation at room temperature. The phase dissolved at cooling and formed again when the temperature returned to the room one. This time the formed phase was liquid and its formation was effectively stimulated by KCl and HCl additions. The compact micellar phase was able to extract the micro-admixtures of a different nature from the water solutions. The separation of the micellar-rich phase by decantation did not meet with problems and the low volume of the phase provided the achievement of the high concentrating coefficients. The influence of the concentration conditions on the surfactant-rich phase formation was investigated. It was shown the specificity of extraction with the micellar NS phases at cooling in compare with cloud-point extraction and conventional extraction with organic solvents.

# EFFECT OF QUATERNARY AMMONIUM SALT EXCHANGE CENTER STERIC ACCESSIBILITY ON EXTRACTION OF CADMIUM BROMIDE COMPLEXES

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The quaternary ammonium salts (QAS) are widely used as ionophores of ion-selective electrodes and extractants of metals halogenic anion complexes. The influence of the QASes nature with various methyl groups contents on the cadmium extraction from bromide media has been investigated.

The researches, carried out on model solutions, have shown that replacement of one, two or three long-chained substituents bound with a nitrogen atom by methyl substituents results in sharp increase of the ion-exchanging affinity to hydrophilic single-charged anions at the presence of hydrophobic ones, as well as to double-charged anions. If three octyl substituents in QAS molecule are replaced by methyl ones the exchange constant increases 20-30 times when the bromide-ion exchanges for picrate-ion, and 300-500 times when the double-charged cadmium bromide complex exchanges for picrate-ion.

The anion-exchanger concentration is shown not to influence strongly the exchange constants. It indicates that there is no either the extractant or compound formed in the organic phase self-association.

The values  $K_{2An^-}^{CdBr_4^{2-}}$  (where  $An^-$  is one of the next ions: chloride, iodide, thiocyanate, perchlorate) for QASes with three methyl substituents are comparable with corresponding values for QASes without such substituents. This fact can be used for the extraction and determination of cadmium.

Thus, the QASes of the asymmetrical structure with improved steric accessibility of the exchange centre show the high selectivity to double-charged cadmium bromide complex ions relative to single-charged ions.



# FUNCTIONAL ORGANOSILICA FOR CONCENTRATION AND SEPRATION OF MICROQUANTITIES OF METAL-ANALOGUE IONS

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Sorption activity investigation of multifunctional sorbents including on KU-2-8-ionite basis and amino acids as well as amorphous silica that have been modified with dimethylchlorosilane (K-7-30) are represent great interest. At the same time separation of element-analogues is based on their different possibility to hydrolysis and acid-basic properties of corresponding forms. It is known that simple oxyhydrated sorbents has graded these differences owing proceed of additional hydrolysis process of researched elements on the hydrated surfaces.

The purpose of these work are consist in comparative research of sorption properties unmodified aerosile A-300 and its modified analogue - K-7-30 for selective evolving of microquantities of *Al (III)*, *Ga (III)*, *In (III)* at consistent presence, as well as *Mo (VI)* and *W (VI)*.

There was studied dependence of sorption rate values of microamounts high listed elements from time of their contact with sorbents, pH media and means of equilibrium concentration. It is shown that owing to exchange of sorbents surface characteristics, its hydrating rate value and heterogeneity of sorbate and hydrolyzed forms of metals investigated interaction with surface can simultaneously proceed on several mechanisms. The contributions of various factors into adsorption of elements-analogues are depended from sorption conditions and nature of sorbent surface.

Sorption activity differences of listed elements on aerosile A-300 and K-7-30 have been established depending from pH media. It was marked that disparity of pH sorption optimum values ( $\text{pH}_{\text{opt}}$ ) is caused by changes of composition and structure of hydrated cover of sorbents. The presence of hydrated and a solvate surface layer on K-7-30 is the reason of differences at degree of hydrolysis of taken elements and composition of their hydrolyzed forms.

On basis of results obtained the possibility of separation of microquantities *Al* from *Ga* and *In* have been shown at pH 5 at the presence of ethanol, *Ga* and *In* at pH 2,5 at acetone presence and *Mo* and *W* at pH 6 at the presence of ethanol.

# CHEMICAL ANALYTICAL AND ADSORPTION PROPERTIES OF HYDRATED ALUMINA

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Hydrated alumina is one of the most widespread hydrophilic polar sorbents for concentration and separation of different substances. In water  $\text{Al}_2\text{O}_3$  shows cation or anion exchange properties and its protolytic and adsorption characteristics depend on a way of obtaining.

In the present work the acid-base surface properties of three  $\text{Al}_2\text{O}_3$  samples for a chromatography are investigated: acidic (I), basic (II) and neutral (III) ones with the using of heterogeneous titration of their suspensions by HCl and NaOH solutions. To establish the correlations between the acid-base and adsorption properties studied  $\text{Al}_2\text{O}_3$  the representatives of cationic dyes – diamond green (DG), fuchsine (F) and anionic dyes - eriochrom black T and chromic dark blue have been used.

It was noted that the content of functional groups on the surface of studied  $\text{Al}_2\text{O}_3$  was  $0,92 \cdot 10^{-4}$  mol/g of acid character for (I),  $1,08 \cdot 10^{-4}$  mol/g of basic character for (II). The total content of the groups of both types was  $1,70 \cdot 10^{-4}$  mol/g for (III). The absence of appreciable point deviations from a flat area of titration curves in all cases proves simultaneously charges neutralization character on the same adsorption centers and non-depending on their density. The isoelectric points of oxide surfaces have been determined from titration curves and have been confirmed by “drift” method.

The (I)-(III)-samples sorption ability investigation for cationic dyes microamounts has shown that for DG the maximum rate of extraction is within 70-90 % at pH 3. The isotherm of S-type proves the physical character of sorption process and a „seeming” ionic exchange. Maximal rate of F extraction for all samples was 40-60 % at pH 8 due to electrostatic forces. The anionic dyes have more significant affinity to surface researching  $\text{Al}_2\text{O}_3$ -samples comparatively with cationic. The forms of obtained sorption isotherms at  $\text{pH}_{\text{opt}}$  have mixed character of H,L-type: chemisorption mechanism of formation of a primary monolayer with the further bilayers formation due to H-bonds and hydrophobic interactions. The different values of  $\text{pH}_{\text{opt}}$  for sorbents and dyes confirm their multifunctional character and distinctions in the acid-base properties of adsorption centers.

# **SOLID-PHASE SPECTROPHOTOMETRIC METHOD FOR THE DETERMINATION OF ANIONIC SURFACTANTS WITHOUT LIQUID-LIQUID EXTRACTION**

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Large amounts of synthetic anionic surfactants have been used in industrial and domestic detergents. The main source of commonly used anionic surfactant sodium lauryl sulfate, viz., sodium dodecyl sulfonate, sodium hexadecyl sulfonate and sodium dodecyl benzenesulfonate (sulfanol), in water bodies are household commodities and personal care products, e.g., detergents, soaps, shampoos, fabric and cosmetic materials. Wide assortment and increase in production of anionic surfactants leads to increase of their content in environmental water. Synthetic anionic surfactants are toxic pollutants in natural water, it is necessary to determine these surfactants in water. Almost all methods for spectrophotometric determination of anionic surfactants are based on formation of ion associates with basic dyes or complex metal ions and their subsequent extraction into organic solvents. However analytical methods without using different organic solvents which combine ecological purity with high sensitivity and rapidity are most interesting. Methods with sorption preconcentration meet these requirements.

In this work hybrid method is suggested to determine anionic surfactants in waters. It is based on preconcentration of anionic surfactants as their ion associates with cationic dyes on the membrane filter and measurement of colour intensity by solid-phase spectrophotometry method. Effect of different basic dyes, nature and hydrophobicity of anionic surfactants, size of membrane filter pores, filtration rate on sensitivity of their determination was studied. Various cationic dyes, such as Methylene Blue, Crystal Violet, Malachite Green, Rhodamine 6G, Safranin T, Acridine Yellow were used as counter ions. The difference in reflection between the blank and the sample was significant when Crystal Violet or Rhodamine 6G or Acridine Yellow were used.

The lower limit of detection is  $1 \mu\text{g}/\text{dm}^3$  for sodium hexadecyl sulfonate,  $2.5 \mu\text{g}/\text{dm}^3$  for sodium dodecyl benzenesulfonate and  $10 \mu\text{g}/\text{dm}^3$  for sodium dodecyl sulfonate with sample volume of  $0.1 \text{dm}^3$ . The method proposed is highly sensitive, simple, rapid and guarantees environmental safety of analysis.

# METHODOLOGICAL ASPECTS OF CLOUD POINT PRECONCENTRATING OF MICRO-ADMIXTURES BY PHASES OF NON-IONIC SURFACTANTS

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The study of the mechanism of cloud point micellar extractions by phases of non-ionic surfactant (NS) is an aspect often disregarded in most literature reports and, thus, is of general interest. The effective application of the micellar extraction in the analysis is connected with the principled and the least studied problem about the influence of hydrophobicity, structure and substrate charge on the distribution between the water and non-ionic surfactant-rich phase.

The regularity of micellar extraction of large grope of organic reagents and their complexes with metal ions was investigated.

***Charge influence.*** The non-ionic surfactant-rich phase is able to extract high charged ions, in contrast to organic solvents. The tendency of a decrease in distribution coefficients with a simultaneous charge increase was observed. The difference between distribution coefficients when the electroneutral and monoanion forms are compared is greater in comparison with the transformation from a monoanion to a dianion or from a dianion to a three charged anion. The data obtained indicates the expediency of micellar extraction preconcentrating using the electroneutral molecular forms of microcomponents.

***Hydrophobicity influence.*** Despite of the diphilic character of the NS-rich phase the efficiency of micellar extraction raises with general substrate hydrophobicity increase. The hydrophobicity of ligand is the main factor, which determines the cloud point extraction of complexes.

***Structure influence.*** The specificity of interphase transfer in the micellar-extraction systems is the independent and cooperative influence of the substrate molecular structure ( ${}^1\chi$  - the first-order molecular connectivity indexes) and hydrophobicity ( $\log P$  - the distribution coefficient value in the water-octanole system) on its distribution between the water and the surfactant-rich phases. The possibility of substrates distribution and their D-values prediction in the cloud point extraction systems using regressions, which consider the  $\log P$  and  ${}^1\chi$  values was shown. Here the specificity of the micellar extraction is determined by the appearance of the host-guest phenomenon at molecular level and the high level of structural organization of the micellar phase itself.

# SOLID-PHASE EXTRACTION ON SIMULTANEOUS SPECTROPHOTOMETRIC DETERMINATION TRACE IONS IN WATER WITH 1-(2-PYRIDILAZO)-2-NAPHTOL

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Significant practical objective in analytical chemistry is control on contents of metal ions in various objects including natural. Effective method for practical uses is one of simultaneous determination of content of various metals in object, because it decreases time of analysis, quantity of reagents and probe.

In practice of simultaneous determination contents of metal ions in various objects reagent 1-(2-pyridilazo)-2-naphthol (PAN) is used widely. PAN as reagent for determination metal ions has row of preferences. PAN forms complex compounds with most of metals to be controlled. These complexes have high coefficients of absorption; each complex has a line of primary absorption, what make them appropriate for simultaneous determination. The complexes also possess high constants of stability that allows moving them from one phase to another without destruction including solid-phase extraction. The passing of the reaction of complex formation depends on pH of medium, therefore allocation of several groups of metal ions depend upon pH of formation is possible.

In this work analytical procedure combines solid-phase extraction and spectrophotometric determination. Higher coefficients of concentrating in solid-phase extraction in comparison with liquid extraction make first to be perspective. The procedure of concentrating analytical form of determining elements was developed. Dependence of desorption complex compounds from silica-gel surface was investigated for a row of organic solvents including mixible with water. The procedure of sorption complexes of metals from water and one of forming complexes on silica-gel surface with uncovalent immobilized reagent were tried. First procedure was chosen.

The results of the analysis of the row of model mixtures of elements having been investigated are shown. These results allow thinking that limit of determination lays at range of  $(2-5) \cdot 10^9$  mol/l.

# **MICROWAVE-ASSISTED SOLVENT EXTRACTION AND A NEW METHOD FOR ISOLATION OF TOTAL PETROLEUM HYDROCARBONS (TPH) FROM PLANTS WITH COLUMN CHROMATOGRAPHY (SILICA GEL AND ALUMINA) AND DETERMINATION WITH SPECTROFLUOROPHOTOMETRY**

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The efficiencies of total petroleum hydrocarbons (TPH) transfer into various solvents from plants by microwave enhanced process were extracted.

Microwave extraction realized at 120 °C for 30 min with Hexane – Acetone (3:2 V/V) as the extraction solvent was identified as the most effective extraction procedure for isolation of TPH from biotic matrices. The aim of this research is to develop a silica gel and alumina fractionation procedure for plant sample extraction. Column chromatography with two solvents (chloroform and hexane: dichloromethane) as a mobile phase were used for clean-up of extract. In this research the efficiency of recovery received from chloroform as a mobile phase.

With this mobile phase colour compounds and carotenoids separated with 15 ml of chloroform (first fraction) and the second fraction with 20ml chloroform contained total petroleum hydrocarbons. At the end Spectrofluorophotometry was employed for quantification of analytes.

# EXPERIMENTAL DESIGN APPLIED TO THE OPTIMIZATION OF A DISTILLATION PROCESS FOR FLUORIDE DETERMINATION IN ANHYDRITE

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Fluorine is a small atom with a large ego. Fluorine has a high electronegativity so it makes it very reactive, bonding with a great number of atoms.

Fluoride production consists on reacting fluorspar mineral ( $\text{CaF}_2$ ) with  $\text{H}_2\text{SO}_4$  (cc) to form HF and calcium sulphate. However, reactions do not achieve 100 % yield, so fluorogypsum or anhydrite ( $\text{CaSO}_4$ ) obtained contains small amounts of fluoride as  $\text{CaF}_2$  in its structure. The application of this kind of subproduct is well-known as construction material, so that the fluoride content has to be controlled.

Fluoride analysis requires a previous separation process step, which is known as Willard-Winter distillation using a mixture of  $\text{HClO}_4/\text{H}_3\text{PO}_4$ , to isolate fluoride from interferences like: Al, Cl, etc.

The aim of this work is the optimization of distillation process using  $\text{H}_2\text{SO}_4$  for fluoride separation and potentiometric determination in anhydrite samples by means of chemometric tools.

A full factorial design was used to determine the main factors which affect fluoride recovery in the distillation process. Anhydrite amount, volumes of  $\text{H}_2\text{SO}_4$  and distillate were studied, being the first two variables the most significant. Therefore, the analytical conditions obtained with these variables were applied in a central composite design. The results showed that anhydrite amount was the most influent factor in the fluoride distillation process. The application of the optimal experimental conditions gave good results using  $\text{H}_2\text{SO}_4$ , compared with the recovery of fluoride obtained using a mixture of mineral acids in the distillation process.

The fluoride amount recovery by Willard-Winter distillation process using a mixture of mineral acids (50 % v/v) was  $3.2 \pm 0.1$  % F. The new analytical conditions using  $\text{H}_2\text{SO}_4$  obtained from the chemometric study gave the result of  $3.3 \pm 0.2$  % F.

Therefore, the use of  $\text{H}_2\text{SO}_4$  during Willard-Winter distillation process is able to separate fluoride from the anhydrite matrix, with the additional advantages such as economy, security and environmental benefits.

## SEPARATION OF PLASTID PIGMENTS BY THIN LAYER CHROMATOGRAPHY

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In the course of an investigation on plastid pigments, a rapid technique for separation of small quantities of these pigments was needed. A search of the literature revealed a lot of paper on the application of thin layer, column, HPLC and paper chromatography for the separation of plastid pigments from various biological materials, but it is not applied to our investigated biological material. That's why it was worked out rapid technique for thin layer separation of these pigments.

Plastid pigments were received by extraction and crystallization. Crystals of these pigments were dissolved in suitable solvent.

It was used 200×200 mm plates of "Silufol UV 254" as a fixed layer. Unfixed layer "Silica gel LC 5/40 μ" was spread on the 200×200 mm glass plates.

Chromatography was carried out by following solvent mixes:

- 1) chloroform – ethyl alcohol (9:1);
- 2) chloroform – ethyl alcohol (19:1);
- 3) benzene – ethyl acetate (7:3);
- 4) chloroform – ethyl alcohol (20:1);
- 5) chloroform – ethyl alcohol (40:1);
- 6) chloroform;
- 7) hexane;
- 8) chloroform – ethyl alcohol – hexane (20:1:10);
- 9) chloroform – ethyl alcohol – hexane (20:1:20);
- 10) chloroform – ethyl alcohol – hexane (20:1:30);
- 11) chloroform – hexane (1:1);
- 12) chloroform – hexane (1:5);
- 13) chloroform – hexane – ethyl alcohol (20:100:1).

The best separation of plastid pigments were received chloroform – hexane – ethyl alcohol (20:100:1) solvent mix.

It was separated five pigments:  $R_{f1} = 0.08$  (orange – yellow zone),  $R_{f2} = 0.23$  (red zone),  $R_{f3} = 0.31$  (yellow zone),  $R_{f4} = 0.43$  (light yellow zone),  $R_{f5} = 0.86$  (red-brown zone). The last zone corresponds to zone of beta-carotene. Other pigments were not yet determined.



# THE USE OF ORGANOSILICON ION-EXCHANGE AND COMPLEXING ADSORBENTS IN ANALYSIS OF NATURAL OBJECTS

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The long and systematic investigations of the present authors have resulted in the creation of organosilicon adsorbents, ionites and complexing agents. The wide series of such sorption materials were synthesized with such ionogenic and complexing groups as -SH, -S-, -SS-, -SO<sub>3</sub>H, NHC(O)CH<sub>3</sub>, -NHC(S)CH<sub>3</sub>, SCH<sub>2</sub>COOH, -S(CH<sub>2</sub>)<sub>2</sub>NH<sub>2</sub>, -S(CH<sub>2</sub>)<sub>2</sub>S, -NHC(O)NH-, -NHC(S)NH-, -NH-NHC(=S)S<sup>+</sup>NH<sub>3</sub>, -NHC(=NH)NHC(=NH)NH<sub>2</sub> etc.

These adsorbents have cross-linked silsesquioxane structure. They are stable up to 230-270°C and do not lose their sorption activity in 10-18 M H<sub>2</sub>SO<sub>4</sub> at 100°C in boiling concentrated hydrochloric acid.

Ion-exchange and complexing properties of organosilicon adsorbents were studied on the example of 50 elements of Periodical System. Among synthesized adsorbents it was found an effective complexation agents toward rare-earth elements. The sorption of elements is accompanied by bright display of tetradic effect. Adsorbents were synthesized, which opened wide chances of sorption isolation and division of rare-earth elements.

In addition the very effective adsorbents for noble metals have been obtained. Their high sorption capacity (SSC) and coefficients of interphase distribution (D) are evidence availability of their use for concentration and isolation the microquantities of these metals from natural and induced objects.

In the present time our organosilicon adsorbents found the practice application in such as fields such as, for example: 1) the method of spectral-chemical determination of gold Clarke quantities in poor ores and rocks has been applied in analytic practice of geological establishments and research institutes; 2) at the first time sorption process was used in hydro-chemical analyze of fresh water. This method has been allowed to analyze of Baikal water; 3) for purification metallurgical waters and waste solutions of chemical-metallurgical plants due to toxic elements; 4) for creation the filters for extraction of rare elements, for example, uranium; 5) for silver utilization from wasted of cinema-photo manufactory. This method has been applied to obtain the silver of high purity.

# ATOMIC ABSORPTION DETERMINATION OF Cu(II), Cd(II), Zn(II), Pb(II) USING PRECONCENTRATION BY SOLID-PHASE EXTRACTION ON PROPYLTHIOETHYLEAMINE MODIFIED SILICA

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The determination of heavy metals at trace levels is important in the field of environmental analysis. This problem can be solved by the help of highly selective sorbents.

Effective metal ion adsorbent has been prepared by the immobilization of propylthioethyleamine ligand onto the surface of silica gel (SN-SiO<sub>2</sub>). The effectiveness of this material to bind metal ions has been attributed to the complexation chemistry between the ligand and the metal. We are investigating properties of propylthioethyleamine grafted on the surface of silica and possibility of application of the obtained surface for preconcentration of heavy metals such as zinc, lead, cadmium, copper, etc. from water solutions.

The capacity factors of SN-SiO<sub>2</sub> for metal ions were determined under a range of different conditions of pH, metal ions concentrations and time of interaction. Preconcentration of Cd<sup>2+</sup>, Pb<sup>2+</sup>, Zn<sup>2+</sup> and Cu<sup>2+</sup> were used for their preliminary determination by flame atomic absorption spectroscopy. The optimum pH values for quantitative sorption are 5.8, 6.2, 6.5, 7.0 for Pb, Cu, Cd and Zn, respectively. The sorption ability of SN-SiO<sub>2</sub> to metal ions decrease in line: Pb>Cu> >Zn>Cd. The sorption capacity of the sorbent is 2.7, 7.19, 11.12, 28.49 mg·g<sup>-1</sup> for Cd, Zn, Pb, and Cu, respectively. The sorbent distribution coefficient calculated from sorption isotherms was 10<sup>5</sup> ml·g<sup>-1</sup> for studied cations. All these metal ions can be desorbed with 5 ml of 0.1mole·l<sup>-1</sup> HCl (sorbent recovery average out 96-100%).

The results of sorptional properties investigation have shown the possibility of SN-SiO<sub>2</sub> application for Pb<sup>2+</sup>, Cu<sup>2+</sup>, Zn<sup>2+</sup>, Cd<sup>2+</sup> selective preconcentration. The preconcentrated Cu, Pb, Cd, Zn ions at pH 6-7 were eluted by acid and determined by atomic-absorption method.

The method has been successfully applied to the analysis in drinking water. The results show sufficiently high recoveries.

# ANION-EXCHANGE EXTRACTION OF ZINC THIOCYANATE COMPLEXES BY NON-SYMMETRIC QUATERNARY AMMONIUM SALTS

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High tendency of  $Zn(SCN)_4^{2-}$  ion to extraction into organic phase is widely used for zinc determination by extraction photometry method. Recently it was shown that when single-charged anions are exchanged for double-charged ones, the selectivity of this process depends on the number of methyl substituents in quaternary ammonium salt (QAS) cation.

In this work, the results of study of zinc thiocyanate complexes anion-exchange extraction by non-symmetric QASes in toluene are discussed. The non-symmetric QASes have the common formula  $[(C_{43}H_{79}O_3)_nN(CH_3)_n(C_8H_{17})_{3-n}]^+X^-$ , where  $C_{43}H_{79}O_3$  – highly lipophilic substituent, (2, 3, 4-*tris*-dodecyloxy)benzyl. It was found that exchange constants  $K_{2Pic^-}^{Zn(SCN)_4^{2-}}$  increase in the following sequence: trinonyloctadecyl ammonium > dimethyl QAS > trimethyl QAS > monomethyl QAS. Thermodynamic exchange constants of zinc thiocyanate complexes by different QASes in toluene are given in the table below.

QAS type	$K_{2Pic^-}^{Zn(SCN)_4^{2-}}$
TNODA	$(2.12 \pm 0.43) \cdot 10^4$ (n=8, $\alpha=0.95$ )
TDDBTMA	$(5.64 \pm 0.54) \cdot 10^3$ (n=8, $\alpha=0.95$ )
TDDBDOMA	$(4.00 \pm 0.55) \cdot 10^3$ (n=8, $\alpha=0.95$ )
TDDBTOA	$(2.56 \pm 0.23) \cdot 10^3$ (n=8, $\alpha=0.95$ )

The correlation found is substantially different from one that is observed in case of exchange of single-charged anions for small doublecharged ones. In the latter case, the exchange constants regularly increase with the number of methyl groups at the nitrogen atom. The results observed are interpreted in terms of peculiarities of exchange center steric accessibility influence on QAS cation association constants with single-charged and double-charged anions, depending on the size of exchanging anions. The results obtained allow us to recommend the most sterically hindered QASes as the most promising extractants for zinc thiocyanate complexes.

# THE CLOUD-POINT EXTRACTION OF ALIPHATIC AMINES INTO THE NON-IONIC SURFACTANT-RICH PHASES

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Micellar extraction based on the phase separation at cloud point temperature of the non-ionic surfactants (NS) solutions is considered lately as a convenient and environmentally safe alternative to extraction with organic solvents. The simplicity of combination of cloud point extraction with different detection methods allows the usage of micellar extraction for elaborating of high-sensitive hybrid analytical methods. But despite of the availability of extensive evidence in this area, the influence of substrate's hydrophobicity and structure on the distribution between NS-rich and water phases is not yet investigated. Organic amines are suitable and convenient group of compounds for this problem solving.

The interphase distribution of aliphatic ( $n=4-9$ ) and some aromatic amines in micellar-extraction system based on the non-ionic surfactant OP7 at cloud point temperature was investigated. The distribution of amines was controlled by pH-metric titration of the water solution or the NS-phase. From the data obtained the extraction degree and the distribution coefficients ( $D$ ) of amines in water - NS-phase system were calculated. It was shown that with OP7 concentration increase the extraction degree of amines raises. Analogously to traditional extraction with organic solvents the  $\lg D=f(n)$  correlation is close to linear. The increments of the methylene and amine groups into the distribution coefficient value were calculated and compared with corresponding increments for different water-organic extraction systems.

On the basis of data obtained the possibility of substrates distribution and their  $D$ -values prediction using the regressions which consider the hydrophobicity and structure of amines was investigated. The hydrophobicity of amines was estimated by the distribution coefficient value in the water-octanole system ( $\lg P$ ). The molecular structure of aromatic amines was characterized by the first-order molecular connectivity indexes ( ${}^1\chi$ ). It was shown the independent and cooperative influence of the  $\lg P$  and  ${}^1\chi$  parameters of amines on their distribution. Evidently, this fact demonstrates the "host-guest" phenomenon which is inherent to the organized media. The obtained in the research data were used for optimization of the conditions of micellar-extraction preconcentrating of metal ions with amines into the NS-rich phase with the following determination by atomic-absorption method.

# CHARACTERISTICS OF SORPTION OF MOLYBDENUM, TUNGSTEN AND VANADIUM ON CHEMICALLY MODIFIED SILICA GELS

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In the recent years intensive studies related to modification of silica with organic compounds of various chemical nature have being conducted in order to concentrate selectively metal ions from solutions and then to perform their analytical determination directly in the sorbent phase, or after that, to elute with appropriate reagents in solution.

In order to determine the concentration of molybdenum (VI), tungsten (VI) and vanadium (V) the reagents of triphenylmethane series, in particular brompyrogallolic red (BPR) and pyrogallolic red (PR) are widely used.

We have performed fixation of these reagents on the surface using silica gels with 3-aminopropyl and ethylenediamine groups covalently bound to SiO<sub>2</sub> surface. This fixation is realized due to acid-base interaction between aminogroups of the silica gel surface and sulfonate groups of the dyes. Such fixing on SiO<sub>2</sub> surface BPR and PR does not lead to significant changing their analytical properties as their complexing centers (o-oxyquinone groups) remain unchanged.

Comparison of electronic absorption spectra of BPR and PR in solution with electronic absorption spectra of BPR and PR on NH<sub>2</sub>-S and en-S surfaces has been made. In contrast to aqueous solutions, where shift of the absorption maximum of dyes is occurred when pH is changed, significant shift of maxima is not observed on aminosilica gels surface during pH changing. Both reagents BPR and PR have an absorption maximum in the field of 17900-18100 cm<sup>-1</sup> at different pH values. However use of BPR is more preferable than that of PR as qualitative sorption of BPR occurs at wider pH range.

Sorption processes of complexes of Mo(VI), W(VI) and V(V) with BPR as well as these complexes in the presence of dodecylpyridinyl chloride from aqueous solutions on aminosilica gels surfaces have been considered. The presence of dodecylpyridinyl chloride increases significantly the sorption degree of metals and broadens pH range of their quantitative extraction.

Electronic absorption spectra of metals sorbed on NH<sub>2</sub>-S surfaces in the presence of BPR have a maximum in the field of 19000 cm<sup>-1</sup>-18000 cm<sup>-1</sup>, adding of DPC to the solution leads to forming complexes, which is characterized by bathochromic shift to the range of 17000-16000 cm<sup>-1</sup>. Thus the absorption maximum is shifted bathochromically by 50-70 nm.

# SEPARATION TECHNIQUES IN DETERMINATION OF ALKYLPHOSPHONIC ACIDS

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Analysis of alkylphosphonic acids is a topical question for environmental protection since they are important degradation products of nerve agents as well as chlorovinylarsonous acid and lewisite oxide are the degradation products of lewisite. In order to achieve adequate verification, reliable and sensitive procedures are necessary, commonly based on versatile analytical instrumental methods. There are only a few reviews concerning modern separation techniques in the determination of chemical warfare agents and their degradation products [1, 2]. Analysis of the derivatives in aqueous and/or environmental matrixes is challenging. They are nonvolatile compounds; therefore, the derivatization procedure for gas chromatography (GC) is required. In the past decade, and capillary electrophoresis (CE) has generated considerable interest because relatively simple and inexpensive instrumentation can be used to create fast and highly efficient separation. Since the degradation products have no chromophoric groups, the CE-UV detection is problematic and usually the indirect detection was used.

The recent development and comparative application of modern separation techniques with regard to determination of alkylphosphonic acids and lewisite derivatives have been demonstrated. This report highlights advantages and shortcomings of GC equipped with mass spectrometry detector and HPLC as well as CE with UV-Vis detector. The comparison was made from the sampling point of view and separation/detection ability. The derivatization procedure for GC of main degradation products of nerve agents to determine in water samples was applied. Direct determination of lewisite derivatives by HPLC-UV was shown. Also optimization of indirect determination of alkylphosphonic acids in CE-UV was developed. Finally, the new instrumental development and future trends will be discussed.

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## ION EXCHANGE DETERMINATION OF TRANSURANIUM ELEMENTS CONTENT IN ENVIRONMENT OBJECTS

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The radioecological monitoring of a surrounding medium provides determination of the contents and densities of all spectrum of radionuclides do not dependent on a radiant of their receipt. The determination of the contents long-lived, alpha-emitting radionuclides <sup>238</sup>Pu, <sup>239+240</sup>Pu, <sup>241</sup>Am and <sup>244</sup>Cm in plants of a surrounding medium is one of major problems in rehabilitation of territories contaminate as a result of emergency on Chernobyl NPP.

In the report the radiochemical procedure of simultaneous selection of <sup>238,239,240</sup>Pu, <sup>241</sup>Am and <sup>244</sup>Cm from one sample for determination radionuclide of a composition of contaminating is submitted.

The procedure provides pre-concentration and separation <sup>238,239,240</sup>Pu, <sup>241</sup>Am and <sup>244</sup>Cm by anion exchanger column AV-17 in NO<sub>3</sub><sup>-</sup> form and cation exchanger column KU-2-8 in NH<sub>4</sub><sup>+</sup>-form, Pu, Am, and Cm elutriated step-by-step by 2-hydroxy-*iso*-butyric acid with pH 4,75. The separation of <sup>241</sup>Am + <sup>244</sup>Cm and rare earth elements is carried out on a cation exchanger column KU-2-8 in H<sup>+</sup>-form by strip saturated HCl containing 20 % C<sub>2</sub>H<sub>5</sub>OH.

The chemical yield of plutonium determined on tracer <sup>236</sup>Pu or <sup>242</sup>Pu, makes of 60 -70 %, americium and curium, determined on tracer <sup>243</sup>Am makes 50 - 70 %.

At development of a procedure for optimization of requirements of selection of plutonium and the determinations of stages on which occur losses of plutonium used gamma-emitting isotope of plutonium <sup>237</sup>Pu. In the report the data's on losses of plutonium at all stages of radiochemical selection are reduced.

This procedure has been applied to thousands soil and sediment samples and hundreds biological and water samples taken in the exclusive zone of Chernobyl NPP and different regions of Ukraine. The methods developments are described.

Advantages, difficulties and limitations of the method are discussed.

**EFFECTS OF AMINES IN OXIDATION OF HYDROQUINONE  
WITH HYDROGEN PEROXIDE CATALYZED BY COPPER(II)  
IN THE PRESENCE OF MALONONITRILE CARRIED OUT  
ON PAPER FILTERS WITH CHEMICALLY ATTACHED GROUPS**

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Activating and inhibiting effects of amines in oxidation of hydroquinone with  $H_2O_2$  catalyzed by Cu(II) in the presence of malononitrile carried out on filter paper with chemically attached hexamethylenediamino groups (HMDA-filters) were investigated. Copper(II) was preconcentrated from aqueous solution by pipetting or pumping copper-containing solution on or through HMDA-filter (Cu-HMDA-filter). The catalytic reaction was monitored by measuring of reflection of wet filters at 525 nm. The effect of amine in the indicating reaction depends on the ratio Cu: amine on the filter; structure of amine and the type of sorbent. Many investigated amines (triethylamine,  $\alpha$ -,  $\beta$ -,  $\gamma$ -picolines) have got activating action at the ratio Cu : amine =  $1000 \pm 10$  (the range  $10^{-12}$ – $10^{-10}$  mmol on the filter).  $\alpha$ -Picoline activates indicating reaction carried out on Cu-HMDA-filters at the range  $10^{-9}$ – $10^{-3}$   $\mu$ mol, and  $\gamma$ -picoline only inhibites at same conditions ( $10^{-12}$  –  $10^{-1}$   $\mu$ mol). Different effects of diamilamine in the reaction carried out on filter paper and HMDA-filter were observed: inhibiting on filter paper and activating on HMDA-filter.



## DEVELOPING SAMPLE PREPARATION AND DETERMINATION OF TOTAL IODINE IN COMPLEX ORGANIC MATRIX

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Sample decomposition is the critical operation in determination of total iodine in complex organic matrix. Iodine in simple form ( $I_2$ ) is highly volatile, so it should be transformed into nonvolatile analytical form (iodide or iodate) to prevent losses during the decomposition.

Some experimental and literature data of sample preparation were discussed:

- 1) dry alkaline ( $KOH$  or  $K_2CO_3 - ZnSO_4$ ) digestion in oven with the next water extraction in form iodide;
- 2) combustion in oxygen atmosphere in closed autoclave;
- 3) wet digestion acid-oxidant or acid mixture ( $H_2SO_4 - K_2Cr_2O_7$ ,  $H_2SO_4 - HNO_3 - HClO_4$  or  $HClO_3 - HNO_3$ ).
- 4) extraction of iodine by hydroxide tetraalkilamonium. Method used for determination iodine in dietary products fortified by Iodine.
- 5) wet digestion ( $HNO_3$  - microquantity of  $HClO_4$ ) under microwave treatment.

The methods 1- 4 of sample preparation are classics. As a rule they give a high value of blank and some of them take a lot of time. Microwave sample preparation is perspective, more convenient and much more faster procedure than classical mineralization. There are some problems with the combination Cendall-Kolthoff's kinetic method and microwave sample preparation which discussed. The experimental data of different complex organic matrix are demonstrated (food products on fat, peptides, hydrocarbone matrix, urine etc).

# EXTRACTANT CONCENTRATION GRADIENT IN THE AMERICIUM(III) / CURIUM(III) SEPARATION BY COUNTERCURRENT CHROMATOGRAPHY

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Modern strategy for the management of high-level liquid nuclear wastes (HLLW) arising from reprocessing of spent nuclear fuels includes the partitioning of minor actinides (Am, Cm and Np) and some fission products, followed by their immobilisation in a solid matrix (e.g. glass, mineral, ceramic) or their transmutation into shorter lived or stable isotopes before storage.

Solvent extraction of long-lived transplutonium elements, particularly Am and Cm, from HLLW, is primarily based on two classes of compounds:

- (i) acidic and neutral organophosphorus reagents and,
- (ii) amidic extractants. Close values of the distribution ratios of Am(III) and Cm(III) in the above mentioned systems make it difficult to separate these elements without a multi stage methods. One of them is the Countercurrent Chromatography (CCC).

Separation of Am(III) and Cm(III) from aqueous acidic nitrate media by CCC using two different extraction systems have been studied:

- (i) “diamide - hydrogenated tetrapropylene (TPH) -  $\text{HNO}_3$ ” (pentaalkyl propanediamides (malonamides) are bifunctional extractants with the general formula  $\text{RR}'\text{-N-C(O)-CHR}''\text{-C(O)-NRR}'$ , where R and R' are alkyl groups and R'' is an alkyl or oxyalkyl group),
- (ii) “tri-*n*-oktylphosphine oxide – phenylmethylbenzoylpyrazolone-5 – cyclohexane -  $\text{HNO}_3$ ”.

The acceptable separation of Am(III) and Cm(III) by countercurrent chromatography (CCC) was achieved using both isocratic elution, and a new approach to the creation of the reagent concentration gradient in the stationary phase [1]. This way allows reduce the experiment length.

It is shown that these liquid systems and different experiment modes can be used for the effective separation of Am(III) and Cm(III) by CCC.

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# MEMBRANE EXTRACTION AND SEPARATION OF COPPER(II) FROM PLATINUM(IV) BY DI(2-ETHYLHEXYL)PHOSPHORIC ACID DURING ELECTRODIALYSIS

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Membrane extraction is a promising technique for removal and separation of valuable and toxic metal ions. Di(2-ethylhexyl)phosphoric acid (D2EHPA) is widely used for copper(II) removal from neutral and weakly acidic solutions by liquid membranes. Application of a direct electric field significantly intensifies the transport of ions through the liquid membranes and facilitates the stripping of metals from the organic phase. The aim of the present work is to study the membrane extraction of copper(II) from binary hydrochloric mixtures with platinum(IV) by bulk liquid membranes of D2EHPA – dichloroethane with tri-n-octylamine (TOA) admixtures under conditions of galvanostatic electrodialysis.

The experiments were carried out in a five-compartment cell:

(+) Pt, H <sub>2</sub> SO <sub>4</sub>	CuCl <sub>2</sub> H <sub>2</sub> PtCl <sub>6</sub>	D2EHPA, TOA 1,2-dichloroethane	HCl	H <sub>2</sub> SO <sub>4</sub> , Pt (-)
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The liquid membrane (thickness 0.2 cm) was separated from the aqueous solutions by two vertical cellophane films. The electrode compartments were filled with 0.05 M sulfuric acid solutions and were separated by the solid anion-exchange membranes MA-40. Binary mixtures contained, as a rule, 0.04 M Cu(II) and 0.018 M Pt(IV) in 0.01 M HCl. 0.1 M HCl was used usually as the strip solution.

The copper(II) flux is directly proportional to the current density up to 10 mA/cm<sup>2</sup>. The extraction degree of platinum(IV) into the strip solution is less than 0.1% per hour of electrodialysis. About 55% of copper(II) is removed from the feed solution under optimal conditions. The copper(II) extraction process is characterized by high selectivity. Maximum separation factor  $\beta_{\text{Cu/Pt}}$  exceeds 900 in the studied system.

The copper(II) transport rate increases, as a rule, as Cu<sup>2+</sup> initial concentration in the feed solution increases. The increase of the carrier's concentration from 10 to 30 vol.% results in a decrease of both metal fluxes and in an increase of Cu<sup>2+</sup> transport selectivity. The increase of TOA concentration in the liquid membrane up to 0.1 M leads to a reduction of the copper(II) flux, and the platinum(IV) flux increases as  $C_{\text{TOA}} > 0.2$  M. Composition of the strip solution (HCl, H<sub>2</sub>SO<sub>4</sub>, HNO<sub>3</sub>, HClO<sub>4</sub>, H<sub>2</sub>O) does not exert significant influence on the transport of extracted components through the liquid membranes at electrodialysis.

# SOLID PHASE EXTRACTION AND DETERMINATION OF TRACE AMOUNT OF $\text{Co}^{2+}$ BY MODIFIED ANALCIME ZEOLITE WITH A NEW SCHIFF-BASE LIGAND

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The Schiff bases derived from salicylaldehydes polydentate ligands are known to form very stable complexes with transition metal ions [1].

In order to one of the most effective separation and preconcentration procedure in trace metal analysis is solid phase extraction (SPE) of analyte.

The methods which involve complexation of the metal ion with chelating agents followed by adsorption on a solid phase such as octadecylsilane (ODS) [2], Zeolite [3] or activated carbons [4] have been reported.

In this work, a simple, rapid and sensitive Flame Atomic Absorption Spectrometry (FAAS) method has been developed for the determination of trace amount of  $\text{Co}^{2+}$  in various samples after adsorption of its complex on modified Analcime using a Schiff base Bis-[(2,2'-dihydroxy)-N,N'-diethylenetriamino-1,1'-naphthalidimine] by column method in the pH range (4-7) at flow rates  $1 \text{ ml}\cdot\text{min}^{-1}$ .

The influence of flow rates of eluent and sample solution, amount of ligand, types and least amount of eluent for elution of Cobalt ion from column were investigated.

The effects of various cationic interferences on percent recovery of Cobalt were studied. The method was successfully applied for the determinations of Cobalt ion from synthetic and water samples.

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# USING OF THE MICELLAR MEDIUM, BASIC DYES AND PRECONCENTRATION ON THE POLYURETHANE FOAMS FOR THE DETERMINATION OF PHOSPHORUS AND ARSENIC

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Ionic associates (IA) of polyoxometalates (POMs) with threphenylmethane dyes remain as perspective analytical forms for the determination of some nonmetals including P(V), As(V) and Si(IV). Several reasons hinder to the improvement of analytical characteristics of these reactions. Separation of dye excess and its IA with reagent are most important. Procedure for extractive separation is often timeconsuming, complex and does not allow complete separation from reagent excess.

IA of POM  $\text{AsMo}_{10}\text{W}_2\text{O}_{40}^{3-}$  with crystal violet (CV) in presence on nonionic surfactant were used for As(V) determination. Using of molybdo-tungsten POMs instead of molybdenum is advantageous due to their higher stability. Decrease in the reagent concentration and consequently in the blank absorbance become possible. In micellar medium spectrum of CV is slightly changed. At the same time spectrum of IA significantly differs from dye spectrum. In presence of nonionic surface-active substances most part of free dye is discolored. In optimal conditions of the method 0,07-0,7  $\mu\text{g/l}$  of As(V) can be determined.

Adsorption of IA of POMs with CV and Malachite Green (MG) on the polyurethane foams (PF) and some other adsorbents is investigated. While IA is fully adsorbed on the PF in wide pH range (0,4 M  $\text{H}_2\text{SO}_4$  – pH 4) extent of dye adsorption does not exceed 0,4%. IA are adsorbed faster than POMs. Extent of sorption of IA is 60-70% at 5 minutes and is complete after 15 minutes. IA can be eluted from PF most effectively by methylbutylketone, acetone or alcohols can be used too.

Test method using IA with MG and spectrophotometric procedure were developed for the phosphate determination. Test method allows determination of P(V) in the 10-100  $\mu\text{g/l}$  concentration range. Spectrophotometric procedure able to determining lower than 3  $\mu\text{g/l}$  P(V) was used for determination in waters.

# COMPARISON FOR SEPARATION OF AMINO DERIVATIVES OF 3-CHLORO-1,4-NAPHTOQUINONE BY RP-HPLC WITH METHANOL AND ACETONITRILE ELUENT

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Early [1, 2] it was reported about RP-HPLC the separation of amino derivatives of 3-chloro-1,4-naphtoquinone with methanol mobile phase. In some cases changing organic modifier in eluent leads to the progress in effectiveness of separation. In present work the comparison was performed for separation of some amino derivatives of 3-chloro-1,4-naphtoquinone by RP-HPLC with methanol and acetonitrile eluent. It has been shown that certain differences exist for various derivatives mentioned above.

Experimental part was provided by device Model Knauer-Compact with UV-detector ( $b=3$  mm) at 250 nm and column Spherisorb-ODS-2 (250×4,6 mm). Sample volume was 1-2  $\mu$ l injected by Reodyne 7725. Concentration range was 0.4-0.5 mg/ml for solutions of studied substances in DMSO. The organic modifier concentration range was 75-85 % w for methanol and 40-60 % w for acetonitrile in eluent (flow rate -1 ml/min).

Generally it was found that resolution  $R_s$  is practically the same for isoeluotropic mixtures methanol and acetonitrile with water. The dependencies were obtained between capacity factors for derivatives of 3-chloro-1,4-naphtoquinone at their retention with methanol and acetonitrile. Previous prediction of RP-HPLC behaviour of the compounds was made by ChromDream software. Some complications are observed at weak acetonitrile eluent with 40 % w content when for some substances the existence of peak bifurcation.

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# SELECTION OF CONDITIONS OF SOIL MICROWAVE DECOMPOSITION FOR ICP-MS ANALYSIS

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Analysis of soils is an important task in the environmental researches. Reliability of ICP-MS results of soil analysis mainly depends on chemical sampling. Recently microwave systems are widely used for preparation of different samples. Influence of microwave radiation on sample ensures a complete decomposition of sample, greatly increases the mineralization, and allows possible losses of volatile elements to be minimized. In the given study to intensify decomposition of soils we applied the microwave sample preparation system MULTIWAVE (Anton Paar, Austria and Perkin-Elmer, USA) equipped with rotor from 6 autoclaves with TFM reaction chambers of 50 ml volume.

Conditions of microwave sampling were selected using soil reference materials P-1, SP-1, SP-3, PKP, PDPV (Russia).

Chemically high purity hydrofluoric acid and nitric acid twice distilled and ultra pure water produced by Elix-3/Milli-Q purification system (Millipore, France) were used. Two techniques of microwave decomposition were investigated: first – one-stage (sample with HNO<sub>3</sub> and HF mixture was heated in the microwave oven for 15 min at power 1000 W); second – two-stage (at first step sample was treated with HNO<sub>3</sub> and heated for 10 min at 700 W, at second step HF was added and vessels were heated at 1000 W for 20 min). Then solutions obtained were transferred into PTFE vessels and evaporated on a hot plate in order to remove matrix. Acidity of the analyzing and calibration solutions was adjusted with HNO<sub>3</sub> to 2 %. Thermal acid decomposition was used as a control technique. The influence of a preliminary burning of samples on results was estimated by analysis of samples prepared with burning under 500 °C and without burning.

HR-ICP-MS ELEMENT-2 (Finnigan MAT, Germany) equipped with a standard introduction system (quartz water-cooled spray chamber, concentric nebulizer, torch with 1.5 mm i.d. injector and nickel cones) was used for measurements. The following operating conditions were used: RF power 1150 W, coolant gas flow rate 16 l min<sup>-1</sup>; auxiliary gas flow rate 0.85 l min<sup>-1</sup>; nebulizer gas flow rate 1.2 l min<sup>-1</sup>. Sample uptake rate was 0.8-1 ml min<sup>-1</sup>. Measurements were performed with low and middle resolutions. Rh was used as an internal standard. For calibration working standard solutions were prepared by diluting the multielemental stock solutions CLMS (SPEX, USA) with water to concentration range from 5 ng l<sup>-1</sup> to 5 µg l<sup>-1</sup>.

Comparing results obtained by concerned decomposition techniques with the data certified (recommended), the two-stage microwave sample preparation procedure is preferable.

# SYNTHESIS, RESEARCH AND APPLICATION OF CHITINCONTAINING SORBENTS

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Last years the concern of the scientists and contributors to chitin, chitosan and chitincontaining connections has increased. It is connected to their widespread occurrence in the nature, particular properties, and also feasibility in many areas of a national economy. The raw sources for obtaining chitincontaining of products are the testas of crabs, lobsters, shrimps, and also cabbage-weeds, funguses.

On department of chemistry of the Cherkassk state technological university the secure ecological way of obtaining chitincontaining of sorbents (ChCS) from fungus mycelium of *Aspergillus niger* – the waste of production of citric acid are developed, which one differs by “soft” conditions of processing of an initial biomass. The aim of our work was analysis of the physico-chemical characteristics ChCS and also their sorbate properties in relation to ions of heavy metals.

Element structures of chitincontaining sorbents are determined using standard methods. Behind the data of an element structure the contents of chitin in ChCS was calculated. The analysis of morphological frame of ChCS was conducted by a electron-microscopic method on a raster supermicroscope at increase from 500 up to 1000 times. For matching is samples ChCS were conducted IR research in the field of 400 - 4000  $\text{cm}^{-1}$ .

The sorption of ions of heavy metals (Cu(II), Zn(II), Cr(VI), Cd(II), Pb(II)) on ChCS in static and dynamic conditions were studied. For an estimation of selective sorbate ability ChCS the distribution factor was determined. Sorption, physical and chemical properties of complexes received by different methods were analyzed by a comparative method.

The effect of a way of obtaining ChCS, time of realization of a sorption, temperature of a sorption, density and pH of sorbate on process of a sorption was studied. It is established, that chitincontaining sorbents are strong at  $\text{pH} \leq 5$  and are capable for effective heavy metals ions absorption from acid water solutions.

In conditions of a dynamic sorption the calculation of parameters sorbate pillars was conducted at usage initial curve in co-ordinates  $C/C_0 - f(t)$ .



## SEPARATION OF HEAVY METALS IN AQUEOUS SOLUTIONS BY A NEW ION EXCHANGER BASED ON CELLULOSE

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A new ion exchanger based on cellulose was synthesized by esterification of hydroxyethyl cellulose with 1,2,3-propane tricarboxylic acid. Ion exchanger characteristics such as swelling percentage (19.8 %), ion exchange capacities ( $3.3 \text{ meq}\cdot\text{g}^{-1}$  as wet and  $4.1 \text{ meq}\cdot\text{g}^{-1}$  as dry) and chemical stability were determined. The effect of pH on the ion exchange capacity was investigated. The exchange capacity was attained a maximum value at pH 6. In order to determine the chemical structure of the synthesized resin, degree of substitution (252.4), acid and hydroxyl values (78.5 and 178.2) were determined. The ester value (173.9) was calculated by means of acid value and degree of substitution.

Sodium trimetaphosphate was used as an eluting agent for the removal of heavy metals such as Pb, Cd, Co, Cu, Fe, Ni, Zn and Cr from aqueous solutions. Distribution coefficients of these elements have been determined regarding five different concentrations of sodium trimeta phosphate ( $3\cdot 10^{-3} \text{ M}$ ;  $5\cdot 10^{-3} \text{ M}$ ;  $0.01 \text{ M}$ ;  $0.05 \text{ M}$ ;  $0.1 \text{ M}$ ) on this resin. By considering these distribution coefficients, the separation of heavy metals has been performed using a concentration gradient of  $3\cdot 10^{-3}$  -  $5\cdot 10^{-3} \text{ M}$  sodium trimetaphosphate. Qualitative and quantitative determinations were realized by ICP-AES.

It has been seen that this resin has also some important advantages over the other resins in the literature like high total ion exchange capacity, easy synthesis, lower cost, simple regeneration. Furthermore, very good separations were obtained using a concentration gradient of elution. In these elutions, very low concentrations of sodium trimetaphosphate were used. As a result, the resin synthesized can be used as an adsorbent for the effective removal of Pb, Cd, Co, Cu, Fe, Ni, Zn and Cr from aqueous solutions.

# COMPARISON OF MICROWAVE ASSISTED EXTRACTION METHODS FOR THE DETERMINATION OF PLATINUM GROUP ELEMENTS IN SOIL SAMPLES BY ELECTROTHERMAL ATOMIC ABSORPTION SPECTROMETRY AFTER PHASE SEPARATION-EXTRACTION

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Elemental analysis of organic and inorganic samples requires partial or total dissolution of the sample prior to spectrometric analysis. Microwave-assisted extraction (MAE) provides an alternative to traditional digestion methods and it is recognized as one of the most efficient methods for the dissolution of soil samples.

In this study, the extraction and subsequent determination of Platinum Group Elements (PGEs) in road dust and urban soil is presented. The method is based on a three step process: microwave-assisted digestion from the solid matrix, preconcentration and finally detection by electrothermal atomic absorption spectrometry (ETAAS). An initial series of experiments were carried out with 1 g of sample to evaluate the most effective combination of  $\text{HNO}_3$ ,  $\text{HCl}$ , aqua regia,  $\text{HF}$  and  $\text{HClO}_4$  acids. Samples were heated with various acid mixtures in the microwave oven for varying lengths of time and varying power settings to establish approximate conditions that would promote the most effective dissolution, but would not result in the microwave vessels venting (with the possible result of losing part of the sample) during digestion. Once extracted, the metallic elements were preconcentrated as their APDC complexes with the aid of Cloud Point Extraction (CPE) method. The preconcentrated extract was then re-dissolved in a small amount of  $\text{HNO}_3$  and measured with ETAAS for its content in PGEs. The overall procedure was validated through the analysis of a certified reference material. Preliminary investigation in urban road dust and soil samples from Ioannina city (Northwestern Greece) is also presented.

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MINISTRY OF NATIONAL EDUCATION  
AND RELIGIOUS AFFAIRS  
MANAGING AUTHORITY OF OPERATIONAL  
PROGRAMME "EDUCATION AND INITIAL  
VOCATIONAL TRAINING"



ΥΠΟΥΡΓΕΙΟ ΕΘΝΙΚΗΣ ΠΑΙΔΕΙΑΣ ΚΑΙ ΘΡΗΣΚΕΥΜΑΤΩΝ  
ΕΣΩΤΗΚΗ ΥΠΗΡΕΣΙΑ ΔΙΑΧΕΙΡΙΣΗΣ ΕΠΙΧΕΙΡΗΣΙΑΚΗΣ  
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ΣΥΓΧΡΗΜΑΤΟΔΟΤΗΣΗΣ  
ΕΥΡΩΠΑΪΚΟ ΚΕΝΤΡΙΚΟ ΤΑΜΕΙΟ  
ΕΥΡΩΠΑΪΚΟ ΤΑΜΕΙΟ ΠΕΡΙΦΕΡΕΙΑΚΗΣ ΑΝΑΠΤΥΞΗΣ



ΠΑΙΔΕΙΑ ΜΠΡΟΣΤΑ  
2<sup>ο</sup> Επιχειρησιακό Πρόγραμμα  
Εκπαίδευσης και Αρχικής  
Επαγγελματικής Κατάρτισης

# PIROMETALLURGICAL PROCESSES OF FIRE ASSAY PRECONCENTRATION OF NOBLE METALS UNDER AN OPERATION OF ULTRASONIC

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Our researches of a method fire assay (FA) of ores have shown that the losses of noble metals (NM) in scoria's FA hardly depend on composition of used fusion mixture. Usage of ultrasonic (US) oscillations of low frequency allows lowering on 50-100° temperature FA, to reduce time in 3-4 times. Even under unfavorable conditions thus the extent of extraction NM is conserved at FA on NiS ( $\text{Ni}_2\text{S}_3$ ) or Sn and is augmented at usage as a collector Pb or Cu.

In the given work the researches of dependence of an extent of testing concentrating from some arguments US are lead with the purpose of a heightening of efficacy of his application.

*Frequency US.* At usage US with frequencies 22 and 44 kHz is not detected of essential differences on an eventual result of definition NM.

*Intensity US.* Examined US by intensity up to 10 W/cm<sup>2</sup>. Dependence of intensity US and time indispensable for deriving of alloy, which one obeys of analysis, is described by the equation  $I = C - k \cdot \text{Int}$ .

At FA of a shot of mass 5 g for deriving alloy with usage US by intensity of 9 W/cm<sup>2</sup> there are enough 10 minutes of handling. The common time FA depends on furnace efficiency, and in our works compounded 15-25 minutes.

*Geometrical arguments of the concentrator.* For handling melts have utilized concentrators manufactured of a heat-resisting steel of the cylindrical form about a dia 10 mm (phylum 1), and fungoides form about a dia of "cap" from 5 up to 15 mm (phylum 2). Is established, that peak efficiency at FA of shots of mass 5 g the concentrator 1 type educes at submergence in a melt on spacing interval of 5-7 mm from bottom of a crucible (3-5 mm from a surface of a collector), and concentrator 2 such as - on 5-15 mm (3-13 mm from a surface of a collector). At decrease of spacing interval of submergence the probably strong dispergation of a collector in a melt, and for his final congregating in one drip is necessary to withstand a melt at the temperature of FA after US not less than 20 minutes.

# ETAAS, SPECTROSCOPIC AND TEST DETERMINATION OF HEAVY METALS IN NATURAL OBJECTS AFTER THEIR PRECONCENTRATION BY ADSORPTION

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Most heavy metals even at low concentrations are dangerous.

The development of methods using sorbents modified with analytical reagents that enable analytical signal measuring directly on the surface by solid-phase spectrometry, visually or by electrothermic atomic absorption spectroscopy (ETAAS) after elution is now a subject of growing interest.

Brombenztiazo (BBT) is known to be one of the best reagents for extraction-photometric determination of cadmium(II). The reagent also forms complexes with Co(II), Cu(II), Fe(II), Ni(II), Zn(II). The aim of this work was to develop a solid-phase reagent on the base of BBT immobilized on silica gel for sorption-spectroscopic and visual test determination of Cadmium, and also for sorption-atomic-adsorption determination of total heavy metals contents in natural waters.

BBT sorption on unmodified sorbents of different nature was studied. Silica gel Merck 60 (SG) was chosen for further investigations. BBT immobilization on SG was realized by adsorption from chloroform-hexane solution (1:10) in batch mode. The isotherm of BBT adsorption can be referred to H3-type. Interaction of Co(II), Cu(II), Cd(II), Ni(II), Zn(II) ions with immobilized BBT has been studied in batch mode as a function of pH of solution, time of phase contact and concentration of metals in solution. In the presence of sodium citrate absorbance (at  $\lambda = 620$  nm) of immobilized BBT grows with the increase of Cd(II) concentration in solution. No interference was observed from Zn(II), Pb(II), Cu(II), Ni(II), Co(II) and macrocomponents of natural waters. This was assumed as a basis of sorption-spectroscopic and visual test determination of Cd(II). Heavy metals eluted from BBT-SG easily and quantitatively with a small volume of HNO<sub>3</sub>-ethanol mixture. This became a basis of sorption-atomic-absorption determination of the total concentration of heavy metals in natural objects.

The analytical characteristics of the sorption-spectroscopic and sorption-atomic-absorption methods developed have been checked up by the analysis of standard solutions, natural, artesian, mineral waters and food salt.

## IMPROVEMENT OF SOME METHODS OF PRECONCENTRATION OF SELENIUM

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Selenium is a vital microelement for people. It has dual properties. Selenium is an essential nutrient at low concentration levels and it becomes toxic at higher concentration levels. Deficiency of selenium results in weakness and hard diseases. Selenium is a building material of many hormones and ferments; it neutralizes free radicals, radioactive radicals in organism. The range of selenium safety concentration in food and water is very narrow. The daily normal amount of human consumption of selenium is 10-20 µg, maximum safe concentration of selenium in water is 5-10 µg/l. It becomes toxic at 20-30 µg and bigger content in different objects.

The content of selenium in biological and environmental objects is low and comprises 10<sup>-5</sup>-10<sup>-7</sup>%. This causes necessity of development of new and improvement of existing effective methods of preconcentration and determination of Se traces.

The possibility of preconcentration of selenium in form of SeO<sub>3</sub><sup>2-</sup> by evaporation of low alkali water solution (for 20-1000 µg/L) has been investigated. Considerable losses of selenium have been observed during evaporation of acidic and neutral solutions owing to volatility of selenium compounds. During evaporation of low alkali solutions at pH 9-10 there are no losses of selenium. Relative error of selenium determination is 1-2% for 1000 µg/L solution and 3-5% for 20-100 µg/L. Concentration factor is 10.

The possibility of preconcentration of selenium (IV) by coprecipitation with iron (III) hydroxide and lanthanum (III) hydroxide with subsequent determination by flame atomic absorption spectroscopy has been investigated also. The effect of nature and concentration of collector and interfering ions on precision accuracy and reproducibility of analytical signal A has been studied. Application of Fe(OH)<sub>3</sub> as copreconcentrant leads to small relative error (less than 5%). S<sub>r</sub> is 0.1-0.2 for 5-100 µg Se in the sample. Concentration factor is 6. The effect of concentration of hydrochloric acid on precision and accuracy of AAS determination of Se has been studied. The best results were obtained with HCl (1 : 1).

# **SENSORS AND TESTS**

*Keynote lectures*

# ELECTROCHEMICAL BIOSENSORS FOR PESTICIDE DETERMINATION

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Biosensors are widely used to the detection of hazardous contaminants in foodstuffs, soil and fresh waters. Due to high sensitivity, simple design, low cost and real-time measurement mode biosensors are considered as an alternative to conventional analytical techniques, e.g. GC or HPLC. Although the sensitivity and selectivity of contaminant detection is mainly determined by a biological component, i.e. enzyme or antibodies, the biosensor performance can be efficiently controlled by the optimization of its assembly and working conditions. In this report, the prospects to the improvement of pesticide detection with cholinesterase sensors based on modified screen-printed electrodes are summarized. The following opportunities for the controlled improvement of analytical characteristics of anticholinesterase pesticides are discussed:

1. The optimization of the biorecognition layer by the modification of a transducer used. Nanostructured polyaniline composite comprising Prussian Blue or poly-ionic polymers has been synthesized and successfully used in the assembly of cholinesterase sensors. In comparison with non-modified sensors, this improved signal selectivity toward electrochemically active species and decreased the detection limits of Chloropyrifos-Methyl and Methyl-Parathion down to 10 and 3 ppb, respectively.
2. Sample pre-treatment. Novel procedures of electrochemical sample treatment have been proposed to decrease the signal interference with native cholinesterase inhibitors present in fruits and vegetables. Polyphenolic compounds were removed by electrolysis with soluble Al anode followed by the oxidation of thionic pesticides with electrogenerated chlorine. The procedure proposed makes it possible to decrease the background current and the matrix effect by 80-90%. Thus, the detection limits of about 5 ppb of Parathion-Methyl and Chloropyrifos-Methyl were obtained in spiked grape juice without any additional separation or pre-concentration stages.

The effect of electrochemical sample treatment on the signal selectivity in multi-component mixtures is discussed.

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# DESIGN OF SENSING MATERIALS FOR ELECTROCHEMICAL SENSORS

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Electrochemical sensors operate on the principle of controlled change of some electrical parameter, e.g. conductivity, current or voltage, caused by the change of the chemical environment. Specifically, in electrochemical gas sensors the change of conductivity or work function is measured in response to the change of partial pressure of the analyte. Selectivity of the interaction with the analyte in any given application is usually the most important figure of merit for design of a new sensing material. Other parameters that are important for defined practical applications are speed of response and long-term stability. In that respect we have investigated modification of organic semiconductors with room temperature ionic liquids, co-polymerization with polyelectrolytes, grafting and irradiation induced crosslinking to obtain improved performance of solid state sensors based on conjugated conducting polymers.

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## DNA BASED CHEMICAL TOXICITY ELECTROCHEMICAL SENSORS

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Association interactions and structural attack to biopolymers such as deoxyribonucleic acid (DNA) belong to general ways of effects of toxic species which are important particularly from the point of view of human health and ageing processes. Today, DNA is typically used as a biocomponent at the biosensors with rather specific application area at the determination of DNA sequence and the evaluation of damage to DNA as well as DNA host-guest interactions. High sensitivity, small dimensions, low cost and cheap exploitation belong to general advantages of electrochemical biosensors.

In this work, simple (single-use) biosensors with a layer double stranded (ds) calf thymus DNA attached to the surface of screen-printed carbon electrode assembly have been prepared. The sensor efficiency was significantly improved using nanostructured films like carbon nanotubes, hydroxyapatite and montmorillonite in the polyvinylalcohol matrix.

The biosensors were applied to the study and detection of various potentially toxic chemicals. DNA binding interactions of biologically widely active quinazoline derivatives, amino-, hydroxy- and nitroderivatives of polycyclic aromatic hydrocarbons and drugs were investigated. Simple procedures for the detection of a deep DNA degradation by reactive oxygen species formed *in situ* in the presence of risk chemicals such as inorganic and organic arsenic and tin compounds, quinazolines and others as well as for the detection of natural and synthetic antioxidants were developed and validated using conventional methods (spectrophotometry, gel electrophoresis and others).

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# TEMPLATED NANAOSTRUCTURED POLYMERS AS SENSITIVE MATERIALS

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Bulk and surface imprinting strategies are straightforward tools to generate artificial antibodies. Combined with transducers such as QCM (quartz crystal microbalance), SAW (surface acoustic wave resonator), IDC (interdigital capacitor) or SPR (surface plasmon resonator) they yield powerful chemical sensors for a very broad range of analytes.

Aromatic solvents or polycyclic aromatic hydrocarbons (PAH) in water, e.g. can be detected by QCM coated with bulk-imprinted polymer layers. Here, the interaction sites are not confined to the surface of the sensitive material but are distributed within the entire bulk leading to very appreciable sensor responses. Additionally, these materials show high selectivity: aromatic solvents e.g. can be distinguished both by the number of methyl groups on the ring (toluene vs. xylene, etc.) and by their respective position. Selectivity factors in this case reach values of up to 100.

In the case of PAH, adding a second template leads to highly increased selectivity and sensitivity of the materials. With fluorescence e.g. a detection limit of some ng/l is achieved.

Due to the very flexible synthetic approach, imprinted layers are highly suitable for sensor measurements in complex mixtures: Sensor coatings consisting of a carbonic-acid-imprinted sol-gel material e.g. incorporate oxidative degradation products from engine oil leading to a chemical lubricant sensor.

Bioanalytes, such as enzymes, viruses and cells, are much larger than the aforementioned compounds, so surface imprinting techniques are applied due to much slower analyte diffusion. The resulting surface structures range from some nm to some  $\mu\text{m}$ . Selectivity studies show that not only the sterical features of the analyte species are important, but also the surface chemistry. For example it is possible to distinguish between different blood groups (A, B, O) with a sensor as a result of different glycolipids on the cell surface.

Viruses are also detectable with imprinted sensor materials thus leading to the first true rapid on-line analysis for these species that are too small for e.g. light scattering experiments. So we e.g. succeeded in determining the tobacco mosaic virus (TMV) in plant saps as well as the Human Rhinovirus (HRV).

## SENSORS BASED ON CARBON CERAMIC MATERIALS

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Carbon ceramic electrodes have been prepared by the sol-gel processing method and these materials have been used to develop a new series of chemical sensors and biosensors. The  $\text{SiO}_2/\text{ZrO}_2/\text{C}$ -Graphite carbon ceramic composites were prepared by the sol-gel processing method in two different proportions: 60% $\text{SiO}_2$ / 20% $\text{ZrO}_2$ /20% C-Graphite and 50% $\text{SiO}_2$ /20% $\text{ZrO}_2$ /30% C-Graphite (where the amounts are in wt. %). They were investigated by X-Ray Diffraction (XRD), Scanning Electron Microscopy (SEM) connected to an X-ray dispersive energy analyzer (EDS), Transmission Electron Microscopy (TEM) and X-Ray Photoelectron Spectroscopy (XPS). The images obtained by SEM for the carbon ceramic composites reveal a higher fragmentation of the material morphology as the graphite concentration increase. The zirconium mapping for the  $\text{SiO}_2/\text{ZrO}_2/\text{C}$ -Graphite by EDS shows that the zirconium atoms are highly dispersed in the matrix and no evidence of islands of zirconium oxide can be observed. The graphite was found as nano-crystallites incorporated in the middle of the  $\text{SiO}_2/\text{ZrO}_2$  amorphous matrix and the interplanar distances evaluated by TEM were 0.34 nm and 0.22 nm, a quite similar value to that found by XRD. Copper hexacyanoferrate was immobilized on the surface of the carbon ceramic electrode composite and their electrochemical properties were evaluated by Cyclic Voltammetry (CV) and Electrochemical Impedance Spectroscopy (EIS). The XPS data showed that potassium ion was incorporated into the inorganic lattice in very low content. The cyclic voltammetry of the resulting modified carbon ceramic electrode shows a well-defined reversible redox couple due to the  $[\text{Fe}(\text{CN})_6]^{3-/4-}$  system. The value of charge transfer resistance for modified carbon ceramic electrode calculated by EIS was also very low, which indicates that the film behavior is similar to a conductor, whereby different species undergo oxidation/reduction reactions governed by their redox potential. The modified carbon ceramic electrode shows a good electrocatalytic activity towards the electrochemical reaction of hydrazine.

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## ORGANIC SEMICONDUCTOR THIN-FILM TRANSISTOR SENSORS

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Organic semiconductor thin-film transistors (OTFT) have seen a dramatic improvement of their performance in the last decade and recently they have been also exploited as gas sensors. These are semiconducting organic-based sensors that offer the advantage of remarkable response repeatability as standard deviations are within 2% for several hundreds subsequent exposure to an analyte. The devices are operated in the pulsed mode and full base-line recovery can be achieved, operating the OTFTs at room temperature, by strategic use of the gate bias. It has been also shown that OTFT response can be enhanced by properly choosing the imposed gate bias potentials. Selectivity and specificity is being pursued by choosing ad hoc chemically or biologically functionalized semiconducting organic active layers. In this respect, interesting is the recent work showing that it is possible to operate OTFT sensors in water and to integrate them to microfluidics. They have also been proposed as bio-sensors for lactic acid, glucose and streptavidin as well as large-area flexible pressure sensors for artificial skin applications. Scaling down OTFT dimensions to the nanoscale may be yet another way to further improve their response. It is however not clear at this point if this will result in a sensitivity improvement. Cost is a key driver as well, particularly for consumer-oriented sensor systems. In these regards, the advantages of organic electronics are well known. This newborn technology can take full advantage of the rapid developments occurring in the field of organic electronics where OTFTs have been already implemented in complementary-metal-oxide-semiconductor (CMOS) circuits and in flexible plastic displays.

*Oral presentations*

## ION-SELECTIVE ELECTRODES REVERSIBLE TO DOUBLE-CHARGED ANIONS: PROBLEMS AND TRENDS

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Many double-charged anions, such as sulfate, hydrophosphate, oxalate etc., are highly widespread in natural sources and at the same time lack any convenient technique for their determination. Therefore, development of ion-selective electrodes (ISEs), responsive to these anions, is of great practical importance. However, for a long time all attempts directed toward creation of such electrodes were unsuccessful (except for carbonate ISEs based on trifluoroacetylbenzene derivatives), and only in recent years this field has shown significant progress.

In this work, the most important problems, connected with development of ISEs for double-charged anions, have been analyzed and possible ways for their overcoming have been discussed. The main difficulties in creating such ISEs are caused by:

- a) high degree of hydration for double-charged anions, as compared to single-charged ones;
- b) low efficiency of their interaction with traditionally used anion exchangers, due to steric hindrance for simultaneous interaction of two cation centers with one anion;
- c) much weaker complexing ability of double-charged anions, compared to metal cations, that limits the possibility for synthesis of highly selective neutral carriers.

Opportunities for creation of ISEs to hydrophilic double-charged anions with practically acceptable selectivity are based on latest achievements of anion receptor chemistry and modern ISE theory. The following mechanisms of anion recognition are utilized: coordination of the target anion with a metal atom being a part of some lipophilic complex or organometallic compound; multi-center hydrogen binding or ion-ion (ion-dipole) interaction of the target anion with highly preorganized tweezer-type or tripodal ionophores, providing ditopic or three-dimensional recognition, etc. Significant effect is also achieved by increasing efficiency of anion exchanger interaction with double-charged anions, attained by using anion exchangers with enhanced steric accessibility of the exchange center. The most successful examples of ISEs, responsive to hydrophilic double-charged anions, are given.

## **A NOVEL STRATEGY FOR THE DEVELOPMENT OF BIOSENSORS BASED ON NAD-DEPENDENT ENZYMES**

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A lot of analytical techniques have been proposed in recent decades and most of them are based on enzymes, called dehydrogenases, which are not sensitive to oxygen and need cofactors such as NAD<sup>+</sup>. The key problems which seriously hamper a wide commercialization of biosensors and enzymatic kits based on NAD-dependent enzymes are: necessity to add exogenous cofactor (NAD<sup>+</sup>) into the samples to be analyzed; to incorporate into the biologically active membrane of sensors covalently bounded NAD<sup>+</sup>; to supply the analytical technique by NAD<sup>+</sup>-regeneration systems.

For the first time, NAD<sup>+</sup> is non-covalently incorporated into a bio-selective sensor membrane in high concentration which supplies a sufficient level of the cofactor for a great number of assays - as preliminary calculated up to 1000 measurements per sensor can be performed. To reach a high level of NAD<sup>+</sup> in bio-membrane two new approaches are proposed: a) usage of positively charged polymeric carriers which bind with phosphate-anions of NAD<sup>+</sup> (for example, DEAE-dextran); b) usage of an additional negatively charged membrane covering NAD<sup>+</sup>-containing one which creates a diffusion barrier preventing a leakage of the cofactor from biomembrane (for example, Nafion).

Novel glycerol and formaldehyde selective sensors based on pH-Sensitive Field Effect Transistors as transducers and Glycerol Dehydrogenase and Formaldehyde Dehydrogenase as biorecognition elements have been developed. The main analytical parameters of the sensors have been investigated and will be discussed.

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## COMPOUNDS OF d-ELEMENTS IN SENSITIVE COATINGS OF SENSORS

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There were synthesized new functionalized mixed-ligand and polynuclear coordination compounds (MLC) of 3d-transition metals with some types of polyaminocarboxylates, oxyacids, carbonic acids, aminoacids, amines. The design of composition and structure of these MLC was carried out with account of the necessity that they will be able to multicenter interaction with analytes vapors (water, ammonia, hydro-carbones) and due to their properties will be suitable their own or as components of mesoporous composite coatings (MCC) for use as sensitive coatings of piezoelectric sensors on such analytes. Conditions and methods of formation of sensitive coverings, containing individual compounds, and also MCC containing these compounds and mesoporous  $\text{TiO}_2$  or  $\text{SiO}_2$  materials, on a surface of electrodes of the piezoquartz resonator are researched. Results of screening of the received MLC as components of sensitive coverings of sensors have certified their rather high sorption ability to specified analytes. The initial converters received with their use had comprehensible time of the response and a relaxation. As sorption active coating of humidity and ammonia sensitive piezoelectric sensors were proposed sodium salts of some heteronuclear MLC of 3d-transition metals (first of all Cu and Zn). Such compounds have very high sensitivity to vapors of water and ammonia (the stoichiometric sorption factor ( $n$ ) changes from 6 up to 42 depending on relative humidity and complex structure). Such coatings in water vapors provides linear dependence of values of responses of sensor on relative humidity in a range from 50 up to 75 % and the greater gain of values of responses of sensor at change of relative humidity in comparison with the nearest analogue (270 Hz on 1 % of relative humidity). The mesoporous hydrophobized composite coatings on the ground of  $\text{TiO}_2$  or  $\text{SiO}_2$  and coordination compounds demonstrated high sensitivity toward vapors of different hydrocarbones but were not selective to separate compound, and gives the different response to presence of each compounds in mixture. It opens an opportunity of creation on the basis of such sensors of multisensor intellectual system which operates with use of programs of images recognition. The specified compounds and MCC were recommended [Patents of Ukraine 57360A, 60031A, 60032A, 60033A, 60034A] as components of sensitive coverings for vapors of water, ammonia and hydrocarbones.



# COMPUTER MODELING OF IONOPHORE-BASED ION-SELECTIVE MEMBRANES USING MULTISPECIES APPROXIMATION

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Ion-selective electrodes (ISEs) with ionophore-based membranes allow for quantification of a large number of analytes in various matrixes. Tailoring of the composition of the membranes: to comply with the analytical task, requires advanced theory of membrane response. Most of theoretical descriptions include nonrealistic extra-thermodynamic assumptions, in the first place it is assumed that some kind of species strongly predominate in membranes. Ideally, a rigorous theory of ISE response should be based on strict thermodynamics. However, real ISE membranes are too complex. Therefore, known attempts aimed at rigorous thermodynamic description of ISEs proved to be fruitless.

The so-called chemical approach, *i.e.* taking into account chemical reactions between various species in membranes, seems to be a good alternative to rigorous thermodynamic description. The species presented in the real-world ISE membranes are free ions (primary and interfering), their complexes with neutral and charged ionophores, and the respective associates: ion pairs and triplets. Careful consideration of all of these species allows obtaining a system of equations describing membrane potential. By means of this approximation which is called here “multispecies approximation”, computer modeling of ISE behavior becomes possible. Modeling using multispecies approximation is not limited by *a priori* assumptions on whether some kind of species predominates in membrane, being therefore advantageous when compared with more traditional descriptions.

A number of simulations are presented, which demonstrate the capabilities of multispecies approximation to quantify various kinds of ISEs behavior:

- The peculiarities in selectivity dependences on membrane or on solution composition;
- The anion interference with cationic response (or vice versa);
- The non-Nernstian responses at equilibrium;
- The potentiometric response to nonionic species;
- The response from sandwich membranes: measurements of species interactions *in situ*.

# **POLYELECTROLYTE-SILICA COMPOSITE FILMS USING SURFACTANT FEATURE: OPTICAL AND VOLTAMMETRIC CHARACTERISTICS**

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A new generation of mesoporous silica (SG) materials obtained by sol-gel technique where polymers and ionic or non-ionic surfactant act as structure – directed templates is widely developed during last years. Final materials can be synthesized as thin films and used as sensitive elements of optical and electrochemical sensors.

In the present work it was studied the dependence of analytical characteristics of the composite SG - polyelectrolyte films obtained by sol-gel technique on the content of non-ionic surfactant in initial sol. Triton X-100 and Tween 20 were examined as surfactants; polystyrene sulfonate (PSS), polyvinyl-sulfonic acid (PVSA) or polydimethyl-ammonium chloride (PDMDA) were used as polyelectrolytes. The final films were applied as modifiers of glass slides and pyrolytic graphite (PG) electrode surfaces.

The ion- exchange properties of the composite films were studied by spectrophotometric and voltammetric methods using sorption of  $\text{Fe}(\text{Phen})_3^{2+}$  and rhodamine 6G for PVSA-SG or PSS-SG films and methyl orange or lumogallion (LG) for PDMDA-SG films. Tween-20 at its cmc and higher level was shown to be better structure directed additive than Triton X-100.

PVSA-SG film was used for determination of  $\text{Fe}(\text{Phen})_3^{2+}$  and  $\text{Zn}^{2+}$  as ternary complex  $\text{Zn}^{2+}$ -Phen-bengal rose by spectrophotometric method. The calibration graph was linear in the concentration  $5 \cdot 10^{-6} - 5 \cdot 10^{-5}$  mol/l for Fe(II) and  $1 \cdot 10^{-6} - 5 \cdot 10^{-5}$  mol/l for Zn(II). The film can be regenerated and reused. LG-PDMDA-SG film was shown to be perspective modifier of the PG electrode surface and used for voltammetric detection of Mo(VI) at ppb level.

PSS-SG composite film was tested for sorption of heme proteins: hemoglobin (Hb) and myoglobin (Mb). The peroxidase activity of adsorbed proteins were studied and evaluated by optical and voltammetric methods. Mb-PSS-SG film on PG electrode was shown to be perspective for detection of dissolved oxygen and hydrogen peroxide by voltammetry with linear calibration in the range 2-30  $\mu\text{M}$ , and detection limit  $\sim 1.5 \mu\text{M}$ . Obtained composite films can be modified by different types of biological active compounds which is important for the development of sensitive elements of biosensors.

## **TEST ANALYSIS: NEW SYSTEMS AND METROLOGICAL PROVIDING**

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Test method of analysis has wide application in the practice of analytical chemistry and requires unified reliable approach to the evaluation of such metrological characteristics as limit of detection (LDC) and limit of determination (LDM).

The algorithm for estimating the LDC and LDM for techniques of test analysis with visual indication is suggested. It includes the steps to check the sufficiency of experimental material [1]. The hypothesis choice about the type of frequency distribution in unreliable reaction (UR) region is based on the calculation of criteria complex:  $\chi^2$ , Kolmogorov-Smirnov criterion, asymmetry and excess coefficients. The approach is applied to 19 test-systems. The carrier materials were reagent indicating paper (RIP), polyurethane foam (PUF), metylsilicic acid (MSA), gelatin film. Some indicator reactions were studied in solutions.

New test-systems are offered to determine:

- 1) sum of heavy metals with 4-(2-pyridylazo)resorcinol on the bases of PUF, MSA, gelatin film;
- 2) 2,4-dichlorophenoxyacetic acid 2,4,5-trichlorophenoxyacetic acid with butylrhodamine on the bases of PUF;
- 3) Co (II) with 2-nitroso-1-naphtol in the presence of diphenylguanidine and NiSO<sub>4</sub> on the bases of PUF and MSA;
- 4) Co (II) with nitroso-R-salt on the bases of gelatin film;
- 5) pH solutions by indicators of bromphenol blue, bromcresol green, neutral red, malachite green immobilized in gelatin film.

To characterize the quality of test-system the notion "relative width of UR region" was suggested for the first time. The less the value of UR region relative width is the test-system the more tolerant to the random interferences and better in analytical sense. In the work the dependence of LDC on the reaction type, observation condition of test-means staining, the carrier material type, UR region relative width and the number of observations was analysed.

1. Reshetnyak E.A., Nikitina N.A., Kholin Yu.V., Svetlova N.V., Ostrovskaya V.M.// Kharkov University Bulletin. Chem. Series. Issue 10 (33). 2003. No. 596, p. 90-97. (in Russian)

# NANOSCALE LANGMUIR-BLODGETT FILMS AS SENSITIVE LAYERS OF CHEMICAL SENSORS

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One of the new trends in chemical analysis appeared in the last decade is that the miniaturization. It becomes apparent in the miniaturization of analytical devices, separation procedures, measuring tools, analyzing samples and as a consequent the term “micro” have appeared. Further development of this trend have led to transfer from the term “micro” to “nano” one (nanoparticles, nanofluides, nanoprobes, nanoelectrodes, nanotubes, nanoscale, nanobarcode, nanoelectrospray, nanoreactors, etc). Thereupon a nanoscale films produced by Langmuir-Blodgett (LB) technique are proposed for modifying of chemical sensors.

Among the important advantages of sensor layer created by LB technique are its high homogeneity combined with the directed mutual orientation of molecules and their functional groups, as well as the feasibility of the layer thickness control within the precision of single molecule. Other advantages of such ultrathin films are virtually unlimited variability of molecules of organic and inorganic nature constituting the basis of sensor element. Besides, LB films possess a relatively high ratio between the active surface of molecular layers and their overall bulk that facilitates a rapid equilibrium establishing on the interaction with the detected substance. It is of importance also that the microheterogeneous medium in the film containing diphilic molecules resembles that in an active centre of enzymes, and simulates the cellular biomembranes in many respects.

The new approach for development of pH sensor with wide acidity range (2.5 M H<sub>2</sub>SO<sub>4</sub> – pH 5.5) based on the use of Congo Red and Benzopurpurin 4B immobilized in polyamido- or arachidic acid nanosized sensitive matrix will be demonstrated.

The use of arachidic acid and different amphiphilic calixarenes for modifying of field effect transistor sensors and determination of some volatile organic contaminants will be considered.

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# **SENSORS BASED ON FREE-STANDING MOLECULARLY IMPRINTED POLYMER MEMBRANES. COMPUTATIONAL MODELLING OF SYNTHETIC MIMICKS OF BIORECEPTORS**

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Development of highly-stable and selective sensor systems for environmental monitoring is one of the challenging goals of sensor technology and biotechnology. Therefore, development of highly stable and inexpensive materials with the ability of selective recognition of toxic substances is of great importance. This presentation will concentrate on development of sensors for herbicide detection based on synthetic mimicks of bioreceptors. Triazine herbicides were used in the present research as model analytes. Polymers-biomimicks were synthesized in the form of free-standing membranes using the method of molecular imprinting in combination with the method of computational modeling. The choice of functional monomer in this study was based on the results of computational modeling. Methacrylic acid, itaconic acid, and acrylamide were identified as optimal functional monomers for atrazine. The optimal ratios atrazine/functional monomers in the monomer mixture were identified and their binding energies were determined. The method of synthesis of highly cross-linked molecularly-imprinted polymers in a form of thin, flexible, and mechanically-stable membranes was developed. It was shown that compositions based on copolymers of tri(ethyleneglycol)dimethacrylate and oligoethaneacrylate MM2600 as well as on aliphatic and alicyclic epoxy resins can be successfully used as selective elements of conductometric sensors. Effectiveness of the computational modeling was analyzed and correlation between the estimated binding energy and the ability of functional monomers to form atrazine-selective receptor sites was revealed. The developed sensors were characterized by low detection limit (5–15 nM) of atrazine detection as well as high selectivity. Working parameters of the sensor systems were determined and optimized. The approaches towards improving the sensitivity of the developed sensors were proposed.

# ELECTROCHEMILUMINESCENT HYBRIDISATION CHIP USING ELECTRIC FIELD AIDED HYBRIDISATION AND IMMOBILISATION

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There is a growing interest in miniaturised DNA- and bioassay platforms. We present an electrochemical hybridisation chip based on electrochemiluminescence (ECL) detection of ruthenium-labeled oligonucleotides. ECL is a method where light is generated on the surface of an electrode upon electrochemical polarisation in the presence of a suitable coreactant. A ruthenium label (Ru1) composed of two bipyridine and one phenanthroline ligand was synthesised and covalently coupled to amino-modified oligonucleotides. The hybridisation chip having gold microelectrodes as immobilisation and detection platform and reservoirs made in poly(dimethylsiloxane) (PDMS) is fabricated. Amino modified 15-mer oligonucleotides are immobilised on gold using self assembled monolayers (SAM) of mercaptohexadecanoic acid (MHA) and NHS/EDC coupling. Parameters of SAM formation, such as concentration of MHA and deposition time are optimised. Ru1-labeled targets are added into reservoirs and left to react with probes for 2 hours or shorter. Upon removal of nonhybridised targets the ECL buffer is added and the ECL signal is measured upon application of the potential of 1 V at the working electrode. Electric field influence on the immobilisation and hybridisation is also tested. The best ECL signal is obtained in the presence of 0.1% of SDS at pH 7.8. The best MHA concentration is between 200-500  $\mu\text{M}$  of MHA, while higher concentrations lead to passivation of the electrodes. At optimal conditions complementary target is detected at low nanomolar level. Application of potential of 300 mV for 1 min during immobilisation and hybridisation increases the speed of both processes, while upon application of negative potential of -200 mV both immobilisation and hybridisation are greatly reduced. Thus, electric field aids discrimination between complementary and uncomplementary strands and reduces time needed for the analysis.

## MESOPOROUS SILICA MATERIALS AS SENSITIVE COMPONENTS FOR CHEMO- AND BIOSENSORS

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The field of chemical and biosensors is one of the fastest growing areas both in research and commercial fields. Most of the research work in this field is concentrated towards reducing the size of sensors and at identification and quantification of multiple species. Also, quick response, minimum hardware requirement, good reversibility, sensitivity, and selectivity are qualities expected of an excellent sensor and hence there is a need for further research.

Inorganic supports with favorable surfaces for the immobilization which result in high sensor activity have been highly sought. However, formation of the channels and the pores of the sol-gel matrix is not controlled, and various sizes of pores and channels are formed, ranging from 0.1 to 500 nm in size. Often interconnected micropores and channels are formed, allowing only the smallest of the substrates to penetrate, while the bigger substrates clog the channels, slowing the reactions. The hexagonal mesoporous silica have great potential for high organic molecules loading, provided that pore size is sufficiently large for some organic molecules (enzyme, pesticide, toxine, biomolecules) to be anchored and also for it substrate to access and diffuse easily through pore channel such as appropriate functional groups provide high affinity for various biomolecules.

Self-organized materials with high surface area and pore size 3-25 nm was produced used templating and coassembly. The highly porous nature of the ordered combined with low adsorption and emission in the visible spectrum, facile diffusion makes them good candidate for optical and chemical sensor and provide new avenues for encapsulation/ immobilization processes and solve the problems mentioned above.

We showed that these mesoporous silica materials, with variable pore sizes and susceptible surface areas for functionalization, can be utilized as good separation devices and immobilization for biomolecules, where the ones are sequestered and released depending on their size and charge, within the channels. Mesoporous silica with large-pore-size structures, are best suited for this purpose, since more molecules can be immobilized and the large porosity of the materials provide better access for the substrates to the immobilized molecules. The mechanism of bimolecular adsorption in the mesopore channels was suggested to be ionic interaction. On the first stage on the way of creation of chemical sensors on the basis of functionalized mesoporous silica materials for selective determination of herbicide in an environment was conducted research of sorption activity number of such materials in relation to 2,4-D.

# THE SOLID-PHASE REAGENTS IN ANALYSIS. A NEW APPROACH

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One of the predominant trends of modern analytical chemistry is the determination of toxic elements, their species and bioactive compounds in various objects. And hyphenated techniques are the most suitable for these purposes. The silica gels (SG) modified with analytical reagents permit to combine the recovery and preconcentration of elements with their rapid detection on the surface of sorbent by means of spectroscopy or after elution (ETAAS). Moreover, the using of specific reagents as modifying agents allows to increase the selectivity of determination. SG are the most perspective support for analytical reagents immobilized. The adsorption of reagents on such matrix is known as effective and simple method of surface modification.

The aim of the present work is to create the effective analytical forms for the hyphenated spectroscopic technique and test methods which can be used not only under stationary laboratory conditions, but also "in site". The investigation of immobilization of more than 40 organic reagents of different classes, their complexes and ion associates resulted in the definition of main factors causing the hard reagent binding on the surface and chemical-analytical properties of immobilized reagents. On the base of the study of complexing ability of immobilized reagents the reasons of reagents selectivity increase at their grafting onto surface were found. The obtained correlation equations make possible to foresee and change the chemical-analytical properties of solid phase reagents. The proposed sorption-spectroscopic and visual approximate methods have considerable advantages in comparison with the best existing analogues. A number of solid-phase reagents on the base of SG modified with metal chelates, ion associates, redox reagents, heteropolyacids were proposed for sensitive and selective determination of metal ions, metalloids, anions and organic reductants in water and food-stuffs. The solid-phase redox reagents for the evaluation of such quality criteria as total antioxidant activity of herbal products were worked out. For the study of the speciation of some heavy metals in natural water the ion-exchange and gel-permeation chromatography coupled with membrane filtration, photochemical oxidation and their sorption-spectroscopic detection were applied. The perspective fields of analytical application and tendencies of further investigation were outlined.



*Poster presentations*

# SOLVATION AND IONIC ASSOCIATION EFFECTS IN THE SELECTIVITY OF ISES RESPONSIVE TO PRIMARY - QUATERNARY ALKYLAMMONIUM CATIONS

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The sufficient selectivity to a principal component is the most important condition determining the possibility of ion-selective electrodes (ISEs) practical appliances. In this work, the relationship between the potentiometric selectivity of alkylammonium-selective electrodes and factors such as the nature of plasticizer, ion-exchanger and substitution degree of cationic nitrogen atoms of the principal and foreign ions, is discussed.

The selectivity coefficients ( $K_{ij}^{pot}$ ) of ISEs with poly(vinyl chloride) membranes plasticized either with dibutyl phthalate (DBP) or *o*-nitrophenyl octyl ether (*o*-NPOE) and containing either tris(nonyloxy)benzenesulfonic acid (TNOBS) or tetrakis(4-chlorophenyl) borate (TpCIPB) (as ion-exchangers), to some primary – quaternary alkylammonium cations, have been determined.

It has been found that the influence of the membrane composition on the ISE selectivity is mainly governed by substitution degree of the nitrogen atom, but virtually does not depend upon the length of hydrocarbon substituents. The key factor in the selectivity of DBP-plasticized membranes with both kinds of ion-exchangers and of the *o*-NPOE-TNOBS-membrane is the ionic association. Values of  $\lg K_{ij}^{pot}$  of the tetrabutylammonium-selective electrode to primary – tertiary alkylammonium cations for TpCIPB-containing membranes are less than for TNOBS-containing membranes. The selectivity coefficients to primary – tertiary cations are also shown to decrease when DBP is replaced by *o*-NPOE. It is worth mentioning that the selectivity to  $\text{Et}_4\text{N}^+$  (i.e., quaternary ammonium cation, just like the principal ion) is almost the same for all the membranes studied. The facts are explained by solvation and ionic association processes.

The results obtained indicate that the ion-exchanger nature, generally not taken into account when developing ISEs for alkylammonium cations, actually influences strongly the selectivity of such ISEs and should be paid attention to when choosing optimal membrane composition. These data will be useful for finding ways to control the ISEs selectivity by rational choice of the membrane composition.

## MODIFICATION OF SILICA GEL BY BASIC DYES

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One of the most important trends of the development of analytical chemistry is analysis test methods work out. The use of modified by dyes sorbent based on silica is a possible variant of test systems. Investigations of the systems basic dye (BD) – silica gel (Sg) were not practically carried out. It is known, however, that ion associates based on BD are effective analytical forms for different types of spectrophotometric analysis. We have studied the sorption process of BD of different classes based on silica gel: astrazone violet 3R, astrafloxin FF, crystal violet, methyl violet, brilliant green, mehtyl green, methylen blue, kationic golden-yellow, hinaldin red and other.

Isotherms have been constructed and quantities of maximum sorbent capacity have been calculated for all the dyes. For instance, isotherms of astrazone violet 3R and astrafloxin FF dyes sorption refer to S2 type. Maximum sorbent capacities made up 0,761 and 1,264  $\mu\text{mol/g}$  correspondingly.

The kinetic characteristic – the time of sorption equilibrium stabilization – has been studied. It ranges from 5 to 30 minutes for different dyes. In particular, equilibrium of crystal violet stabilizes for 10 min. and that of astrafloxin FF – for 30 min. Strength of dyes keeping on the surface of silica gel has been evaluated as well. In the order: water - acetone – DMFA – methanol – DMSO the degree of desorption increates. Corresponding of this number of solvents and data of dyes sorption of aqua-organic mixtures has been also traced. Under the condition that the content of organic solvent (DMFA), methanol, DMSO in aqua-organic solutions over 80 % sorption of BD is completely suppressed. It should be mentioned that analogous regularities were observed during the investigation of dyes extraction from aqua-organic mixtures. It may be indirect illustration of sorption and extraction BD from aqua-organic solutions mechanisms similarity.

As a result of the research carried out samples of modified BD silica gel has been obtained. Their behaviour (coloring change) in the presence of different anions: simple (chlorides, nitrates, sulphates) and metal complexes (tetrachloraurate) has been studied. Silica gel modification by astrafloxin FF has been shown possibility of creation of semi-quantitative  $\text{AuCl}_4^-$  determination test system.

Expediency of the use of scanned samples computer simulation method for analytical signal evaluation and interpretation has been analyzed.

# SOLID-PHASE SPECTROPHOTOMETRIC AND TEST DETERMINATION OF CATIONIC SURFACTANTS ON PAPER FILTERS AS ION ASSOCIATE WITH BROMPHENOL BLUE

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Actually, the successful use of cationic surfactants (cSurf), as flotation reagents, frothers, metal corrosion inhibitors, pharmaceutical products, cosmetic materials, stimulates considerable increase in their production and as a result increases their content in natural water. As cationic surfactants are toxic pollutants in natural water and their maximum contaminant level (MCL) of natural water is 0.15-4.0 mg/dm<sup>3</sup>, it is necessary to use methods for which provide rapid and reliable determination with sensitivity equal to at least 0.1 of MCL. Practically most sensitive methods of cationic surfactant determination include the preconcentration by extraction or sorption. Analytical methods without using organic solvents are more preferable due to their ecological safety.

In this work hybrid method is suggested to determine cationic surfactants in water. It is based on preconcentration of cationic surfactants in the some of ion associates with acidic dyes on the paper filter and measurement of color intensity by solid-phase spectrophotometric method or visual comparison.

Effect of pH, dye concentration, size of pores of paper filters and their hydrophobic characteristics, filtration rate, nature and hydrocarbon radical length cSurf on sensitivity of their determination was studied.

The investigation leads to the elaboration of solid-phase spectrophotometric and test methods of different cationic surfactants determination in water. The detection limits of cationic surfactants with hydrocarbon radical length C<sub>10</sub> is 0.7 mg/dm<sup>3</sup>, C<sub>12</sub> is 0.2 mg/dm<sup>3</sup>, C<sub>14</sub> is 0.009 mg/dm<sup>3</sup> and C<sub>16</sub> is 0.003 mg/dm<sup>3</sup> by using a 100 cm<sup>3</sup> sample. Metrological performance of method was examined on the natural samples. Proposed method is highly sensitive, simple, rapid and guarantees ecological purity of analysis.

# SILICA BASED THIN FILMS OBTAINED BY SOL-GEL TECHNOLOGY IN THE PRESENCE OF NON-IONIC SURFACTANTS AND MODIFIED WITH POLYELECTROLYTE FOR DETERMINATION OF Zn(II) PHENANTHROLINATE COMPLEX

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Low temperature sol-gel technology is promising approach for preparation of modified with organic molecules silica (SG) thin films. Such films are perspective as sensitive elements of optical sensors. Incorporation of polyelectrolytes into SG sol gives the possibility to obtain composite films with ion-exchange properties. The addition of non-ionic surfactants as template agents into SG sol results formation of ordered mechanically stable materials with tunable pore size.

The aim of the present work was optimization of synthesis of SG – polymeric cation exchanger composite films by sol-gel technology in the presence of non-ionic surfactants and their application for determination of Zn (II) as phenanthroline (Phen) complex.

SG sols were synthesized by hydrolysis of tetraethyloxysilane in the presence of polyelectrolyte and surfactant. Poly (vinylsulfonic acid) (PVSA) or poly (styrenesulfonic acid) (PSSA) were used as cation exchangers, Tween-20 or Triton X-100 were used as non- ionic surfactants. Obtained sol was dropped onto the surface of glass slide and dried over night. Template extraction from the composite film was performed in water- ethanol medium. The ion-exchange properties of the films were studied spectrophotometrically using adsorption of cationic dye Rhodamine 6G or  $\text{Fe(Phen)}_3^{2+}$  and potentiometrically by sorption of protons.

SG- PVSA composite film obtained in the presence of Tween 20 possessed the best cation exchange characteristics. The maximum sorption capacity of SG-PVSA composite film obtained under optimal condition was, mol/g:  $6,2 \cdot 10^{-7}$  for  $\text{Fe(Phen)}_3^{2+}$ ,  $2,3 \cdot 10^{-7}$  for Phodamine 6G and  $2,5 \cdot 10^{-5}$  for protons. The optimal content of PVSA in sol was 4%.

It was shown that  $\text{Zn}^{2+}$  adsorbed onto SG-PVSA composite film as  $\text{Zn(Phen)}_2^{2+}$  complex. It can be detected spectrophotometrically after treatment with anionic dye Bengal Rose (BR). Ternary complex  $\text{Zn}^{2+}$  - Phen-BR formed on the surface under optimal conditions. SG-PVSA film was used for determination of  $\text{Zn}^{2+}$  by spectrophotometric method. The calibration graph was linear in the concentration range  $2,5 \cdot 10^{-6} - 5 \cdot 10^{-5}$  mol/l.

# **STUDIES ON A Pb<sup>2+</sup>-SELECTIVE ELECTRODE WITH MACROCYCLIC LIQUID MEMBRANE. POTENTIOMETRIC DETERMINATION OF Pb<sup>2+</sup> IONS**

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This paper presents the experimental and theoretical data regarding the design, characterization and analytical applications of a non expensive liquid-membrane ion-selective electrode for Pb<sup>2+</sup> ions. The membrane is the solution of the active complex formed by the Pb<sup>2+</sup> ions with dibenzo-18-crown-6 ionophore (DB-[18]-C-6) extracted in propylencarbonate (PC) and is supported on a micro porous alumina rod. The influence of pH, Pb<sup>2+</sup> ions concentration, was studied. The dynamic response and reproducibility of the electrode is also described. Interference of various ions and selectivity properties of the electrode is presented. Successful analytical application of the developed electrode for Pb<sup>2+</sup> ions determination in aqueous solution of synthetic samples and natural water samples both by direct potentiometry and potentiometric titration is presented. The results are statistically interpreted and are compared with the results obtained by AAS method. For the presented analytical results there are insignificant systematic errors between potentiometric method with developed ion-selective electrode and the atomic absorption spectrometry.

## **CHEMICAL REACTIONS ON THE SURFACE OF VO<sub>2</sub>**

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Adsorption of methanol and ethanol from gas phase on the surface of VO<sub>2</sub> was studied by isotherms of resistance (R, Om – t, s).

Adsorption and chemical reaction type “hydrophylic adsorbate” (alcohol) – “hydrophobic agent” (benzene vapor) and “hydrophobic adsorbate (benzoic acid) – “hydrophilic agent” (alcohol vapor) takes place in the temperature range:

$$[T] = [(T_k - \Delta T) \div T_k],$$

where T<sub>k</sub> - temperature of alcohol boiling, ΔT= 12 - 15K.

The treatment with γ quantum promotes the increasing of mobility of charged particles- protons during chemical reactions. According to FTIR spectroscopy during γ-irradiation of the sample by 3-80 kGy dozes the dehydration of the surface takes place.

It was shown by adsorption of cationic dye Rodamine 6G that in water VO<sub>2</sub> is negatively charged. It is known that the surface of dehydrated films is positively charged.

Thus vanadium oxide (IV) could be of interest for sensor systems.

# NEW COMPLEX CHALCOGENIDES AS SENSITIVE MATERIALS FOR ION SELECTIVE ELECTRODES

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In the last years the need for analytical devices to be used for environmental, industrial or medical controls has been growing very quickly.

Intensive investigations in the field of ion-selective electrodes on the basis of crystalline chalcogenide materials or their glassy counterparts have been carried out during the last two decades. Different chalcogenide materials for the detection of heavy metals in aqueous media were presented. The advantages of chalcogenide sensors are the high chemical stability of these materials, their good long-term stability of the low detection limit. Even though they usually do not give very precise data chemical sensors could bring some interesting solutions. In particular chemicalsensors based upon chalcogenide materials are well adapted to the detection of chemical species in solution. Moreover their very versatile composition allows the fabrication of specific membranes for many different types of ions.

The present work is related to the use of electrodes of two different types: the plastic membrane (I) and carbon paste electrode (II). The new crystalline complex chalcogenides ( $\text{Ag}_2\text{HgSnS}_4$ ,  $\text{Ag}_6\text{HgGeS}_6$ ,  $\text{Cu}_2\text{CdGeS}_4$ ,  $\text{Cu}_2\text{ZnGeS}_4$ ,  $\text{Cu}_2\text{CdGeSe}_4$ ,  $\text{Cu}_2\text{ZnGeSe}_4$ ,  $\text{SnBi}_2\text{Te}_4$  and  $\text{SnBi}_4\text{Te}_7$ ) as sensitive materials for ion selective electrodes were studied.

The electrochemical system of the conventional electrode may be represented as follows: *types I*:  $\text{Cu}|\text{filling solution}|\text{membran}|\text{test solution}||\text{saturated KCl}|\text{AgCl}|\text{Ag}$  or  $\text{Ag}|\text{filling solution}|\text{membrane}|\text{test solution}||\text{KNO}_3$  salt bridge $||\text{saturated KCl}|\text{AgCl}|\text{Ag}$ ; *types II*: carbon paste electrode/test solution//saturated  $\text{KCl}|\text{AgCl}|\text{Ag}$ .

The results of the first calibration previous to conditioning differed from the subsequent ones by lower values of both standard potential and slopes. After few measurements the sensor characteristics of the fabricated electrodes became more stable. Electrodes on the basis of  $\text{Ag}_2\text{HgSnS}_4$ ,  $\text{Ag}_6\text{HgGeS}_6$  show an electrode function in relation to the  $\text{Ag}^+$ -ions, and on the basis of  $\text{Cu}_2\text{CdGeS}_4$ ,  $\text{Cu}_2\text{ZnGeS}_4$ ,  $\text{Cu}_2\text{CdGeSe}_4$ ,  $\text{Cu}_2\text{ZnGeSe}_4$ ,  $\text{SnBi}_2\text{Te}_4$  and  $\text{SnBi}_4\text{Te}_7$  - the  $\text{Cu}^{2+}$ -ions within the concentration ranges  $3 \cdot 10^{-6}$  -  $1 \cdot 10^{-1}$  M. The limit of detection was close to  $(1-2) \cdot 10^{-6}$  for different electrodes. The fixed interference method was used to determine the selectivity coefficients towards different ions.

# ION-SELECTIVE ELECTRODES REVERSIBLE TO PHYSIOLOGICALLY ACTIVE AMINE CATIONS: THE MAIN WAYS FOR CONTROLLING POTENTIOMETRIC SELECTIVITY

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Despite the fact that a great lot of ion-selective electrodes (ISEs) with liquid and film polymeric membranes for the determination of physiologically active amines (PhAA) has been described, the factors responsible for their selectivity have not yet been studied sufficiently. In this work, the influence of plasticizer and ion-exchanger nature on the selectivity of ISEs reversible to PhAA cations of various structures has been discussed.

The potentiometric selectivity coefficients ( $K_{ij}^{pot}$ ) of ISEs with poly(vinyl chloride) membranes plasticized with either dibutyl phthalate (DBP) or *o*-nitrophenyl octyl ether (*o*-NPOE) and containing either tris(nonyloxy)-benzenesulfonic acid (TNOBS) or tetrakis(4-chlorophenyl) borate (TpClPB) as ion-exchangers, to gangleronum, spasmolytinum, pachycarpinum, papaverinum, dimedrolum, dibasolum, remantadinum, chininum, trimecainum, novocainum, were determined by modified separate solution method (E. Bakker et al., *Analyt. Chem.* 2000 V.72. P.1127) at PhAA concentrations  $1 \cdot 10^{-3}$  and  $1 \cdot 10^{-4}$  M.

The results obtained show that the  $K_{ij}^{pot}$  values to dimedrolum, papaverinum and spasmolytinum against gangleronum (chosen as a standard ion) are almost independent of both ion-exchanger and plasticizer nature. The selectivity coefficients to trimecainum and novocainum are virtually independent of the ion-exchanger nature but increase approximately by 0.3 and 0.4 order respectively, when DBP is used instead of *o*-NPOE. The selectivity coefficients to dibasolum, remantadinum and chininum increase 3-10 times, when DBP is used instead of *o*-NPOE as a plasticizer, and 2-8 times when TNOBS is used instead of TpClPB as an ion-exchanger. The maximum effect (up to 2.7 order) of the selectivity change caused by the choice of a plasticizer and ion-exchanger, is observed for the pair remantadinum – pachycarpinum.

It has been shown that the effects found are caused by specific solvation of both the PhAA ionogenic and other polar groups by the plasticizers used, as well as by the influence of ion-exchangers nature on the PhAA cations–anionic sites complex formation constants.



# HYDROGEN PEROXIDE SENSOR WITH ADVANCED ANALYTICAL PERFORMANCES

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Monitoring of low levels of hydrogen peroxide is of great importance for modern medicine, environmental control and various branches of industry. The most progressive method of H<sub>2</sub>O<sub>2</sub> monitoring is its amperometric detection on electrode, modified by Prussian Blue (PB). PB modified electrodes allow low-potential detection of H<sub>2</sub>O<sub>2</sub> down to 10<sup>-7</sup>M [1]. The use of the sensors in clinic diagnostic and for ecological monitoring requires further reduction of the detection limit. We have reported before on the possibility for nanostructuring of PB by its electrodeposition through liquid crystal template for improving of analytical performances [2].

In this work we report on the possibility to simplify the PB nanostructuring procedure. It may be done by electrodeposition of nanostructured PB films without using template. Analytical performances of the resulting PB based nanoelectrode arrays have been studied in course of hydrogen peroxide detection in FIA mode. The value of sensitivity for obtained sensors was 0.2 AM<sup>-1</sup> cm<sup>2</sup>, which is two times more than for electrodes modified by PB electrodeposited through liquid crystal template. Detection limit was 10<sup>-8</sup> M and a linear calibration range was extending over six orders of magnitude of H<sub>2</sub>O<sub>2</sub> concentrations, which are the most advantageous analytical performances in hydrogen peroxide electroanalysis nowadays.

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# SENSORS WITH RESPONSE ON SOME XANTHENE DYES BASED ON MOLECULARLY IMPRINTED ELECTROSYNTHESIZED POLYMERS

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The development of highly selective chemical sensors for complex matrixes of medical, environmental, and industrial interest has been the object of greate research efforts in the last years. Recently, the use of artificial materials – molecularly imprinted polymers (MIPs) - with high recognition properties has been proposed for designing biomimetic sensors, but only a few sensor applications of MIPs based on electrosynthesized conductive polymers (MIEPs) have been reported [1-3].

In the present work, the synthesis of two MIEPs is described and their application for sensing and separation two xanthene dyes – rhodamine and fluorescein – has been reported.

Two MIEPs investigated were poly(*o*-phenylenediamine) (PPDA) and poly(N-phenylglycine) (PPG). They were synthesized on device for cyclic voltammetry (CVA) with Pt working electrode, Ag|AgCl reference electrode and Pt counter electrode of solution which cntained 0.05 M functional monomer (*o*-phenylenediamine or N-phenylglycine), 0.05 M sulphuric acid, 0.1 M crosslinker (resorcinol), 2% dimethylsulfoxide (DMSO) and 0.02 M template molecules (rhodamine or fluorescein). Electropolymerization was carried out over 300 cycles between +0.2 V and +1.0 V at a scan rate 0.1 V/s. After electropolymerization, working electrodes were soaked initially 25 ml water followed by washes each using methanol.

The made electrodes had linear characteristics of functions  $E = f(pC)$  and good selectivity of rhodamine electrode concerning fluorescein electrode and *vice versa*. The PPG electrodes had some better characteristics in selectivity and linearity than PPDA electrodes. The MIEP films based on PPG and PPDA may be used for separation of rhodamine and fluorescein mixtures.

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# DEVELOPMENT OF A DNA SENSOR BASED ON ALKANETHIOL SELF-ASSEMBLED MONOLAYER-MODIFIED ELECTRODES

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In recent years there has been a considerable interest in the development of DNA sensors, due to its theoretical and practical significance in many fields. The detection of DNA hybridisation is of central importance in the diagnosis and treatment of genetic diseases, detection of infectious agents, industrial processing and reliable forensic analysis [1,2]. In this work an electrochemical DNA biosensor based on recognition of double or single stranded DNA (ds-DNA/ss-DNA) immobilised on a modified gold electrode is presented for denaturation and hybridization detection. DNA is covalently bond on a self-assembled 3-mercaptopropionic acid (MPA) monolayer by using water soluble N-3-(dimethylaminopropyl)-N'-ethylcarbodiimide hydrochloride (EDC) and N-hydroxisulfosuccinimide (NHSS) as linkers. The interaction between the immobilised DNA and methylene blue (MB) is investigated using square wave voltammetry (SWV). Under the optimized label SW voltammetric measurement and ss-DNA probe immobilization conditions, both hybridization and denaturation events can be detected by using the oxidation signals obtained after accumulation of MB on the DNA sensors. The MB stripping signal was significantly lower at the ds-DNA-modified electrode than at the ss-DNA-modified electrode. Denaturation and hybridization events directly at the electrode surface were also optimized. The reproducibility and increase of the magnitude of the MB peak current after DNA denaturation are highly promising features towards the preparation of reusable DNA sensors. RSDs of 6.2% and 7.5% were obtained for 75  $\mu$ M MB responses (n=5) at the ss-DNA-EDC/NHSS-MPA-AuE and the ds-DNA-EDC/NHSS-MPA-AuE, respectively, indicating a good stability of DNA when immobilized atop the SAM-modified electrode. The fabrication procedure of the DNA sensor was reliable (RSDs of 5.3% and 6.0% for five ss-DNA and ds-DNA-modified electrodes, respectively, allowing reproducible electroanalytical responses to be obtained with different sensors.

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# MICRO ELECTRO-MECHANICAL SYSTEMS FOR THE DETECTION OF BIOANALYTES USING ELECTROCHEMILUMINESCENCE

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Miniaturization of analytical systems proved to be advantageous with regard to reduction of the volumes of samples and reagents required, allowing medical diagnosis from a drop of blood, and the development of in-vivo sensors and of on-site analysis systems. Moreover, analysis times are usually shorter, several assays can be integrated in a single system without extending the size and complexity of the device, and several steps of the analytical procedure can be integrated and automated within the system. These ideas led to the concept of "labs-on-chips" or micro total analysis systems ( $\mu$ TAS).

Microfabrication techniques used for the production of MEMS (micro electro-mechanical systems) have been successfully used to produce highly efficient microfluidic systems.

Electroosmotic flow (EOF) is thus the mechanism by which liquids are moved from one end of the separation capillary to the other, obviating the need for mechanical pumps and valves. This makes this technique very amenable to miniaturization, as it is far simpler to make an electrical contact to a chip via a wire immersed in a reservoir than to make a robust connection to a pump. More important, however, is that all the basic fluidic manipulations that a chemist requires for microchip electrophoresis, or any other liquid handling for that matter, have been adapted to electrokinetic microfluidic chips.

The reduction of dimensions also reduces volumes which are accessible to the detector. Thus, detection principles related to geometric dimensions of the detector cell are not ideally suited for coupling to microsystems, whereas surface sensitive principles, such as electrochemical methods or optical methods utilizing the evanescent field of a waveguide, or methods which can be focussed on a small amount of liquid, such as electrochemiluminescence (ECL), are better suited. This is why electrochemiluminescence detectors are combined to microsystems. Moreover ECL has found wide applications in biochemistry because of its high sensitivity, relatively simplicity and feasibility under mild conditions.

In this work we discuss some bioanalytes such as amino acids assay by electrokinetic microfluidic chip with ECL detection.

# TEST-METHOD OF NITROXOLINE DETECTION AND DETERMINATION WITH THE REAGENTS IMMOBILIZED IN GELATIN MATRIX

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5-nitro-8-hydroxyquinoline (nitroxoline) is an active ingredient of the drug 5-NOX, which is widely used in medical practice. Nitroxoline forms coloured slightly soluble complexes with cations of d-elements, that was used for development the test-techniques of it detection and semiquantitative determination. The slightly soluble hexacyanoferrates:  $\text{Co}_2[\text{Fe}(\text{CN})_6]$ ,  $\text{Cu}_2[\text{Fe}(\text{CN})_6]$ , and  $\text{Ni}_2[\text{Fe}(\text{CN})_6]$ , physically fixed in gelatin, were used as reagents for identification of nitroxoline. Gelatin-immobilized (GIM) reagents allow to receive test-tools in the form of transparent hydrophilic films with well developed surface.

The region of unreliable reaction at use of created test-tools for visual detection of nitroxoline has been studied. The distribution of frequencies of the detection in region of unreliable reaction for system with  $\text{Cu}_2[\text{Fe}(\text{CN})_6]$  the best fit to the function of normal distribution, for other systems – function Weibulle. A detection limit ( $c_{\min}$ ) and other characteristics of test-systems are reduced in the table:

GIM-reagent	Change the colour	Region of unreliable reaction, mmol/ml	$\delta$	$c_{\min}$ , mmol/ml
$\text{Co}_2[\text{Fe}(\text{CN})_6]$	Green–yellow	10–28	1,8	28
$\text{Cu}_2[\text{Fe}(\text{CN})_6]$	Brown-pink–green-yellow	0,3–9,2	28	9,2
$\text{Ni}_2[\text{Fe}(\text{CN})_6]$	Colourless with green hue–brightly yellow	1,7–8,8	4,2	8,8

Relative width of region of unreliable reaction ( $\delta$ ) was estimated as the ratio of difference between maximum and minimal concentrations to minimal concentration in this region. The test-system containing  $\text{Co}_2[\text{Fe}(\text{CN})_6]$  is the most resistant to uncontrolled factors, the lowest detection limit characterizes a film with  $\text{Ni}_2[\text{Fe}(\text{CN})_6]$ . The possibility of test-films application for quantitative determination of nitroxoline is testified.

## SENSOR FOR DETERMINATION OF PHOSPHORUS IN STEEL

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For research of alloys in the liquid state the chemical analysis can be applied only then, when high-temperature samples sharply to chill, that is to temper. But it can cause changes in the state of the system. That is why it is the best to determine composition of alloys in the liquid state.

The quality of steels and alloys depend on content at them alloying elements, oxygen, phosphorus, and sulfur. The presence of harmful admixtures worsens properties of materials that show up in formation of cracks, decline of plasticity and malleability. In this connection great value has operations, which allow in this as result to decrease content of solute oxygen, phosphorus, sulfur - desoxidation, desulfuration, dephosphorization.

For the improvement of processes of desoxidation, desulfuration and dephosphorizations of metallurgical melts it is necessary to develop the methods of quick and exact determination of concentrations of carbon, phosphorus, hydrogen, sulfur in the process of receipt of steel, cast irons and alloys. It is most effectively possible to execute by electrochemical sensors. Now such sensors are developed only for express determination of content of oxygen in metallic melts. Similar sensors must be constructed for determination of content of phosphorus and other harmful admixtures in metallurgical melts, to regulate their composition directly during melting. Elaboration they can be carried out in laboratory conditions, using modern materials and newest scientific achievements.

We developed a sensor for determination of content of phosphorus in metallurgical melts. In quality of ion conductor used orthophosphate of calcium which pressed in tablets  $\varnothing 10$  mm. Tablets (mass 1-2 g) annealed at a temperature  $400^{\circ}\text{C}$  during 7-10 h. Tablets melts then in a quartz tube and placed the alloy of iron containing 1 mass % P. Control of sensor lead on Fe – P melts. Information on activities (effective concentration) of phosphorus in Fe – P melts was received. It is set that the isotherm of activity of phosphorus shows negative deviations from the Raouls law. Comparison them with reliable literary information showed that they agree between itself. Thus, reliable data on activities (effective concentration) of phosphorus in metallic melts it is possible to received by created electrochemical sensor for express determination.

## CALIXARENE BASED POLYMERS: SYNTHESIS AND SENSOR CHARACTERISTICS

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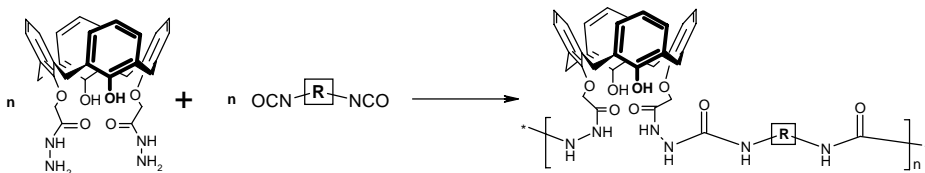
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Structural and chemical modification of urethane containing polymer matrices with macrocycles – calixarenes having reactive hydrazide groups have been carried out and structure, physico chemical and sensor properties of polyurethane semicarbazides (PUS) synthesised have been studied. The polymers obtained (on the base of polypropylene glycol MM 1000 and polysiloxane diol MM 860, hexamethylene diisocyanate and calixarene dihydrazide) are identified by IR-spectroscopy, size exclusion chromatography (SEC), DSC, WAXS and SAXS methods.



Characteristics of PUS' thin films as sensitive support layers towards to a different organic vapors are determined using 8-channel QCM (Quartz crystal microbalance resonator) based sensor array, working cell, gas-supplying pathways, syringe for vapor injection, air filter-drier for providing fresh dry air for purification sensors between sampling, valve for switching “sampling” – “purification” and electronics. According to the results obtained, the analytes analyzed (standard concentration 1000 ppm) regarding their ability to be detected on the surface of calixarene containing polymer sensors are arranged in the following range: methylene chloride > chloroform > benzene > hexane.

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# NOVEL OPTICAL pH SENSORS BASED ON CATECHOL AZO DYE DERIVATIVES

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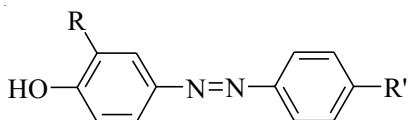
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The glass pH electrode has been the most widely used tool for measurement of pH. Optical pH sensing is one of the most well established methods of pH determinations, which is based on measurements of the absorption spectrum of an indicator, either dissolved in the test solution or immobilized on a substrate.

In this work, we studied optical properties of six catechol azo dye derivatives were synthesized in our laboratory, which general formula are as follow: Among these derivatives, only C<sub>8</sub> and C<sub>9</sub> had good optical properties on triacetylcellulose films.



C<sub>1</sub>: R = H, R' = SO<sub>2</sub>NH<sub>2</sub>, C<sub>5</sub>: R = OMe, R' = Me, C<sub>6</sub>: R = OMe, R' = SO<sub>2</sub>NH<sub>2</sub>,  
C<sub>7</sub>: R = OMe, R' = H, C<sub>8</sub>: R = H, R' = NO<sub>2</sub>, C<sub>9</sub>: R = OMe, R' = NO<sub>2</sub>

C<sub>9</sub> pH-sensitive film had a dynamic range from 6 to 8 and C<sub>8</sub>-film responded at higher pH values (8-10). The membranes showed good reproducibility, reversibility and a short response time (<10 s). They also can be used for at least 3 months without any considerable absorption deviations. These sensors can be used for direct determination of pH in drinking water; detergent and dishwasher liquid that have good agreement with pH meter data.



# AN AMPEROMETRIC ENZYME IMMUNOSENSOR BASED ON SCREEN-PRINTED ELECTRODE FOR THE DETERMINATION OF *KLEBSIELLA PNEUMONIAE* BACTERIAL ANTIGEN

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Precise and rapid detection the pathogenic microorganisms is one the most important problems of clinical medicine. However, some of the conventional approaches are time-consuming and depend on the different conditions observance. Therefore, the immunoassay is widely used for the identification of the small amounts of the biological active compounds due to its selectivity and sensitivity.

The aim of our investigation was the development of the amperometric enzyme immunosensor for the determination of *Klebsiella pneumoniae* bacterial antigen (Ag), causes the different inflammatory diseases. The biosensing part of the sensors consisted of the enzyme (cholinesterase) and antibodies (Ab) immobilized on the working surface of the screen-printed electrode. Bovine serum albumin was used as a matrix component.

The working conditions of the immunosensor (enzyme and antigen concentrations, dilutions of the antibodies, pH of the buffer solution) were found. The cholinesterase immobilized demonstrated the maximum catalytic activity in phosphate buffer solution with pH 8.0. The analytical characteristics of the sensor – the interval of the working concentrations and detection limit – have been obtained. The proposed approach of immunoassay made possible to detect  $5 \cdot 10^{-12}$  mg/ml of the bacterial antigen.

It was established that Ab to *Klebsiella pneumoniae* didn't demonstrate the cross-reactivity to antigens of the relative bacterial species; so, it could be considered that antibodies investigated was highly specific only to the own antigen. The physical-chemical characteristics of the immunological interaction such as constants of formation of Ag-Ab complex were obtained. The binding constants of immune complex were  $Ka_1 = (9.7 \pm 1.1) \cdot 10^{10}$  and  $Ka_2 = (1.7 \pm 0.3) \cdot 10^9$  (mg/ml)<sup>-1</sup>.

The developed amperometric enzyme immunosensor was probed to determine the *Klebsiella pneumoniae* antigen in the human sera samples. The obtained results were juxtaposed with the data of the bacteriological analysis.

## **ADSORPTION OF ORGANIC REAGENTS ON CARRIERS AND ITS APPLICATION IN THE ANALYSIS**

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Recently test-methods of the analysis are widely used; they differ by rapidity, cheapness, simplicity of determination and don't demand availability of the expensive equipment. These methods are used at the control of manufacture, in diagnostic labs, in field and domestic conditions etc. Test - technique have received special distribution in the analysis of objects of environment: natural and sewages, soils, air. The improvement both existing and developing of new methods and techniques of test-determination of elements is an actual problem of modern analytical chemistry.

The researches on fastening of some organic reagents on different carriers (polyurethane foam of marks T 25-3,8, chromatographic paper of marks FN 5 and aerosil) are carried out by us.

The test-techniques of hydrargyrum (II) and zincum (II) ions determination in aqueous solutions with the use of congo red and brilliant green adsorbed on polyurethane foam accordingly are designed on the basis of received data for organic reagents adsorption on it's.

The possibility of magneson, diethyldithiocarbamate of argentums, chloride 2,3,5-tripheniltetrazoly and stilbazo immobilized on a cellulose paper application in the test-analysis is shown. The conditions of reagents immobilization, at which the obtained indicator means give the best metrology characteristics are determined. The test - techniques of magnesium determination by the length of coloured zone of indicator paper stuck in a transparent polymer film, arsenic and cuprum determination by intensity of colouring disks of indicator paper are designed.

The research of congo red and stilbazo adsorption on aerosil is carried out. The test - techniques of hydrargyrum and cuprum determination with the use of obtained solid phase reagents are designed.

The metrology characteristics of designed techniques of elements determination meet the requirements shown to test - methods of the analysis. The time of determination makes 15 - 20 minutes.

# DEVELOPMENT OF CHEMICAL SENSORS FOR VOLATILE ORGANIC COMPOUNDS DETERMINATION

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Methods of analysis of volatile organic compounds admixtures in various objects, as a rule, require separation and concentration followed by the gas chromatographic analysis of concentrate. Besides, for volatile amino-compounds determination a limited number of stationary phases is suitable. Necessary equipment and reagents are not always present in ordinary analytical laboratories, and implementation of the analysis needs a highly skilled staff.

Therefore the problem of development of express, inexpensive and simple in use test-methods for determination of volatile amines is of present day interest.

Methods of analysis based on the use of different sensor systems – electrochemical, optic, fluorimetric, instrumental and visual - mostly meet such requirements.

In this work the results of search of sensor systems suitable for analysis of liquid and solid media for content of volatile aliphatic amines are presented. The most suitable procedure of analysis is “gas extraction - detection”.

Composition materials including indicator reagent and bearer have been investigated as sensor materials. It has been found out that nature of bearer (sorbent or polymer film) is of the main significance. Silica gel, aluminium oxide, porous glass, polyurethane, polyvinylchloride etc have been investigated as bearers.

A decisive influence of acid-basic indicator reagent nature on selectivity of aliphatic amines determination in the presence of aromatic and heterocyclic has been found out.

The influence of different factors on analytical response of the sensors has been investigated.

On the basis of the obtained results simple, reliable and express methods of aliphatic amines determination in natural objects, food stuffs and technological mixtures have been offered.

# DEVELOPMENT OF A CHEMILUMINESCENCE DETECTION OF HERBICIDES RELATIVE TO THE MEDIATED INHIBITION OF THYLAKOIDS IN A $\mu$ -FLUIDIC SYSTEM

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The work presented is part of a European project (Biosensors for Effective Environmental Protection; BEEP) which is aimed at the assembly and application of Photosystem II (PS II)-based biosensors for large scale environmental screening of specific herbicides and heavy metals.

A method of detecting herbicides is proposed; the photosynthetic herbicides act by binding to Photosystem II (PS II), a multiunit chlorophyll–protein complex which plays a vital role in photosynthesis. The inhibition of PS II causes a reduced photoinduced production of hydrogen peroxide, which can be measured by a chemiluminescence reaction with luminol and the enzyme horseradish peroxidase (HRP). The sensing device proposed combines the production and detection of hydrogen peroxide in a single flow assay by combining all the individual steps in a compact, portable device that utilises micro-fluidic components.

The production of hydrogen peroxide by chloroplasts was investigated, and hydrogen peroxide was detected under illumination with concentrations increasing in a time- and light intensity-dependent manner. The presence of herbicides in samples reduces the hydrogen peroxide measured in a concentration-dependent manner. The integration of the above reactions, that have initially been performed in cuvette assays, has been achieved by designing and constructing a microfluidic device, which consists of a flow-channel constructed of machined Perspex sandwiching a laser cut elastomer spacer/flow-channel in which regions of appropriate reagents are immobilised reversibly.

The end device will be responding to a range of pollutants and be used for rapid, low cost pre-screening of large numbers of samples to determine samples that will then undergo further analysis.

## CONSTRUCTION OF A HIGHLY SELECTIVE PVC-BASED MEMBRANE SENSOR FOR La(III) IONS

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A highly La(III) ion-selective PVC membrane sensor based on N'-(1-pyridin-2-ylmethylene)-2-furohydrazide as an excellent sensing material is successfully developed. The electrode shows a good selectivity for La(III) ion with respect to most common cations including alkali, alkaline earth, transition and heavy metal ions. The proposed sensor exhibits a wide linear response with slope of  $19.2 \pm 0.6$  mV per decade over the concentration range of  $1.0 \times 10^{-6}$ – $1.0 \times 10^{-1}$  M, and a detection limit of  $7.0 \times 10^{-7}$  M of La(III) ions. The sensor response is independent of pH in the range of 3.5–10.0. The proposed electrode was applied as an indicator electrode in potentiometric titration of La(III) ion with EDTA.

# **SORPTION-SPECTROSCOPIC AND VISUAL TEST-DETERMINATION OF Pb(II), Zn(II), F<sup>-</sup> AND C<sub>2</sub>O<sub>4</sub><sup>2-</sup> IN WATER AND FOOD-STUFFS**

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Attention has recently been focused on the determination of toxic elements in some objects. The silicas with chromophorous reagents immobilized permit to combine the recovery and preconcentration of elements from high volume of solution with their express visual or sorption-spectroscopic detection. Moreover, the using of specific reagents as modifying agents allows to increasing the selectivity of determination. Silica gels (SG) are the most perspective support for analytical reagents immobilized. The adsorption of reagents on such matrix is known as effective and simple method of surface modification. Xylenol orange (XO) and Methylthymol Blue (MTB) are known to be one of the effective reagents for metal ions spectrophotometric determination. As far as we know, no silicas with XO, MTB and its complexes adsorbed have been proposed for Pb(II), Zn(II), C<sub>2</sub>O<sub>4</sub><sup>2-</sup> and F<sup>-</sup> determination.

In the present work, the technique of XO and MTB immobilization onto silica gel in the form of its complexes with Fe(III) and Bi(III) respectively were found. The acid – base and chemical-analytical characteristics of solid-phase reagents were examined. The optimal conditions of quantitative recovery of Pb(II) and Zn(II) from diluted solutions, such as acidity of aqueous phase, the mass of the sorbents, the volume of solutions and the time of equilibrium reaching, were found. The methods of C<sub>2</sub>O<sub>4</sub><sup>2-</sup> and F<sup>-</sup> determination were based on a competitive reactions of Zr(IV) with immobilized MTB and C<sub>2</sub>O<sub>4</sub><sup>2-</sup> or F<sup>-</sup>. Optimal conditions of C<sub>2</sub>O<sub>4</sub><sup>2-</sup> and F<sup>-</sup> determination in solution using SG, modified ion associates QAS-MTB (pH = 1,5, C<sub>Zr</sub> = 5·10<sup>-5</sup> mol/l). The tolerance limits of metal ions and foreign anions at the optimal conditions were investigated.

The sensitive and selective sorption-spectroscopic and visual test-methods for determination of Pb(II), Zn(II), C<sub>2</sub>O<sub>4</sub><sup>2-</sup> and F<sup>-</sup> in water and food-stuffs were proposed in comparative with known DRS and VT methods.

# APPLICATION OF FUNCTIONAL POLYMERS FOR MODIFICATION OF OPTOCHEMOTRONIC SENSOR ELECTRODES

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Nowadays all over the world considerable attention is focused on development of chemical sensors for the detection of various organic compounds in solutions and gas phase. One of the possible sensor types for organic compounds in solutions detection is optochemotronic sensor – device of liquid-phase optoelectronics that utilize effect of electrogenerated chemiluminescence. In order to enhance selectivity and broaden the range of detected substances the modification of working electrode of optochemotronic cell with organic films is used. Composition and deposition technique of modifying films considerably influence on electrochemical and physical processes in the sensor.

Recently due to rapid development of organic light-emitting diodes a variety of new polymers was synthesized. These polymers contain in their structure different functional groups responsible for charge transfer and efficient light emission. Among utilized light emitting functional groups there are substances that are effective electrochemiluminescers (first of all 9,10-diphenylanthracene (DPA)). DPA is selected because of its luminescent properties stability (high quantum yield, luminescence spectral range etc.) against different external factors and chemical modification, as well as incorporation into polymers. Utilization of such polymers for modification of optochemotronic sensor's working electrode is very promising and attractive. In this work, relying on quantum-mechanical modeling of electronic density distribution in the set of polymers with the inclusion of DPA as a luminescent functional group, the possibility of their application for modification of anode and cathode of DC optochemotronic sensor is analyzed.

# **PHARMACEUTICAL AND BIOMEDICAL ANALYSIS**

*Keynote lectures*



# RECENT DEVELOPMENTS IN ENANTIOSEPARATION OF CHIRAL DRUGS

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Chirality is becoming increasingly important issue in drug development and use. The world-wide market for chiral fine chemicals reached 6.63 billion US dollars in 2000 and is expected to grow at 13.2% annually to 16.0 billion US dollars in 2007. The drug industry is considered to be the driving force of this strong growth, accounting for 81.2% of the total, or 5.38 billion US dollars. These numbers become even more impressive when transferred to drug formulations. Thus, the world-wide market for dosage forms of single-enantiomer drugs was 123 billion US dollars in 2000, up 7.2% from 115 billion US dollars in 1999. The major current trend in enantioseparations is to leave the classical column size and separation scale in two opposite directions: Thus, on one hand chromatography is becoming a valuable tool for obtaining enantiomerically pure drugs on preparative and production scales. On the other hand, the techniques for analytical-scale enantioseparations are continuously miniaturized and microtechnologies, such as capillary liquid chromatography (CLC), capillary electrophoresis (CE) and capillary electrochromatography (CEC) are gaining importance in this field. In addition, lab-on-chip technologies are establishing very rapidly. This presentation will summarize current developments in preparative and analytical scale enantioseparations. Development of more universal, stable and tailor-made chiral stationary phases as well as more efficient and economical separation technologies such as recycling, displacement and especially, simulated moving bed chromatography make chromatography a valuable alternative to the classical techniques for the preparation of enantiomerically pure drugs. With respect to analytical scale enantioseparations for the control of the enantiomeric purity of synthetic intermediates and final products of chiral drugs and dosage forms, stability of formulations or enantioselective metabolism and pharmacokinetics studies, miniaturized techniques such as CE and CLC appear more attractive and should gain popularity in the near future.

# LUMINESCENCE WHOLE-CELL BIOSENSOR ANALYZER FOR WATER TOXICITY ASSESSMENT

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This lecture concerns the development of whole cell biosensors based on immobilized luminescent bacteria for water toxicity assessment. The application of developed biosensors to sample analysis is achieved through incorporation in an automated flow injection analyzer. The analyzer facilitates automated solution handling and transport to the biosensor. Sensing elements are luminescent bacteria immobilized in the biosensor's flow cell. Low level light detection is achieved through photomultiplier tubes incorporated in the biosensor. Cell immobilization techniques are being developed for the *Vibrio fischeri* and *P. leiognathi* luminescent bacteria and evaluated in flow through systems.

This on-going research aims at a) environmental monitoring and b) the development, after further research and collaboration with an instrument manufacturer, of a prototype portable flow toxicity meter as an early warning system for pollution.

# GENERAL LINES OF PHARMACEUTICAL ANALYSIS DEVELOPMENT IN UKRAINE

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Fundamental lines of pharmaceutical analysis development in Ukraine are as follows:

1. Development of new and improvement of existing methods.
2. Analytical support of technological investigations.
3. Standardization and validation of drug quality control procedures.
4. Establishing of the National System of Reference Standards (NSRS) for Medicines.
5. Establishing of the National Program of Professional Testing (PPT) for the Drug quality control laboratories.
6. Estimation of the methods reproducibility in different laboratories.
7. An expansion of the State Pharmacopoeia of Ukraine (SPU).

With regard to the line 1, the development could be noted for the following methods: those, where peroxide derivatives of carboxylic acids are used; methods of multiple-wavelength spectrophotometric analysis; methods of quantitative accounting of a priori information; methods of liquid chromatography (a Unified adsorption center model and a Mobile phase effective concentration conception; an application of micellar chromatography; standardization of TLC-plates).

With regard to the line 2, the progress could be noted for a model of drug release “in-vitro” from ointments and suppositories taking into account time and layer thickness. It was also found an optimal value of thickness of the layer (5 mm) and a critical particle size (60-90  $\mu\text{m}$ ) for suspension ointments and suppositories, when critical size is under this value, the degree of drug release shows no growth. Taking into account mass conversion of enterprises to GMP regulations implementation and generic medicinal product manufacturing, it is obvious that lines 3-7 relating to the procedures standardization and validation, PPT establishing and SPU development, take on a special urgency.

On basis of systematic use of the principle of insignificance, acceptance criteria system of validation characteristics was developed and standardized validation plan of pharmaceutical analysis procedures was proposed, the latter plan found an application in the establishing of NSRS and PPT establishing. Have been developed and issued two editions of the SPU, which is harmonized with European Pharmacopoeia and now is a sole national pharmacopoeia in CIS.

# STANDARD PROCEDURES FOR VALIDATION OF DRUG QUALITY CONTROL METHODS

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According to Pharmacopoeia, methods of drug quality control must be validated. But now there no justified acceptability criteria and standardized validation procedures. It presents problems for analysts during method development.

For criteria development we used systematical application of an insignificance principle (IP). Uncertainty  $\Delta_2$  is insignificant in comparison with  $\Delta_1$  on the level of 95% if their pooled uncertainty  $\Delta_{\text{pooled}}$  is at most 5% exceeds  $\Delta_1$ . It results in an inequality  $\Delta_2 \leq 0.32 \cdot \Delta_1$  that is the main instrument in development of acceptability criteria of validation characteristics.

For standardization of validation procedure we suggested normalized coordinate system (NCS):  $X_i = 100 \cdot C_i / C_i^{st}$ ,  $Y_i = 100 \cdot A_i / A_i^{st}$ , where  $C$  is a concentration,  $A$  – analytical response (absorbance, peak area etc.), index “ $st$ ” indicates reference solution, “ $i$ ” – number of solution. In this coordinate system recuperation coefficient (findings in per cent to entry) is found as  $Z = 100 \cdot Y / X_i$ . As a result, coordinates of all methods are in the unified numerical range (about 100%). It standardizes presentation of data. All main validation characteristics may be obtained from nine-point (+ reference solution) linear regression investigation in the range.

Application of IP and NCS in conjunction with specification tolerance limits enables to substantiate acceptance criteria for linear regression metrological characteristics (residual standard deviation, correlation coefficient, y-intercept), accuracy and repeatability. Acceptance criteria for impurity influence (in spectrophotometric assay), solution stability and intermediate precision are substantiated as well.

Important part of validation procedure is prognosis (on basis of Pharmacopoeial requirements and results of inter-laboratory trials) of sample preparation, final analytical operation and total uncertainties. It enables to forecast method uncertainty in control laboratories.

This approach enables also to substantiate acceptance criteria for detection and qualification limits in impurity control method validation.

Developed standard validation procedure is demonstrated for validation of a spectrophotometric assay of ambroxol hydrochloride tablets. Without any considerable revisions, this approach may be applied to chromatographic methods. Recommendations for validation criteria were included in the State Pharmacopoeia of Ukraine.

# STATE-OF-THE-ART OF BIOOBJECTS ASSAY IN MICROFLUIDIC LAB-ON-A-CHIP DEVICES

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Electrochemiluminescent (ECL) systems combining electro-chemical (substances conversions to ion-radicals and *vice versa* during solutions Faraday electrolysis) and chemiluminescent (non-optical luminescence excitation in pair of particles chemical reactions) proved to be advantageous in assays of different liquid objects such as biological, pharmacological, ecological etc. with organic substances. Two independent channels in those systems, namely electrical (electrochemical) and optical (luminescent), are providing additional advantages for receiving high assay metrological characteristics thus broadening the nomenclature of potential analytes.

The modern trends are the application of high techniques (e.g. microelectromechanical systems and nanotechnology) for miniaturization of analytical systems bringing them to the format of lab-on-a-chip devices. The latter have unique and obvious advantages over conventional 3D macroscale analytical constructions in very small analytes quantities, assay handling, reactant and analyte mixing, diminishing of assay time, portability etc. Rapid upsurge of publications and patents in this field including micro- and nanofluidics over the past decade shows actuality of such technology and devices research and development. This approach has been expanded to ECL assay micro-devices too.

In this paper the critical review and description of the micro-device, i.e. ECL, system and assay technologies for detecting of analytes of biomedical interest are provided. Special attention is devoted to optochemotronic sensor for trace quantities assay, micro- and nanofluidics system peculiarities, the structure of micro-flow cells, types of photodetectors and computer control system of the whole detection process with appropriate software. Performance assay characteristics such as high sensitivity, short response time and good stability are discussed. These results including research and development results obtained in our Laboratory point out that the micro-ECL systems have wide application and good perspectives in different branches for organic analytes determination, first of all in biomedicine, pharmacology etc. anti-terrorist activity including.

## MODERN LIQUID CHROMATOGRAPHY IN MEDICAL ANALYSIS

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Coupling of analytical techniques (detectors) to high-performance liquid chromatographic (HPLC) systems has increased in the last tree decades. Initially, gas chromatography was coupled to mass spectrometry (MS), then to infrared (IR) spectroscopy. Following the main interest was to hyphenate analytical techniques to HPLC.

The most common detectors in HPLC are ultraviolet, fluorescence, electrochemical detector and diffractometer. However, despite all improvements of these techniques it seems necessary to have a more selectivity and sensitivity detector for the purposes of the medical analysis. It should be therefore improvements to couple analytical techniques like infrared IR, MS, nuclear magnetic resonance (NMR), inductively coupled plasma-MS (ICP-MS) or biospecific detectors to the LC-system and many efforts have been made in this field.

Since liquid chromatography-mass spectrometry (LC-MS) was introduced in the field of medical analysis, many challenges were considered using this technique in an attempt to overcome the problems which remained unsolved using other techniques. The studied compounds include abused drugs, hypnotics, antipsychotics, ethyl glucuronide, muscle relaxants, surfactants, natural toxins such as tetrodotoxin and cardiac glycosides, etc. The field of the medical analyses which makes use of LC/MS is indeed expanding.

Hyphenation of HPLC with NMR combines the power of separation with a maximum of structural information by NMR. HPLC-NMR has been used in the detection and identification of drug metabolites in human urine since 1992. The rapid and unambiguous determination of the major metabolites of drugs without any pretreatment of the investigated fluid represents the main advantage of this approach. Moreover the method is non-destructive and without the need to use radiolabelled compounds.

Many different combinations, separation + element-selective detection, have been attempted but HPLC in conjunction with ISP-MS has emerged as one of the best combinations. HPLC is a versatile technique, which due to the variety of separation mechanisms developed, can be applied to a great variety of medically important analytes.

*Oral presentations*

# THE APPLICATION OF CARBOXYLIC ACIDS PEROXIDE DERIVATIVES IN THE CHEMICAL ANALYSIS AND MEDICINE

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The theoretical principles of oxidative ability evaluation of carboxylic acids peroxide derivatives and the choice of reagent and optimal conditions of carrying out the process of peroxyacid oxidation of different nucleophilic functional organic substances groups in the aqueous medium have been developed. It has been found that kinetics and the reaction's mechanism of peroxyacid oxidation of sulphur-(and/or nitrogen) containing compounds are submitted to the general principles of the specific acid-base catalysis. The possibilities and advantages of use of perhydrolysis reactions and hypersensitive chemiluminescent reactions, in which peroxide derivatives of carboxylic acids with a high reactivity have been generated as intermediate products and also reactions of peroxyacid oxidation on the functional chemical analysis of sulphuro- and nitrogen containing organic compounds, etc have been shown.

Specific biological activity of carboxylic acids peroxide derivatives in comparison with their oxidation ability and ionization degree in aqueous solutions has been considered. Peroxyoctanoic, diperoxy-nonandioic and diperoxydecandioic acids give the most intense bactericidal effect among researched carboxylic acids peroxide derivatives. The perspectives of use of the aliphatic middle-chain peracid C8-C9 as anti-infective agents have been discussed.



# NEW APPROACH TO INCREASING OF ROBUSTNESS FOR METHOD OF DETERMINATION OF MOLECULAR WEIGHT DISTRIBUTION IN DEXTRANS

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The main problem of determination of molecular weight distribution (MWD) of dextrans (polysaccharides which are used as active substances for infusion medicines) is low robustness of the existing method. It means that obtained results are strongly dependent on controlled and uncontrolled parameters of chromatographic system; standard substances for calibration; loading on columns etc. It has been showed on practical examples.

Chromatograph Agilent 1100 was used in this work. Dextran standards of "Farmakosmos", Denmark and standard for system suitability test were used for calibration. Different quantities of dextrans were loaded on column set. The largest loading was in compliance with that of recommended by European Pharmacopoeia (loading 1); another loading was 25 % (loading 2) and 10 % (loading 3) of loading 1.

The main criterion of acceptance for results of calculations of MWD for dextran 40 is validity of system suitability test (characteristics of MWD for dextran 40 standard for system suitability test must be in prescribed intervals).

It is found that the validity of system suitability test depends on loading of dextran standard. Characteristics for loading 3 was close to the middle of prescribed interval, for loading 2 it is close to the upper limit, for loading 1 it is outside of the limit.

Methods which are described in Pharmacopoeias (American, British, and European) are based on using "narrow" standards for calibration and "broad" standard for system suitability test. Prescribed limits of system suitability are broad and therefore it may cause large uncertainty of results. But on the other side results are strongly influenced by parameters of chromatographic system.

Robustness of methods based on "broad-on-narrow" approach (one of "narrow" standards is used as "broad" standard for correction of calibration function) is higher but some disadvantages also are observed.

In this work there is proposed approach which allows using 'broad' standards for calibration and system suitability test. The approach is based on main principle of using of standards i.e. maximal closeness of tested sample and standard. It has been showed that the approach allows achieving essential improvement of robustness of method for determination of MWD of dextrans.

# DETERMINATION OF RUTIN BY CATHODIC ADSORPTIVE STRIPPING VOLTAMMETRY

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Rutin which chemically classified as flavonols, has a direct constriction action on the capillary bed and decreases the permeability and fragility of the blood vessels, inhibits lipid peroxidation, reduced the cytotoxicity of oxidized LDL-cholesterol, and inhibits the oxidation of vitamin C. Due to its persistence and water solubility, different methods have been introduced for determination of Rutin in drugs and extractants, mainly based on spectrophotometric method. A defiled electrochemical study of flavonoids with identification of their oxidation products has been performed by Hendrickson et al. Rutin has been determined in vegetable and fruit beverages by HPLC with UV-detection, amperometric, and coulometric method. From the above methods, spectrophotometric and HPLC require sophisticated instrumentation, long analysis time, poor detection limits and selectivity (for spectrophotometric methods), and laborious methods. Therefore, sensitive analytical methods for the determination of Rutin are highly desired. Electrochemical methods, such as adsorption stripping voltammetry are recognized methods for trace determination of reducible or oxidizable compounds that possess surface-active properties. Both of the above methods have higher limit of detection (10 nM) and low selectivity, whereas the proposed method has lower limit of determination (1.0 nM) and higher selectivity. The new method is based on the accumulation of Rutin-Cu(II) complex onto a surface of hanging mercury drop electrode (HMDE) at -0.50 V, then reduction of complex by scanning the potential from 0.05 to -0.40 V vs. Ag/AgCl reference electrode have been applied. Rutin was preconcentrated onto the surface of hanging mercuric drop electrode using Cu(II), for accumulation time of 80 sec. Then the preconcentrated Rutin was analyzed by cathodic stripping square wave voltammetry. The peak potential of copper(II)-Rutin complex was observed at about -0.030 V versus Ag/AgCl reference electrode. The measured current peak at about -0.030 V is proportional to the concentration of Rutin in the range of 2-80 nM. The practical limit of detection is 0.5 nM. The relative standard deviations for six replicate analyses of 10 and 50 nM Rutin were 1.8% and 1.7%, respectively. The influences of chemical and instrumental parameters on the sensitivity were studied. The capability of the method was evaluated in synthetic and real samples.

## OXIDO-REDUCTASES FROM GENETICALLY ENGINEERED YEAST STRAINS AND THEIR BIOANALYTICAL APPLICATION

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Oxido-reductases of microbial origin are of a great bio-analytical importance as the very selective and sensitive bio-recognition elements of biosensors and components of the kits for enzymatic analysis. To construct strains over-producing target enzymes, selection procedures as well as gene engineering approaches are the most effective. Our work has been focused on screening, selection and gene engineering of the yeast strains capable to over-express some oxido-reductases which can be used in bio-analytical technologies to assay practically important analytes, *e.g.* alcohols, formaldehyde, L-lactate. For alcohol oxidase, the over-synthesizing mutant avoid of catalase was constructed and several mutants with modified  $K_M$  values to substrates were isolated from the thermo-tolerant methylotrophic yeast *Hansenula polymorpha*. For formaldehyde dehydrogenase, the construction of the genetically engineered overproducers bearing multi copies of *FDHI* gene was done using integration of the target gene to chromosome from *ARS*-free pYT1-plasmid.

L-lactate-cytochrome *c*-oxidoreductase (flavocytochrome  $b_2$ ) was isolated for the first time from the thermo-tolerant yeast *H. polymorpha*. The mentioned above enzyme preparations were used for construction of the biorecognition elements of electrochemical sensors.

On the base of alcohol oxidase and flavocytochrome  $b_2$ , the enzymatic kits for selective assay of ethanol, methanol, formaldehyde and L-lactate were developed.

*The work was supported by INTAS grant Open Call 03-51-6278, NATO Linkage grant LST.NUKR.CLG 980621 and the grants of the Program "Sensor Systems and Technologies" funded by NAS of Ukraine.*

# SOLID-PHASE REDOX REAGENTS FOR THE DETERMINATION OF BIOANTIOXIDANTS AND TOTAL ANTIOXIDANT ACTIVITY

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Nowadays, the test-methods using chromophoric reagents immobilized on inert matrices attract the growing attention of the researchers. A wide range of test systems have been proposed for the determination of inorganic compounds, mostly metal ions. Instead, the number of the test methods for the determination of organic substances, especially, the bioactive compounds, is rather limited; most of these methods are time-consuming and do not provide sufficient sensitivity and selectivity. No test-methods for the evaluation of such quality criteria of natural products as total antioxidant activity (TAA) have been reported. This work was aimed to elaborate the solid-phase redox reagents for the determination of organic reductants, in particular, polyphenols, and TAA of herbal products.

As modifying agents, the copper-bathocuproine, iron-phenanthroline and copper-tetrabenzotetraazacyclohexadecine (CuTAAB) complexes have been chosen due to their redox properties, stability and high  $\epsilon$  values in visible region. High-dispersed silica with different porosity, particle size and surface area has been investigated as matrices. Immobilization of the reagents by their adsorption was used as this way of reagent fixing on the surface is known to be both simple and reproducible. The conditions of silica modification by *bis*-bathocuproine-copper(II), phenanthroline-iron(III) and CuTAAB chelates and their interaction with organic reductants have been optimized. It was found that the immobilized complexes of planar structure revealed better analytical properties. On the base of the obtained results the methods of solid-phase spectrophotometric and test determination of ascorbic acid have been elaborated and approved in the analysis of pharmaceuticals. As CuTAAB immobilized demonstrated better analytical properties and the ability to react with natural organic compounds, such as polyphenols, it was chosen as an analytical tool for TAA screening. A simple and time-saving “drop-and-measure” test method of herbal product TAA determination has been elaborated. The usefulness of the proposed test method for the evaluation of this quality criterion was confirmed by the correlations between TAA and the contents of the most important groups of bioactive compounds of the analysed phytochemicals and food (Echinacea products, teas, red wines).

## GENERAL BASIS FOR GRUG REFERENCE SUBSTANCES ATTESTATION IN UKRAINE

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The pharmaceutical reference substance system, accepted in USSR, did not meet to modern requirements. For creation of a modern system in Ukraine it was required to develop criteria to uncertainty of analytical pharmaceutical procedures.

The principle of “insignificancy”, enabling use of the given principle for any level of probability is substantiated. The systematic application of the given principle results in developing metrological criteria for pharmaceutical reference substance, analytical validation, evaluation of results of inter-laboratory testing and suitability of the analytical equipment for the pharmaceutical analysis.

It is shown, that for assay of substances and preparations the different approaches («Confirming» and «Inspecting») should be applied. The criteria to analytical procedures uncertainty for tests “Uniformity of dosage units” and “Dissolution” are developed.

The approaches to analytical procedures uncertainty prognosis are developed. The correctness of these approaches is confirmed in 3rd and 4th rounds of pharmaceutical laboratories inter-laboratory testing (“Pharma-Test” program of State Inspection for Quality Control of Medicines, Ministry of Health of Ukraine).

On basis of developed criteria, the theoretical background of reference substances elaboration is developed, and also are developed procedures of elaboration and documentation system for the Ukrainian State Pharmacopoeia RS and for working RS of the pharmaceutical plants. These approaches are successfully applied to elaboration of RS for inter-laboratory testing.

More than 200 species of the Ukrainian State Pharmacopoeia RS are certificated, which are used by all types of Ukrainian pharmaceutical laboratories, and also in countries of former USSR.

# DETERMINATION OF PURINE BASES IN BIOLOGICAL FLUID BY USING MICELLAR THIN-LAYER CHROMATOGRAPHY

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One of trends of development of thin-layer chromatography implies that replacement of aqueous–organic eluents by micellar surfactants solution. This reduces the toxicity, flammability, environmental contamination and cost of the mobile phases, reduce sample preparation in some cases.

The purpose of work is to develop the technique of separation of purine bases (caffeine, theophylline, theobromine) and the technique of detection of purine bases in biological fluid by TLC using micellar mobile phases containing of different surfactants.

The effect of concentration of cationic (cetylpyridinium chloride, CPC), anionic (sodium dodecylsulfate, SDS) and nonionic (Twin-80) surfactants as well as effect of pH value on the characteristics of TLC separation has been investigated. The best separation of three components has been achieved with  $2 \cdot 10^{-2}$  M CPC and  $1 \cdot 10^{-4}$  M Twin-80 solutions, at pH 7 (phosphate buffer). Individual solution of SDS didn't provide effective separation of caffeine, theophylline, theobromine, the rate of separation was low. The separation factor and rate of separation was increase by adding of modifiers – alcohol: 1- propanol (6 % vol.) or 1-butanol (0.1 % vol.) in SDS solution. The optimal concentration of SDS is  $2 \cdot 10^{-2}$  M.

Application of micellar eluent containing Twin-80 or SDS with addition alcohol allows to determine caffeine in blood without previously remove of protein fraction, which moving together with solvent front. The best chromatography characteristics have been achieved by using Twin-80 than SDS in the presence of modifier. Cationic surfactant is unsuitable for this application, since they don't binding of proteins. The technique was tested on blood sample by using the method of known addition at caffeine concentration  $150 \text{ mg} \cdot \text{l}^{-1}$ . The further advantage of micellar eluent in TLC as compared to aqueous-organic solvent has been found, namely, by using of micellar eluent the preliminary conditioning chamber is unnecessary, since micellar solutions have low vapour volatility. This reason make complementary to reduce of analysis time.

# USING CHROMATOGRAPHY-MASS SPECTROMETRY (LC-MS) METHODS FOR THE DECISION OF MEDICAL PROBLEMS

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In recent years, clinical studies on the role of urinary modified nucleosides as the biochemical markers of various types of cancer have been actively undertaken. Most of the urinary modified nucleosides are primarily originated by methylation of either the base part, the sugar hydroxyl part, or in some cases, both parts of the course of biodegradation of tRNA molecules. Hence, their isolation and identification plays a major role in biochemical analysis.

A liquid chromatography-mass spectrometry (LC-MS) method that can quantitatively analyze urinary normal and modified nucleosides in less than 30 min with a good resolution and sufficient sensitivity has been developed. Nineteen kinds of normal and modified nucleosides were determined in urine samples from 10 healthy persons and 18 breast cancer patients. Compounds were separated on a reverse phase Kromasil C18 column (2.1 mm I.D.) by isocratic elution mode using 20 mg/l ammonium acetate – acetonitrile (97:3 % v/v) at 200 µl/min. A higher sensitivity was obtained in positive atmospheric pressure chemical ionization mode APCI(+).

One more serious medical task the determination of corticosteroids in plasma and cerebrospinal liquid of children with acute lymphoblastic leucosis. From the viewpoint of a number of physicians complications often take place from adverse effects of corticosteroids.

The liquid chromatography – tandem mass spectrometry (LC/MS/MS) technique was proposed for the determination of corticosteroids in plasma and cerebrospinal fluid (CSF, liquor) of children with leucosis. Preliminary sample preparation included the sedimentation of proteins, spinning and solid-phase extraction. MS detection was performed by scanning selected ions, with three characteristic ions for every corticosteroids. The limit of detection was found 80 pg/ml of plasma.

**COLLECTION AND IDENTIFICATION OF BIOACTIVE  
ORGANIC COMPOUNDS OCCURRING IN RIVERS AND LAKES.  
ADSORPTION SELECTIVITY OF MONOSACCHARIDES ONTO  
HYDROUS METAL OXIDES**

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As a possible method of concentrating trace amounts of bioactive organic compounds occurring in the hydrosphere, adsorption properties of various compounds have been explored by employing hydrous metal oxides as the adsorbents. To date, a family of organophosphorus compounds and carbonic acids were adsorbed onto hydrous iron oxide, along with the adsorption of monosaccharides onto hydrous zirconium oxide.

In the course of the study, we found that a family of monosaccharides exhibited a definite adsorption selectivity (Langmuir's isotherm adsorption constant), reflecting their molecular structures.

The present paper will describe the results of adsorption experiments toward layered double hydroxides (LDH).

Table. Langmuir's constants of  $a$  and  $W_s$  and the structural parameter R assigned for monosaccharides

Monosaccharides	$W_s$	$a$	R
D-ribose	1.68	5.55	1.00
L-ribose	1.77	5.07	1.00
D-arabinose	0.71	2.98	0.25
D-xylose	0.59	15.21	0.25
D-lyxose	1.17	17.22	0.50
2-deoxy-D-ribose	0.24	0.27	0.00
D-glucose	0.71	4.66	0.25
L-glucose	0.67	4.95	0.25
D-mannose	0.79	10.95	0.50
D-galactose	0.67	3.03	0.42
D-fructose	0.93	25.5	0.83
2-deoxy-D-glucose	0.10	0.33	0.00



# THE INVESTIGATION OF ELEMENTAL DISTRIBUTION IN DIFFERENT PARTS OF MYOCARDIUM IN HUMANS WITH IHD (SRXRF)

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Nowadays the one of the leading cause of death in industrial country is Heart Failure (HF). Under the pathological conditions (e.g., Ischemic Heart Disease (IHD)) the changes in the enzymes activity and ultrastructure of tissue were obtained. The behavior of trace elements may reflect the activity of different types of enzymes. Pathological changes affects only small area of tissue, hence the amount of samples is strictly limited. Thereby, non-destructive multielemental method SRXRF allow to perform the analysis of mass samples in a few milligrams, to save the samples, to investigate the elemental distribution on the sample area.

The analysis was performed by SRXRF at the XRF beam-line of VEPP-3, Institute of Nuclear Physics, Novosibirsk, Russia. For accuracy control the International Certified Reference Materials were used. There were obtained all metrological characteristics, namely precision, accuracy and lower limits of detections.

The complex investigation of the heart of IHD patients with Myocardial Infarction (MI) was performed. The results obtained showed that all investigated elements divided in two groups – the behavior in different parts of the heart of the certain elements (e.g., Se-Rb) were synergetic, the behaviour of another one was antagonistic (e.g., K-Ca, Fe-Br).

The increased concentrations of K, Ca, Fe, Br, Se and Rb in infarction and scar areas are observed for patient with the recent infarction. For the patients with old infarction the levels of these elements are decreased in the same areas. This reflects the intensity of metabolic processes in the pathological area of myocardium. Additionally, the elevated levels of Se was find out in myocardium of right ventricle in both patients, that may be caused by the increasing the activity of the glutathione peroxidase enzyme.

*These investigations are performed in common with the Meshalkin Institute of Pathology of Circulation of the Blood, Novosibirsk, Russia.*

## COULOMETRY IN ANTIOXIDANTS ANALYSIS

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There is an increasing interest in the use and measurement of antioxidants in food, pharmaceutical and biological substrates. Biological antioxidants are compounds protecting biological systems against the potentially harmful effect of processes or reactions that lead to strong oxidative stress caused by free radical formation especially reactive oxygen species. The pathological increase of their generation has already been recognized in over one hundred human and animal diseases including cancer, cardiovascular disease, diabetes mellitus, renal disease and dialysis, cataracts, neurological, liver, periodontal, lung and inflammatory diseases.

Two classes of antioxidants are known: the low-molecular weight compounds (tocopherols, ascorbate,  $\beta$ -carotene, glutathione, uric acid and etc.) and the proteins (albumin, transferrin, caeruloplasmin, ferritin, etc.) including antioxidant enzymes (e.g. superoxide dismutase, catalase, glutathione peroxidase).

Constant-current coulometry allows to determine individual antioxidants in different matrix using electrogenerated reagents particularly halogens (chlorine, bromine and iodine). Electrochemical oxidation of halogenide in acidic medium on the platinum electrode leads to formation of reactive halogen species. They take part in radical, redox reactions and reactions of electrophilic substitution and addition to double bonds of organic compounds. This fact allows to enlarge potential opportunities of galvanostatic coulometry in organic analysis and opens new horizons in application of coulometry.

Wide range of hydrophilic and lipophilic antioxidants including lipoic acid, glutathione, human serum albumin,  $\alpha$ -tocopherol, retinol, calciferols and captopril are investigated by coulometric titration with electrogenerated oxidants using titration end-point amperometric detection. Stoichiometric coefficients of the antioxidants reaction with electrogenerated halogens are established and possible mechanisms of these interactions are discussed. Microgram amounts of antioxidants were determined in model solutions with an RSD of 1 - 6%.

On the basis of the received data, simple, expressive procedures for the coulometric determination of the antioxidants mentioned above in biological fluids and pharmaceuticals have been proposed.

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*Poster presentations*

## ESSENTIAL OIL OF THE ALGERIAN THYME, *THYMUS CILIATUS* DESF.

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*Thymus ciliatus* Desf. is a wild growing plant spread in northeastern Algeria. Although the chemical composition of the volatile oils from several *Thymus* species is well studied, to our best knowledge no research has so far been conducted on this Algerian thyme.

The chemical constituents of the volatile oil obtained by hydro-distillation of the aerial parts of *T. ciliatus* collected at Eastern Algeria in 2002 was investigated, for the first time, by gas chromatography-mass spectrometry (GC/MS). Thirteen components, representing 99.6% of the oil, were detected, of which thymol (79.1%), *para*-cymene (5.6%), carvacrol (4.4%) and *gamma*-terpinene (4.1%) were the major components. Identification of components in the oil was based on retention indices relative to *n*-alkanes and computer matching with the WILEY275.L library, as well as by comparison of the fragmentation patterns of the mass spectra with those reported in the literature. The major component of the oil, thymol is an abundant component of the volatile oil of several thyme species.

## FLOW INJECTION – SPECTROPHOTOMETRIC DETERMINATION OF SELECTED CEFALOSPORINES

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A rapid, sensitive and accurate flow injection method for the determination of cefotaxime, cefuroxime, cefixime and cephalaxime has been developed. It is based on the oxidation reduction reaction between cefalosporines and iron(III). The excess iron(III) is determined spectrophotometrically using thiocyanate coloring agent. Aliquots of each cefalosporines are hydrolyzed using NaOH and filtered to be ready for injection in a simple manifold composed of 3-channels, injector, reaction coil and a spectrophotometer.

Variables such as concentration of reactants, reaction coil length, injection volume, flow rate. etc. are studied and optimized. Reproducibility, linearity, detection limit and statistical evaluation are shown. The methods results are in good agreement to other standard methods.

# APPLICATION OF EUROPIUM-SENSITIZED LUMINESCENCE FOR POST-COLUMN DETERMINATION OF OXYTETRACYCLINE IN BOVINE MILK

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Tetracycline antibiotics have found wide application in animal industries for treatment, preventive maintenance and stimulation of growth of large horned livestock owing to what their residue amounts can be present at milk and meat of animals. Residue amounts of antibiotics are not toxic, however, capable to cause allergic reactions and to promote development of tolerance of the some people pathogenic bacterias. According with the legislative requirements of a number of the European countries it is forbidden to deliver to the population production polluted residual contents of tetracyclines.

For detection residue amounts of tetracyclines in dairy products widely used methods: HPLC, immunoaffinity chromatography, kinetic spectrophotometry, which are expensive and complicated.

The opportunity of use of a ternary complex of ions Eu(III) with oxatetracycline (OxTC) and citrat-ions (Cit) for luminescent detection of OxTC in milk after chromatographic isolation is shown.

To eluate an antibiotic from chromatographic columns as a mobile phase such solvents as methanol, ethanol, propanol, acetone, acetonitrile are usually used. Influence of these solvents on  $I_{lum.}$  ions Eu(III) in a complex with OxTC and Cit has been investigated. It is established, that the used solvents do not reduce  $I_{lum.}$  Eu(III) ions, and sometimes they increase  $I_{lum.}$  by 16-45 %.

The preliminary precipitation of proteins from milk is realized through the addition of solutions of acetic acid (1,7 mol/l) and sodium acetate (1 mol/l) at  $t = 40-45^{\circ}\text{C}$  before chromatographic isolation of OxTC. The precipitated proteins are separated by filtration. OxTC is determined in filtrate after its isolation on chromatographic column. Contents of OxTC was determined on calibration curve which is linear within concentration range 0,01-1,0  $\mu\text{g/ml}$ .

For the determination of the oxytetracycline in milk the detection limit was 5  $\text{ng/ml}$ .

# TLC DETERMINATION OF SACCHARIN IN PHARMACEUTICALS

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Saccharin and its salts are intense sweeteners tasting several hundred times as sweet as sugar. Despite the fact that it may cause bladder cancer in laboratory rats, its ban was rescinded after a public outcry. In 1984, the W.H.O. suggested an intake limit of 2.5 mg saccharin/day/kg b.w. Its content in pharmaceuticals was determined so far by electrochemical, spectroscopic, titrimetric and chromatographic methods. There is only a single report on saccharin determination by thin-layer chromatography [1].

The present study was aimed at development of a simple, sensitive and selective method for determination of saccharin in pharmaceuticals by high performance thin-layer chromatography. For this purpose, silica-gel 60 F<sub>254</sub> plates and ethyl acetate - carbon tetrachloride - glacial acetic acid (3:4:0.5 v/v) as a mobile phase were used. Chromatographic zone corresponding to the spot of saccharin was scanned in the reflectance/absorbance mode at 230 nm. Calibration curve was obtained within the concentration range of 300-1200 ng saccharin per spot. The relationship between the peak area and the amount of saccharin was evaluated by linear regression analysis. The proposed method, applied for saccharin determination in two pharmaceutical preparations (effervescent tablets and a carbomer-based gel) was shown to be simple and reliable providing reproducible results.

1. M. I. La Rotonda, L. Ferrara, *Boll. Soc. Ital. Bio. Sper.*, 51 (1975) 690-5.

## **SIMULTANEOUS DETERMINATION OF LEVONORGESTREL AND ETHINYL ESTRADIOL IN LOW-DOSE ORAL CONTRACEPTIVES BY HPTLC-DENSITOMETRY**

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A high-performance thin-layer chromatography (HPTLC)–densitometric method was developed in order to obtain a novel procedure for routine analysis of steroidal hormones levonorgestrel and ethinyl estradiol in oral contraceptives. Optimization of conditions for the densitometric procedure was reached by eluting HPTLC silica gel plates in a 10 cm×10 cm horizontal chamber. The solvent system consisted of toluene–hexane–methanol (2.0:2.0:0.25, v/v/v). Densitometric analysis of drugs was carried out in the reflectance mode at 225 nm by using a computer controlled densitometric scanner and applying a calibration in the range of 200-800 and 40-160 ng per spot for levonorgestrel and ethinyl estradiol, respectively. The proposed method is precise, reproducible and accurate and can be employed profitably in place of HPLC for the determination of levonorgestrel and ethinyl estradiol in oral contraceptives.

# QUANTUM-CHEMICAL MODELLING OF PROCESSES OF INTERACTION OF ACTIVE FORMS OF OXYGEN WITH PHOSPHOLIPIDES

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Lipids alongside with proteins are the major components of biomembranes which directly and constantly contact with the molecular oxygen dissolved both in intercellular and intracellular liquid. This creates objective preconditions for the process of oxidation in them that goes through the stage of formation of free lipid radicals. Easily carried out and autocatalytically amplified in these conditions lipid peroxidation can result in infringement of biological membranes structure and their functions. But it does not occur due to existence and functioning of the whole hierarchy of protective adaptations - natural antioxidants (AO) - tocopherols, ubiquinones (a synonym coenzyme Q10) and vitamins of group K which are inhibitors of free radical activity.

Deficiency of natural AO in the organism brings to intensification of oxidizing processes in lipids and to occurrence in them of oxidation products in quantities that are above normal.

The aims of the given work are investigation of interaction processes of active forms of oxygen with phospholipids under action of natural antioxidant Q10; development of chemical model on the basis of physical and chemical behaviour of Q10 and corresponding mathematical model.

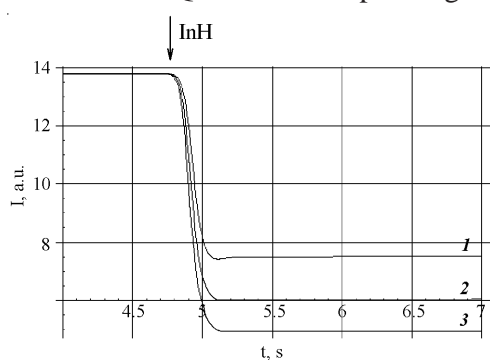


Fig. 1

The mathematical model was based on the scheme utilized in chemiluminescent method that was supplement with the reactions of radicals, formed of inhibitor molecules – AO.

On the fig. 1 is given the family of curves displaying the dependence of chemi-luminescence intensity ver-sus time at injection of AO (the arrow shows the moment of inhibitor injection).

From figure follows, that in case of injection of small concentration of AO in it will be consume rather slowly, that results in slow variation of luminescence intensity during certain time.

*Scientific supervisor – Dr.Phys.-Math.Sc. Prof. Rozhitskii N.N.*

## **DETERMINATION OF ELEMENT COMPOSITION OF HUMAN BLOOD SERUM BY ICP AES**

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It is well known that the abnormality of macro- and microelement levels in an organism results in mineral exchange disturbances. Nevertheless, the data of element analysis of biological tissues and fluids are insufficiently used by modern applied medicine. This connects with the lack of methodical developments in the field of the analysis of biological materials. This fact complicates obtaining reliable quantitative information, which may be used in diagnostic and prophylactic purposes. Thus, the foundation of analytical base for determining element composition of varying biological substrates is of a great interest.

The purpose of the study was the development of multi-elemental technique for inductively coupled plasma atomic-emission spectrometry (ICP AES) analysis of blood serum.

Two methods of sample preparation were investigated. The former is dilution of blood serum with 0.1 % Triton X-100, the latter is acid microwave digestion. As evaluated, the most adequate mineralization procedure for determining the majority of elements in blood serum by ICP AES is acid microwave digestion. However, the ICP AES determination of abundant elements (B, Si, Mn), which present in serum at 0.001-0.01 ppm levels should be follow sample dilution with Triton X-100.

The influence of sodium and organic component on analytical signal values of elements of interest is investigated. ICP parameters (flow rate, power and inner injector diameter) are optimized.

In the course of the study ICP AES technique for determining B, Ba, Ca, Cl, Cu, Fe, K, Mg, Mn, Na, P, S, Se, Si, Sr, and Zn in blood serum is developed. Relative standard deviations vary in the range from 0.02 to 0.25 depending on the element. The correctness of results obtained is confirmed by comparing with those of independent analytical methods.



## **BIODEGRADATION OF PHENOL VAPOUR IN A BENCH-SCALE BIOFILTER**

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The purpose of this study was to investigate the feasibility of biological degradation of phenol from polluted air-stream by means of a biofilter, including microorganism content of activated sludge as a nonspecific microorganism. This project was carried out using two Continuous and Batch methods. The continuous experiments have been conducted during a period of 110 days in a bench-scale column packed with a mixture of compost and wood chips, utilizing the activated sludge as the source of microbial population. The experiments were performed at various inlet phenol concentrations from 23 mg/m<sup>3</sup> up to 125 mg/m<sup>3</sup> and different residence times of 23, 28, 38, 57, and 75 s. Phenol concentrations at inlet and outlet of the system were measured using direct colorimetric method or 4-amino-anti-pyridine. The results showed that, the mean of removal efficiency was 61-75% for phenol concentrations of 23-125 mg/m<sup>3</sup>. It was also shown that, removal efficiency was reduced with increasing in phenol concentration at residence times of 23, 28, and 38 s, while, residence time increment to 57 and 75 s (around 60 s) causes to solve this problem. The results of Batch tests showed that, the mean of removal efficiency was 52% using non-specific microorganism. Although the removal efficiencies obtained during these tests are not considerably high, regarding using nonspecific microorganism instead of the pseudomonas putida, the removal efficiencies can be acceptable.

## **DETERMINATION OF THE FUNCTIONAL PROPERTIES OF THE BIOLOGICALLY ACTIVE PELOBISCHOFITE COMPLEX**

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Determination of the functional properties of the biologically active pelobischofite complex was carried out for the diversification of its application at the manufacture of makeup preparations, dermatologic protective shampoos, creams, gels, face packs, lotions and special detergents. Biologically active pelobischofite complex was prepared from Kujalnik therapeutic muds and Permian formation salts. The research was carried out in some directions: determination of the pelobischofite detergency and emulsifiability; study of the pelobischofite influence on the skin transepidermal water loss (TEWL) *in vitro*; combined Kujalnik peloids and magnesium bischofite complex action on the TEWL value of the mesomorphic gel model; diminution of the negative surfactants influence with the pelobischofite.

The gravity measurements of the pelobischofite and appropriate compositions detergency showed the essential increase of this parameter for pelobischofite-surfactant mixtures. Thus the washing power of pelobischofite-surfactant solutions with concentration 0,1% was 90%. From another hand, similar detergency of bischofite-surfactant mixtures was reached for 1% solutions only.

The pelobischofite-surfactant mixtures emulsifying ability was estimated by measurements of the phase immiscibility time for standard "oil in water" emulsion. The measurements of emulsion particles size were also carried out. The experiments showed the essential increase of phase immiscibility time with the pelobischofite contents increase. Some decrease in average particles size of standard emulsion was also registered. The emulsifiability of other magnesium containing preparations was at least twice worse.

Here the TEWL-value measurements showed that Kujalnik peloids and magnesium pelobischofite complex salutary potentize each other in their mixtures and provide the effective preservation of acidic mantle of the skin. Besides, the pelobischofite addition to the cosmetic cream compositions results in the effective coverlet moistening. Also, the pelobischofite addition provides the decrease of the negative surfactants effect on the skin health. The TWL parameter value is less by half, the water balance of the skin is normalized and the wrinkled skin becomes smoothed out and velvety.

# ELECTROPOLYMERIZED FLAVINS AND AZINES AS ELECTROCATALYSTS FOR NADH OXIDATION

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Oxidation of  $\beta$ -nicotinamide adenine dinucleotide (NADH) to  $\text{NAD}^+$  has attracted much interest from the viewpoint of its role in biosensors reactions. It has been reported that several quinone derivatives and polymerized redox dyes, such as phenoxazine and phenothiazine derivatives, possess catalytic activities for the oxidation of NADH and have been used for dehydrogenase biosensors development [1, 2]. Flavins (contain in chemical structure isoalloxazine ring) are the prosthetic groups responsible for  $\text{NAD}^+/\text{NADH}$  conversion in the active sites of some dehydrogenase enzymes. Upon the electropolymerization of flavin derivatives, the effective catalysts of  $\text{NAD}^+/\text{NADH}$  regeneration, which mimic the NADH-dehydrogenase activity, would be synthesized [3].

Flavin adenine dinucleotide (FAD) has been electropolymerized using cyclic voltammetry. Cyclic voltammograms of poly (FAD) modified electrode were demonstrated dramatic anodic current increasing when the electrolyte solution contained NADH compare with the absence of pyridine nucleotide.

The electrocatalytic activity of novel redox films in regeneration of  $\text{NAD}^+/\text{NADH}$  has been investigated by means of chronoamperometry, hydrodynamic and potentiodynamic methods. In order to achieve the most efficient electrocatalytic properties indicated as both the highest heterogeneous rate constant and maximum sensitivity, the further optimization of electropolymerisation conditions has been made.

The electrodeposited film of flavin derivatives would be utilized as a functional material in combination with number dehydrogenases and pyridine coenzymes for the detection of great number of analytes.

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# ESI-MS AND POTENTIOMETRIC STUDY OF MOXIFLOXACIN – ALUMINIUM(III) ION SYSTEM

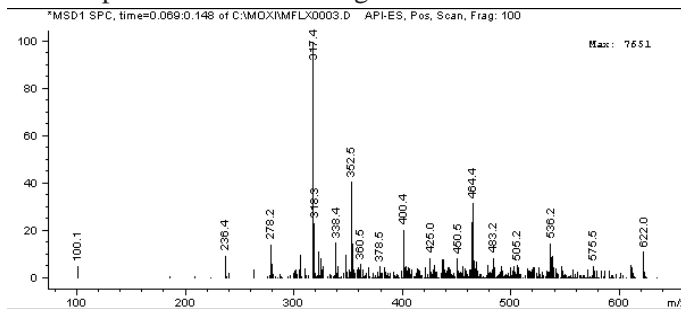
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Moxifloxacin, [1-cyclopropyl-7-(2,8-diazobicyclo[4.3.0]nonane)-6-fluoro-8-methoxy-1,4-dihydro-4-oxo-3-quinoline carboxylic acid] is a fourth generation quinolone effective against acute bacterial sinusitis, exacerbation of chronic bronchitis and community acquired pneumonia. It has been designed to optimize safety and pharmacokinetic profiles. Upon concomitant ingestions of aluminium based antacids and moxifloxacin, bioavailability of moxifloxacin is greatly reduced. The effect was supposed to arise from chelation between aluminium ion and moxifloxacin. In this work we aimed at closer examination of equilibria existing in aluminium(III) - moxifloxacin (mfx) solutions. These were studied by potentiometry and esi-ms measurements.

Potentiometric titrations were performed in the pH interval 3.0-9.0 at  $0.5 \leq C_{Al} \leq 1.0$  and  $0.5 \leq C_{mfx} \leq 1.2$  mmol dm<sup>-3</sup>. The non-linear least squares data treatment using the program Hyperquad 2003 revealed the formation of Al(mfx)<sub>2</sub><sup>+</sup> and Al(mfx)OH<sup>+</sup> complexes with fully suppressed aluminum hydrolysis.

Esi-ms measurements were performed on a Agilent LC\MSD system with the following operational parameters: capillary voltage 4.0 kV, cone voltage, 50 V and solvent flow (methanol – water, 50% v/v) 0.3 mL/min. All esi mass spectral data in the positive ion mode were acquired and processed using HP ChemStation software. The concentration of aluminum was 0.5 mmol dm<sup>-3</sup> while that of mfx were varied in the interval 0.5 – 1.0 mmol dm<sup>-3</sup>. The pH values were pH 4.0, 6.0, 7.2 and 8.5. The spectrum obtained at Al to mfx concentration ratio 1:2 and pH 4.0 is shown in Fig. 1.



**Fig. 1.** Esi-ms spectrum of aluminum-moxifloxacin solution.  $C_{Al} = 0.5$  mmol dm<sup>-3</sup>,  $C_{mfx} = 1.0$  mmol dm<sup>-3</sup>, pH = 4.0

Analysis of ms spectra confirmed the potentiometrically obtained speciation. In addition the complex Al(mfx)<sub>2</sub><sup>+</sup> was identified. Al-mfx chelates are very stable and may increase aluminum solubility.

# COMPARISON OF ESSENTIAL OIL COMPOSITION OF *SALVIA MIRZAYANII* OBTAINED BY SUPERCRITICAL FLUID EXTRACTION AND HYDRODISTILLATION METHODS

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Supercritical fluid extraction (SFE) has been widely used to the extraction processes in pharmaceutical industries. Besides application of SFE in pharmaceuticals, it has been applied on a wide spectrum of natural products and food industries such as natural pesticides, antioxidants, vegetable oil, flavors, perfumes and etc [1-2].

*Salvia* is one of the most important genera of the Family Lamiaceae. Several species of *salvia* are used in folk medicine as antiseptics, astringents and spasmolytics [3].

The effect of different parameters such as temperature, pressure, modifier volume, dynamic and static extraction time on the SFE of the plant were investigated. The orthogonal array experimental design method was chosen to determine experimental plan,  $L_{25} (5^5)$ . In this design the effect of five parameters and each at five levels were investigated on the extraction efficiency and selectivity [4].

Further more, the essential oils of the plant were isolated by hydrodistillation in Clevenger-type apparatus for 5 hours. The chemical compositions of the SFE extract and hydrodistillation were identified by GC-MS and determined by GC-FID.

The main components of *Salvia mirzayanii* were Linalool, Linalyl acetate,  $\alpha$ -Terpinyl acetate,  $\delta$ -Cadinene, Spathulenol, Cubenol and  $\alpha$ -Cadinol. The extraction yield, based on hydrodistillatin was 2.2% (v/w), and based on the SFE varied in the range of 0.65-10.59% (v/w) under different conditions.

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**SIMULTANEOUS DETERMINATION  
OF ACETYL SALICYLIC ACID AND ACETAMINOPHEN  
IN A.C.A TABLETS BY FT-IR/ATR SPECTROMETRY  
WITH MULTIVARIATE CALIBRATION DATA TREATMENT**

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A simultaneous method based on Fourier transform infrared (FT-IR) was developed for the determination of Acetyl Salicylic Acid (A.S.A) and Acetaminophen coupled with an attenuated total reflectance (ATR) accessory. The method is based on the dissolving of drug powder in ethanol followed by FT-IR spectroscopy and prediction of the active components using Partial Least Squares (PLS) regression analysis. Although the drugs mixture showed some regions of spectra overlapping, but they were simultaneously determined with high accuracy, without interference from tablet excipients. A comparison is represented with related multivariate method of Principal Component Regression(PCR) analysis, which is shown to yield less reliable results. In the analysis of real and synthetic samples, precise and accurate values were obtained by PLS-FTIR, providing in all instances standard errors less than 3% and recoveries ranged from 96 to 105%.

Finally, the results were compared with standard method (USP) and good agreements were obtained by PLS-1.

# CYTOCHROME *c* DETERMINATION IN BIOLOGICAL OBJECTS IN NORM AND PATHOLOGY

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Cytochromes *c* (Cyt *c*) can be defined as electron- transfer proteins having one or several haem *c* groups, bound to the protein by one or, more commonly two, thioether bonds. Cyt *c* possesses a wide range of properties and function in a large number of different redox processes.

Investigation of spectrophotometric properties of Cyt *c* has been investigated in this work in order to determine quantity of the enzyme in serum of mice in norm and pathology.

Experimental part was performed on the spectrophotometer SP-46 (LOMO production. Russia). Bovine heart Cyt *c* (Samson-Med production. Peterburg. Russia) (0.25%) have been used as standard solution.

Absorption spectra of standard solutions of Cyt *c* was obtained at different concentration. Maximum of absorption was observed at wavelength 410 nm. It is known haemoglobin and other haems have absorption maximum at the same wavelength. For elaboration of selective method of Cyt *c* determination in serum of mice its reaction with phtalocyanine of copper was investigated. Absorption maximum of Cyt *c* with Cu phtalocyanine in H<sub>2</sub>SO<sub>4</sub> was observed at wavelength 710 nm. Dependence on optical density at 710 nm against concentration of Cyt *c* have linear character in range 0.162·10<sup>-7</sup> - 6.49·10<sup>-6</sup> mol/L.

Absorption spectra of serum of mice with addition of standard Cyt *c* were obtained and its concentration was determined using new approach (table 1).

Table 1. Concentration of Cyt *c* in serum of mice in norm and pathology (n=3, p=0.95).

№	Serum of mice	C·10 <sup>-7</sup> mol/L
1	Norm state	5.94 ± 0.04
2	with LLC (35 days)	1.62 ± 0.03
3	with LLC (20 days)	2.56 ± 0.03
4	Carcinoma Arlicha (5 days)	2.97 ± 0.05
5	Carcinoma Arlicha (7 days)	1.63 ± 0.02

It was shown that Cyt *c* concentration decrease in blood of pathological state of cancer. The greater days carcinoma develops the less concentration of Cyt *c* in serum of mice.

# COMPARABLE CHARACTERISTIC OF ESTIMATING MYCOTOXIN CONTENT USING HPLC AND CHROMATODENSITOMETRY METHODS

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There have been compared the methods of mycotoxin control in food products with aflatoxin B<sub>1</sub> as an example, using both HPLC method with fluorescent detecting on the apparatus Thermo FL 3000 with a column BDS Hypersil C<sub>18</sub> 2.1×150, as well as a chromatodensitometry method on the apparatus CAMAG TLS Scanner 3.

Test preparation for both methods is similar. It comprises an extraction by a water-acetone mixture with its further degreasing; protein isolation and redistribution of aflatoxin B<sub>1</sub> into chloroform, concentrating by means of evaporation of the dissolvent on the rotary evaporator ( $t = 40^{\circ}\text{C}$ ).

There have been determined the conditions of chromatographing. For HPLC method a moving phase: water-acetonitrile (isocratic regime); the length of the excitement wave is  $\lambda_{\text{ex}} = 364$  nm, the length of the emission wave is  $\lambda_{\text{em}} = 416$  nm. For chromatodensitometry method there has been used a double successive chromatographing of the plate in one direction of the movement of the moving phase. For the first and second chromatographings there has been used a mixture of benzene-ether-hexane and chloroform-benzene-acetone, respectively; the length of the excitement wave is  $\lambda_{\text{ex}} = 365$  nm, the length of the emission wave is  $\lambda_{\text{em}} = 450$  nm.

There have been also found the quantitative characteristics of the methods. They are as follows: for HPLC method the linearity is 0.1 ng to 2 ng; the detecting limit is 0.1 ng; the limit of the quantitative estimation makes up 0.0004 mg/kg; a coefficient of variation is 2.74%; for the chromatodensitometry method the linearity is 2 ng to 10 ng; the detecting limit is 0.6 ng; the coefficient of variation is 2.37%. The data obtained have been treated using a regressive analysis.

The comparison of the obtained quantitative parameters of the methods evidences that HPLC method is better by its perceptibility. However, the chromatodensitometry method is more efficient by the indices of expressivity, as far as in a routine analysis it makes it possible to conduct a greater amount of tests during the same period of time, as well as by the criterion: cost – efficiency.

Both methods allow to realize a medical chemical control of the safety of food products by aflatoxin B<sub>1</sub> at the level of 0.005 mg/kg.



# HPTLC IN ANALYSIS OF PARAFARMACEUTICAL PRODUCTS

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Great variety of parapharmaceutical products (PP) is available to customers and their part in self treatment is growing rapidly. But in Ukraine they do not pass proper standardization and there are no guaranties for their content and safety.

Main purpose of our work was too developing methods for standardization of these products. Among methods traditionally used in analysis of plant material and herbal preparations HPTLC has shown to be fast, convenient and not to expensive. Because the goal of analysis is not to prove presence of certain compound, but to check if the product was made of proper raw material accomplishing technological conditions the best standard, in most cases, was properly prepared raw material sample.

Among the verity of PP those containing flavonoids and lipophilic plant ingredients were selected as widely used and rather labile. Sample preparation varied to accommodate certain product type. Samples were chromatographed on "Sorbfill" HPTLC plates in saturated twin trough chamber.

Best results were achieved in following conditions: **Flavonoids** *mobile faze*: ethyl acetate, methanol, water, formic acid (50:2:3:6); chloroform, acetone, formic acid (130:53:17); ethyl acetate, formic acid, acetic acid, water (100:11:11:26); ethyl acetate, methanol, water (77:15:8); *detection* Natural Product reagent (diphenylborinic acid aminoethylester), 1% ethanolic  $AlCl_3$  (less convenient but cheaper) visualization in UV; vanillin-sulfuric and anisaldehyde-sulfuric reagents – white light. **Lipophilic ingredients** *mobile faze*: toluene, ethyl acetate (8:2); toluene, ethyl acetate, acetic acid (7:3:0.1); toluene, ethyl acetate, formic acid (90:10:1); dichloromethane, acetic acid, acetone (2:4:5); *detection* sulfuric and phosphoric acid reagents, visualization – UV; anisaldehyde-sulfuric and phosphomolybdic acid reagents – white light.

The results of this work show that new reliable and fast methods of standardization are needed for PP because many of such products do not contain declared constituents or they are altered because of improper technological conditions. HPTLC with raw material as a standard can be used as effective and fast method in PP standardization.

## THE ANALYSIS OF BIOMEDICAL OBJECTS BY X-RAY FLUORESCENCE

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The new proved scientific data confirming the important role of chemical elements in maintenance of biological processes in human organism have appeared during the last three decades.

Among the vitally necessary elements the most important are Fe, Zn, K, Ca, S. Some of them are imbedded in the structure of many ferments, amino acids, intracellular liquid, the other define transmembrane electrical potential. In the paper the contents of elements in whole blood and serum by X-ray fluorescence spectrometry is studied.

The liquid was applied and dried on cellulose filter (diameter 25 mm). In the present work as an analytical signal we took the relative intensity of analytical lines. This approach reduces non-homogeneity and inequality of a probe. Influence of filter type and sample mass on features of the procedure was studied. The dependence of analytical lines intensity from probe mass was linear for most of above listed elements except Ca presented in most types of filter paper. The relative intensities (reduced to one of the analysis element) was constant or dependent from mass was weak in determined limits. This fact allows to exclude mass control in sample pretreatment. For Ca this dependence was non-linear, therefore, it is necessary to correct analytical signal. Analysis of thin layer is characterized by minimal influence of elements; hence, the relative intensity explicitly determines the relative concentration. As reference sample we used solid synthetic samples with unlimited lifetime.

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## A KINETIC ENZYMATIC METHOD FOR DETERMINATION OF UREA

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A new kinetic enzymatic method for the routine determination of urea in serum has been evaluated. This method is based upon an enzymatic reaction and formation of a coloured complex. The method is based on a modified Berthelot reaction. The reaction was monitored spectrophotometrically at 700 nm ( $t = 25 \pm 0.1$  °C). The optimal pH value, chosen for the investigation of complex, is 7.8.

A differential variant of the tangent method was used for the processing of the kinetic data, because a linear correlation exists between the absorbance at 700 nm and time during the first 6 min after mixing.

Following this procedure urea can be determined with a linear calibration graph from  $0.143 \mu\text{g}\cdot\text{ml}^{-1}$  to  $1.43 \mu\text{g}\cdot\text{ml}^{-1}$ , and a detection limit of  $0.04 \mu\text{g}\cdot\text{ml}^{-1}$ , based on  $3\sigma$  criterion. Results show precision, as well as a satisfactory analytical recovery. The selectivity of the kinetic method itself is improved due to the great specificity that urease has for urea. There were no significant interferences in urea determination among the various substances tested. Method was applied for the determination of urea in serum.

## RESEARCH OF LIGNANS AND ESSENTIAL OILS FROM THE ROOT ARCTIUM LAPPA L.

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*Arctium lappa* L. (burdock) is used as food, preventive and medical remedy. East medicine usually uses it as a fresh root of its first year of vegetation. In some countries burdock is cultivated for use as food and a medicinal herb. Thus the development of analytical documentation for this plant raw material is essential.

The preliminary investigation of the root by chromatography methods have shown high content of phenolic compounds among which flavonoids, oxycinnamonic acids, lignans were found. The last class of the compounds presents the specific interest. In the investigation provided by prof. Maksyutina N.P. there was stated amplification of anti-inflammatory action of oxycinnamonic acids by essential oil.

Lignans show strong antitumor, antiviral and antibacterial activity, as well as influence upon expression of the tumor necrosis factor- $\alpha$ .

The express method of phenolic compounds determination was designed. It is based on heterogeneous azo-coupling reaction of phenols, which different extracts of fresh raw material contain, with aryldiazonium salts grafted on the silica surface. We can carry out phenols analysis on-site, as formation of immobilized azocompounds leads to a drastic change in the sorbent's color. Thus, we propose a new method, that allows to indicate herb phenols in aqueous and non-aqueous medias and to compare it with a well-known Folin-Ciocalteu method.

Separation of chloroformic fraction of raw material by a polyamide sorbent with the following individual fractions elution and crystallization allowed to study lignans of burdock with IR-, mass- and NMR spectroscopy. In result, arctiin, arctigenin, lappaols were identified. Separation of essential oils was provided by the "method two" of State Pharmacopeias of the Ukraine. Essential oils were analyzed by the means of gas chromatography.

These designed methods will allow hereinafter development of the high-performance remedies, using biologically active substances from *Arctium lappa* L. root. Identification of structure and quality contents allows to obtain correct prediction of pharmacological properties of this groups of compounds. Express method allows to make supply of medical herb raw material more rational.

# METHOD DEVELOPMENT FOR THE POTENTIOMETRIC STRIPPING ANALYSIS OF SOLUBLE COPPER IN DENTAL MATERIALS

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Copper is an essential trace metal for all living beings. However, although copper is indispensable for many physiological functions of human organism, the presence of excess amount of copper in the body may be toxic. One possible source of copper in human body that is scarcely investigated is dental materials.

Various materials are used in dental prosthetic practice for the preparation of dental implants, crowns, and bridges. Some of these materials contain copper, which is added in order to improve mechanical or/and chemical properties, but some of them may contain the copper as an impurity. Considering the fact that dental implants remain in the oral cavity for a long time, and that they are exposed to the corrosive action of oral fluids and various kinds of food and beverages, it is necessary to check their possible harmful effects upon the human health.

The aim of this study was to define the method for the determination of soluble copper in dental materials by applying the potentiometric stripping analysis (PSA). We employed the PSA with dissolved oxygen as an oxidant and diffusion conditions of mass transfer during the analytical step. The use of already dissolved oxygen as an oxidizing agent reduced the contamination risk and simplified the copper determination procedure. A glassy carbon electrode with electrodeposited mercury thin film was used for copper determination in acetic acid extracts of various dental materials.

In order to find optimal conditions for the soluble copper determination we examined the influence of electrolysis potential, electrolysis time, and the solution stirring rate on the accuracy and sensitivity of determination. We found that the optimal parameters for PSA determination of copper were: electrolysis potential of  $-0.9$  V vs.  $3.5$  mol/dm<sup>3</sup> Ag/AgCl, electrolysis time of 300 s, and solution stirring rate of 4000 rpm. The soluble copper content in samples investigated in this study varied from 1.85 to 4.85 ppm. Very good correlation between the copper content determined by PSA and AAS indicated that PSA could be successfully applied for the soluble copper content determination in various dental materials.

# **NOVEL EXPRESS METHODS FOR OUTDOOR RAPID DETECTION OF TOXIC IMPURITIES IN ENVIRONMENT AND SOCIALLY INSECURE PHARMACOLOGICAL SUBSTANCES**

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The purpose of this report is creation of fast chemical test-systems with quite enough low detection limits and enough high selectivity.

Ever-growing problems of environmental pollution by man-caused toxic and physiologically active substances, as well as increase of non-medical use of some pharmacological psychotropic drugs necessitate creation of new fast and highly sensitive chemical control methods. In particular, it is important, that such methods of determination could be applied at the place of sampling that is of great importance as in the field conditions, first of all at the analysis of objects of an environment, and in the stationary ones, for example, at the control of technological processes, in the medical and law-enforcement establishments or under domestic conditions. Convenience and simplicity of application, high sensitivity and reliability of determination are the main demands imposed on out-of-laboratory test-methods.

The most suitable method of fast and simple control of the presence of dangerous substances is analytical detection by means of simplified methods - the so-called express-tests which allow quickly and reliably revealing and estimating the content of chemical substances in various objects. Express-tests are based on sensitive reactions which fix analytical effect visually or by means of portable instruments. Among types of indicator reactions were studied reactions of complex formation, oxidation-reduction, diazotization, azocoupling and oxidative condensation of organic substances, which are accompanied with the formation of colored products or with their discoloration.

It is implied that personnel without special skill will be able execute all kinds of testing under out-of-laboratory conditions.

Authors are designed row sensitive and selective test-systems for analysis of heavy metals, active chlorine, phenols, nitrates, nitrites, phosphate etc. for analysis of objects of an environment and for control of ions Fe contents in the technological solutions of  $\text{KH}_2\text{PO}_4$ , as well as for testing some of pharmacological psychotropic drugs: alkaloids (including opiates), cannabis as well as pharmaceutical preparations of phenothiazines, barbiturates and 1,4-benzodiazepines series too.

## COMPLEX APPROACH TO THE INVESTIGATION OF THE PHYSICO-CHEMICAL PROPERTIES OF COSMETIC RAW

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Carbopol is widely used in cosmetic and pharmaceutical practice as a gel-former. Carbopol resins are hydrophilic polymers which swell in water solutions and transform into the gel form at neutralization. At the elaboration of special cosmetic preparations in which carbopol is used, the problem of raw materials compatibility appears. For example, some extracts of aromatic pectin containing materials destroy the gel structure of carbopol. High contents of bivalent metal ions, in particular calcium ions, destructively influence onto the gel-making ability of the system too.

The aim of the investigation was to study the influence of calcium and sodium ions, pectin containing extracts of aromatic vegetative raw materials and mumio on the carbopol gelation; to develop the procedure of calcium and sodium ions mass part determination in extracts of aromatic vegetative pectin containing raw materials; to establish the macro- and microelement composition of mumio.

Determination of  $\text{Ca}^{2+}$  and  $\text{Na}^+$  ions in raw cosmetic materials was conducted with the developed method of flame photometry. A necessity of development of method of samples preparation arose up in the work process, as this spicily-aromatic raw material contained pectin in amount 0.1-0.5% and that prevented preparation of samples by standard method of extracts dilution and required incineration of analyzed sample, time of analysis was increased in 60 times. It was established that  $\text{CaCl}_2$  solution with the concentration 0,4 % caused destructions of the carbopol gel. It was established that the addition of 0,1%  $\text{CaCl}_2$  and 0,1%  $\text{NaCl}$  salts solutions into the system intensified the effect of negative action of these salts onto the gel structure and the gel destructed completely.

The analysis and summarizing of data obtained allowed to establish the norms of Stevia and Sudanese Rose extracts content in compositions of cosmetic preparations in the gel form.

The determined macro- and microelement structure of mumio specifies onto the expediency of the application of this biologically active substance as a cosmetic raw material in the cosmetic compositions, which do not contain carbopol. The developed procedure for calcium and sodium ions determination in pectin-containing vegetative extracts is express and it is recommended for application at elaboration of cosmetic production compositions on the carbopol base.

**ANALYSIS OF THE ESSENTIAL OIL OF *KELUSSIA*  
*ODORATISSIMA* MOZAFFARIAN FROM IRAN**

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*Kelussia odoratissima* Mozaffarian is a new genus and species of Apiaceae which its leaves is used by local people for its sedative effects and also as a food flavouring agent. The leaves in the young plant are yellow but as the plant grows the leaves get green. Phthalides are known to be responsible for the characteristic odor and probably the pharmacological effects of the plant.

In this study in order to compare the green and yellow leaves of plant they were separately collected and their essential oils were extracted by water-distillation method and analyzed by GC and GC/MS. The main constituents were separated and analyzed by TLC, IR, NMR and UV methods.

It was found that phthalides especially Z-ligustilide (90%) were the major components of the oil of young yellow leaves and as the leaves get green the amount of phthalides decreases (22.5%).



## DETERMINATION OF DNA BY ITS ENHANCEMENT EFFECT ON THE FLUORESCENCE OF Tb<sup>3+</sup>-NORFLOXACIN COMPLEX

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Lanthanide cations and their complexes are used as probes and labels for direct determination of organic analytes, nucleic acids and in immunodiagnosics assays. These ions form complexes whose luminescence is the result of an efficient intramolecular energy transfer process from the excited triplet state of the ligand to the emitting level of the lanthanide. These chelates possess narrow emission bands and a large Stokes shift, which can be exploited to decrease the interference caused by the biological background. General requirements for luminescent lanthanide chelates to be used as probes for bioassays are the high quantum yield of the emission, high kinetic stability and good water solubility.

Here we present terbium complex with norfloxacin (L) which is highly luminescent, has high stability and solubility in water and does not require the addition of enhancers such as micelles. The triplet-state energy level of ligand, the relative quantum yield and the excitation maxima of this terbium chelate were determined. The luminescent parameters were analyzed in urotropin HCl-buffer at pH 7.8. The excitation and emission maxima of the complexes are at 330 and 545 nm, respectively. We also observed the fluorescence enhancement in 38 times of the Tb complex with ligand upon titration with nucleic acid (ct DNA). The key factor is the equimolar concentration of Tb<sup>3+</sup> and the ligand (0.5 μmol/l). The potential interference of various substances and effect of ionic strength were studied. Under optimal conditions, the luminescence intensity linearly depends on the concentration of ct DNA within the range of 0.005-1.2 μg/ml. The sensitivity of this method (LOD 0.001 μg/ml) is better to that of the detection for DNA by ethidium bromide (LOD 0.01 μg/ml).

The mechanism of interaction with DNA is suggested. Ethidium bromide (EB) displacement assay was performed. We determine the binding constant of Tb-L to DNA to be in the order of  $\lg K = 6.47 \pm 0.4$ . The bathochromic and hypsochromic effects in the absorption spectra of investigated complex were observed and the interaction is assumed to be mainly of the mono-intercalating type.

# COMPARATIVE STUDY OF SPE AND LLE FOR PRECONCENTRATION OF URINARY 1-HYDROXYPYRENE AS A BIOMARKER OF EXPOSURE TO PAHS PRIOR TO HPLC

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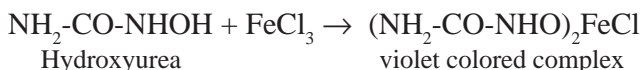
Trace residue analysis of compounds in various matrices is an essential process for evaluation of different exposures to such toxicants, in which, preparation of samples is one of the most time-consuming and error-prone aspects prior to chromatographic analyses. A comparative study of sample preparation was performed to preconcentrate urinary 1-hydroxypyrene (1-OHP) as a major metabolite and biological indicator of the overall exposure to polycyclic aromatic hydrocarbons (PAHs) generated by various industrial and environmental processes. To perform this study, solid phase extraction (SPE) was optimized with regard to sample pH, sample concentration, loading flow rate, elution solvent, washing solvent, sample volume, elution volume, and sorbent mass. The present approach proved that, 1-OHP could be efficiently retained on C18 sorbent based on specific interaction. Further study employed methanol to extract the analyte from spiked urine. Along with, a nonclassic form of liquid-liquid extraction (LLE) also was optimized with regard to solvent type, solvent volume, extraction temperature, mixing type, and mixing duration. The results showed that, 1-OHP could be relatively well extracted by methanol at optimum time of 2 minutes based on moderate specific interaction. At the developed conditions, obtained recovery of SPE was 99.96%, while, the LLE extraction recovery did not exceed 87.3% and also, based on applied sample volume, the limit of detection (LOD) achieved by SPE was 0.02 µg/l showing at least ten times less than that of LLE. The procedures were validated with three different pools of spiked urine samples showed a good reproducibility over six consecutive days as well as six within-day experiments for both developed methods as suitable results were obtained for CV% (less than 3.1% for SPE and between 2.8% and 5.05% for LLE). In this study, a high performance liquid chromatography (HPLC), using reverse-phase column was used. The mobile phase was methanol/water run at constant flow rate of 0.8 ml/min and a fluorescence detector was used, setting at 242 nm and 388 nm. Although the recovery and LOD were obtained for SPE method shows more efficiency, such results for LLE is also relatively efficient and can be applied for majority of similar studies. However, there is a significant difference between the obtained recoveries of SPE and LLE ( $P < 0.05$ ), showing that, SPE is superior.

# SPECTROPHOTOMETRIC DETERMINATION OF HYDROXYUREA AS A COMPLEX WITH FERRIC CHLORIDE AFTER STABILIZATION BY FERROUS IONS

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A simple spectrophotometric procedure for the determination of hydroxyurea (HU) has been developed. This procedure is based on the complex formation between HU and  $\text{FeCl}_3$ . The violet colored complex between HU and  $\text{FeCl}_3$  ( $\lambda_{\text{max}} = 560 \text{ nm}$ ) was not sufficiently stable to allow the spectrophotometric determination of HU. It was found out that the addition of ferrous ions stabilize the complex which could be attributed to the reducing properties of ferrous ions. The later do not produce interfering products with HU. The molar extinction coefficient of the  $(\text{HU})_2\text{FeCl}$  complex was calculated to be  $= 1.41 \cdot 10^2$ . The molar ratio of HU to ferric ion in the complex was found to be 2 to 1 by the mole ratio method, therefore a general formula could be assigned to the complex as  $(\text{NH}_2\text{CO-NHO})_2\text{FeCl}$ . The lower limit of determination was found about 200  $\mu\text{g}$ . The calibration curve was linear within 0-2.4 mg/ml solution. This method is applicable for the determination of HU in capsule formulation.



Harmon RE., Dabrowiak JC., Brown DJ., Gupta SK., Herbert M., and Chitharanjan D. Metal Complexes of 1-Substituted 3-Hydroxyureas. *Journal of Medicinal Chemistry*, 1970, 13(3), 577-579.

## FLUOROMETRIC DETERMINATION OF FLUMEQUINE IN HEN MEAT TISSUES

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Flumequine is a representative of fluoroquinolones which are high-effective antimicrobial medicines used as fodder supplements in cattle-breeding. This causes the necessity in effective testing techniques to determine the content of flumequine in meat products. Fluorimetric determination based on sensitized luminescence of fluoroquinolone chelates with lanthanides is a promising one. The literature lacks information of flumequine determination with the aid of sensitized fluorescence.

The aim of this work was to study the influence of a second ligand, the concentration and nature of surfactants on flumequine-sensitized fluorescence of lanthanides and the usage of such a mixed-ligand complex for fluorimetric determination of flumequine in hen meat tissues.

Flumequine is shown to form a complex compound with terbium(III), whose fluorescence spectrum has one band with a maximum at 545 nm (emission of terbium(III)), it corresponds to the  ${}^5D_4 \rightarrow {}^7F_5$  transition. The emission intensity of the binary chelate rises by 30% in the presence of a second ligand (1,10-phenantroline) whereas the presence of non-ionic surfactants leads to a decrease of the fluorescence intensity of the mixed-ligand chelate. Additives of cationic surfactants slightly increase the emission signal, and introduction of anionic surfactant (sodium dodecylsulfate) micelles raises the intensity by 200%. The influence of the medium acidity on the emission intensity of the analyte is shown. Optimal concentrations of terbium(III) ions, 1,10-phenantroline, sodium dodecylsulfate and the mixing order have been found. The developed technique of flumequine detection in hen meat was put to an evaluation test. The correctness of this analysis was checked by the introduced-found method.  $S_r$  did not exceed 0.03.

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# FLUORIMETRIC DETERMINATION OF HISTAMINE WITH *o*-PHTHALDIALDEHYDE IN THE PRESENCE OF REDUCING AGENTS

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Histamine is the biological amine, playing an important role in living systems, but it can also cause unnatural or toxic effects when it is consumed in large amounts. It can occur with some diseases and with the intake of histamine-contaminated food, such as spoiled fish or fish products, and can lead to undesirable effects as headache, nausea, hypo- or hypertension, cardiac palpitations, and anaphylactic shock syndrome. So, there is a need to determine histamine in biological fluids and food.

Several methods were reported for the analysis of histamine, but the fluorimetric determination with *o*-phthaldialdehyde (OPA) the most widely used. It was shown that adducts, formed in the reaction of histamine with OPA in the presence of reducing agent, is more stable and gives high relative fluorescence intensity. The influences of different tiols on the fluorimetric determination histamine with OPA have been investigated.

2-mercaptoethanol (2ME), 3-mercaptopropionic acid (3MPA) and cysteine (Cys) have been used as reducing agents. Optimal reaction conditions have been found for each reagent. It has been determined that variations in thiol, pH, time of fluorophore formation and the use of phosphate vs borate aqueous buffers have dramatic effects on the corrected relative fluorescence intensity and stability.

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# CONCENTRATION OF ANTIBIOTICS (CEFAZOLINE AND LEVOMYCETINE) ON THE MODIFIED SILICA

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Cephalosporin antibiotics are the largest and varied class of drugs. These medicaments are widely applied in treating different diseases in the present time. Sorption in modified sorbents is used for concentrating these compounds. The method makes it possible to improve degree of extraction, purify sample from interferences and prolong time of chromatographic column life.

The aim of the work is investigate possibilities of application of Cartridges Packed DIAPAK for concentrating antibiotics Cefazoline and Levomycetine and analyze them by Reversed Phase High Performance Liquid Chromatography (RP HPLC).

Sorption of Cefazoline in Cartridges Packed DIAPAK C<sub>16</sub> and DIAPAK –NH<sub>2</sub> was studied in the static and dynamic conditions.

The most part of drugs was sorbated on DIAPAK C<sub>16</sub> (88% Cefazoline and 94% Levomycetine).

The most part of antibiotics was desorbated by 2 ml of acetonitrile – 82% Cefazoline and 69% Levomycetine. 1.2% Cefazoline and 7.2% Levomycetine were desorbated by 5 ml acetonytrile. Degree of extraction of drugs from Cartridges Packed DIAPAK C<sub>16</sub> is 96% for Cefazoline and 86% for Levomycetine. The antibiotics are not practically sorbated by DIAPAK–NH<sub>2</sub> and the first portions of eluent remove them.

Thus, possibility of application of Cartridges Packed DIAPAK for concentrating different antibiotics and analyzing them by RP HPLC was shown. Maximum sorbated quantity of Cefazoline is 1.2 µg on 1 g sorbent.

Cartridges Packed DIAPAK C<sub>16</sub> use better for dynamic concentrating Cefazoline and Levomycetine.

# IONOMETRIC DETERMINATION OF THE TOTAL CONTENTS OF THE ALKALOIDS OF PAPAVER SOMNIFERUM IN THE EXPERT-CRIMINAL OBJECTS

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The analytical control of the total contents of the alkaloids of narcotic material of the vegetable origin carried out by the extraction-photometric, some types of chromatographic methods. They are very long, complex, difficult and expensive; require using of toxic and high-priced reagents.

Therefore the basic task of scientific work is development of sensitive, selective and simple methods of quantitative definition of the total contents of the alkaloids in the expert-criminal objects with the help of electrochemical methods of the analysis.

The reaction between organic cation (OC) of the alkaloids of Papaver Somniferum and  $\text{PMo}_{12}\text{O}_{40}^{3-}$  heteropoly anion (HPA) was studied by the methods of UV-, IR-spectroscopy and amperometry. Correlation of reactive compounds was established by these method and compose OC : HPA = 3:1.

The slightly soluble ion pair was used as electrode-active substance in a plastered membrane of an ion-selective electrode (ISE) for these alkaloids.

The influence of factor series to electrode characteristics has been established. Dependency of the potential of ISE from concentration of defined substance is linear in interval of concentration  $1 \cdot 10^{-2}$  -  $1 \cdot 10^{-5}$  mol/l at the pH 2,0-6,5. Slopping of the graduated graph form 55-56 mV/pC for single-charge cation. Potentiometric factors of the selectivity  $K_{i/j}$  ISE for alkaloids of Papaver Somniferum has been determined.

A method is proposed of ionometric determination of the alkaloids of Papaver Somniferum in the expert-criminal objects. This method is express, selective and characteristic of a high sensitivity ( $10^{-5}$  mole per liter) and good metrological characteristics.

# ANALYSIS OF MEDICINES BY TLC IN MOBILE PHASES CONTAINING SURFACTANTS AND CYCLODEXTRINES

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Many medicines have been found to cause side effects in the human's body (intoxication and allergic reactions, a toxicological shock, malfunction of organs and systems), especially at lingering taking. So the quality of such medicines is subject to control regulations by the State Pharmacopoeia, and this implies the usage of titrimetric, photometric, and chromatographic techniques.

A systematic study was made of the possibility to employ mobile phases (MP) based on surfactants and cyclodextrines (CD) for determination of sulfanilamide preparations, 8-hydroxyquinoline derivatives, vitamins in drugs. The analyses were made by means of upgoing thin-layer (TLC) and high-performance liquid chromatography (HPLC). Sorbfil, Silufol, RP-3, and Polyamide-6 plates were used as stationary phases in TLC while Diacorb C18 sorbents were used in HPLC. Aqueous solutions of cationic (cetyltrimethylammonium and cetylpyridinium bromides), anionic (sodium dodecylsulfate and dodecylbenzolsulfonate), and non-ionic surfactants (Triton-X100, Bridge 35), and alpha-, beta- and gamma-CD were used as mobile phases. Some solvents and strong electrolytes served as MP modifiers, their concentrations were varied to find optimal conditions for chromatography. The results obtained were used to develop quantitative analysis techniques for streptocide, sodium sulfacyl in liquid drugs by means of HPLC, and for chinazol (in Contraceptin T), ascorbic acid (in multivitamins) by means of TLC.

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# DETERMINATION OF ASCORBIC ACID IN POLYVITAMIN PREPARATIONS BY ION-PAIR THIN LAYER CHROMATOGRAPHY

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The new way of quantitative determination of the ascorbic acid (AC) by means of ion-pair thin layer chromatography (TLC) in organo-aqueous mobile phases containing cetyltrimethylammonium bromide (CTAB) has been elaborated.

The following polyvitamin preparations were analyzed: "Kal'tsid" (OAO "Comfort Plus", Russia), "Asvitol" (OAO "INC Marbiofarm", Russia), "Pikovit" (KRKA, d.d. The New Place, Slovenia), "Yeast with vitamin C" (OOO "EKKO Plus", Russia). Chromatographic experiment has been carried out using Silufol UV-254 (Kavalier, Czech Republic) and acetone - ethyl acetate - acetic acid - ethanol (3:5:1:1) - CTAB ( $2 \cdot 10^{-3}$  M) as a mobile phase mixture. The linearity calibration plot, built in coordinate  $S = f(IgqAC)$ , is valid in the interval 5-25  $\mu$ g. Correctness of the determination has been checked by photometry. The obtained results for the ascorbic acid determination are presented below.

Objects	Content, mg/g	Found, mg/g			
		TLC		Photometry	
		$X \pm \Delta X$	$S_r$	$X \pm \Delta X$	$S_r$
"Kal'tsid"	10	$10 \pm 1$	0.08	$10.4 \pm 0.3$	0.01
"Yeast with vitamin C"	9	$8.0 \pm 2.0$	0.13	$8.50 \pm 0.50$	0.02
"Asvitol"	25	$24 \pm 2$	0.07	$24.7 \pm 0.5$	0.008
"Pikovit"	10	$10 \pm 1$	0.09	$9.60 \pm 0.20$	0.007

*The work was supported by the Russian Foundation for Basic Research, Project No. 04-03-32946.*

# LUMINESCENCE DETERMINATION OF NON-STEROIDAL ANTI-INFLAMMATORY DRUGS DICLOFENAC NATRIUM AND IBUPROFEN

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Non steroid anti-inflammatory drugs have commercial names “Diclofenac natrium” (DN) and “Ibuprofen” (Ibp). They contain arylcarboxylic acids - 2-[(2,6-dichlorophenyl)-amino]-phenylacetic (DN) and *d,l*-2-(4-izobutyl-phenyl)-propionic (Ibp) as an active substances. Agents have anti-inflammatory and analgetic effects and are used widely in clinical medicinal practice. It is necessary to develop methods controlling the quality of agents and revealing falsification as well. With this purpose the method of the Ln(III) ions sensibilized luminescence has been investigated for the determination of above agents.

It has been established, that both DN and Ibp form complex compounds with ions Eu(III), Sm(III), Tb(III) and Dy(III), possessing luminescent properties. The most intensive luminescence is observed for complex compounds with ion Tb(III). It has been shown, that complexation has place in low acidic and neutral water solutions at pH 6,4-7,0. From the data of luminescence intensity for the complex the ratio of component Tb: Lig was established equal to 1:2 by the continuous variations method. Presence at a solution of organic bases 2,2'-bipyridil, (Bipy) and 1,10-phenanthroline (Phen) causes the analytical signal amplification up to 250 (75) times as a result of the Bipy (Phen) inclusion in inner coordination sphere and formation of different ligands complexes with component ratio Tb : Lig : Bipy (Phen) = 1:2:1.

The obtained analytical forms are used for quantitative determination of both Diclofenac natrium and Ibuprofen content in medicinal forms as well as for the testing uniformity of batching of the basic substance in tableted forms. The relative standard deviation (RSD) were 3,7-4,6 % (n = 5; P = 0,95).

The proposed chemical system could also been exploited as a post-column detection system for the HPLC determination of these drugs.

# THE LIFE-TIME ANALYSIS OF ELEMENTAL COMPOSITION OF HUMAN LIVER PUNCTURES (SRXRF)

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The elemental homeostasis is the particularity of total homeostasis of organism, the alteration of the parameters of this system may result in pathological changes. The liver is the organ where the detoxication processes take place. The elemental content of the liver may reflect the pathological processes which occur not only in the liver but also in the whole organism.

The specimens analyzed are the punctures of human liver. This provides the life-time investigation of elemental metabolism in liver of patient. This is very important aspect, because the information obtained from autopsy is distorted because of fast processes in the liver post mortem.

The analysis was performed by SRXRF at the XRF beam-line of VEPP-3, Institute of Nuclear Physics, Novosibirsk, Russia. For the accuracy control the different types of the International Certified Reference Materials were used. There were obtained all metrological characteristics, namely precision, accuracy and lower limits of detections. This is the SRXRF method, that allow to analyze the sample mass of 0.5 mg directly without the destruction. The puncture from patient may be picked out more than once.

In present research we pay the special attention not only to the each element determination but to the simultaneous determination different groups of elements and their ratios.

The method of the determination of elemental concentrations in the human liver punctures was developed. The SRM NIST Bovine Liver 1577 was used as the external standard. Following elements were determined: P, S, Cl, K, Ca, Mn, Fe, Ni, Cu, Zn, As, Se, Br, Rb, Sr, Mo. The LLDs (ppm) obtained for some elements: Mn – 1.0, Fe – 0.7, Ni – 0.5, Cu – 0.6, Zn – 0.5, Se – 0.3, Br – 0.2, Rb – 0.2, Sr – 0.2.

The special interest is the determination of Fe, as the acceleration of sclerosed process is connected with the accumulation of Fe in this organ. Copper is accumulated in tissues at the genetic caused diseases (Wilson Disease, Hemochromatosis). This is the alteration in elemental ratios (e.g., Cu/Zn), that is the marker of pathological process.

**SPECTROPHOTOMETRIC DETERMINATION OF  
ATORVASTATIN AND FLUVASTATIN IN PHARMACEUTICAL  
PREPARATIONS AFTER DERIVATIZATION  
WITH 9-CHLOROMETHYLANTHRACENE**

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A selective and sensitive spectrophotometric method for determination of atorvastatin and fluvastatin in tablets have been developed after derivatization with 9-chloromethylantracene. Atorvastatin and fluvastatin were reacted with 9-chloromethylantracene in hexane and then tetrabutylammonium hydroxide for 20' at 90 °C. For spectrophotometric method the derivatives of atorvastatin and fluvastatin were measured at wavelengths, 301 and 303 nm, respectively. The developed method was applied to analyze the atorvastatin and fluvastatin contents in tablets.

# DETECTING POTENTIALLY DANGEROUS CHEMICAL SUBSTANCES MIGRATING FROM ARTICLES FOR MEDICAL USE

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Various polymers and latexes are used in manufacturing different articles for medical use. Safety measures in using such articles require strict control measures which provide for detecting toxic substances on hygienic standard levels or on the permissible migration level (PML) ( $\text{mg}/\text{dm}^3$ ). Chromatographic reaction methods are used to reveal formaldehyde, phenol, and epichlorhydrin.

Interaction of formaldehyde with 2,4-dinitrophenylhydrazine in acid media causes 2,4-dinitrophenylhydrazone (DNPhydrazone) formaldehyde formation. Gas-chromatographic analysis of 2,4-DNP-hydrazone formaldehyde toluene extract with an electron holding detector makes it possible to detect it at the level of  $0,001 \text{ mg}/\text{dm}^3$ . Phenol is detected in the form of tribromphenol yield, the hexane extract of which undergoes chromatography with an electron holding detector which provides the level of phenol detection of  $0.001 \text{ mg}/\text{dm}^3$  (the limit of quantitative detection).

Epichlorhydrin (ECH) detection starts with detecting epoxide cycle using hydrochloric acid in combination with sodium chloride; the reaction product – 1,3-dichlorhydrin – is extracted in diethyl ether and concentrated by removing the latter. Gas-liquid chromatography with a flame-ionization detector is used to detect glycerin 1,3-dichlorhydrin. The sensitivity of the method is  $0.01 \text{ mg}/\text{dm}^3$ .

The method of detecting dimethylterephthalate (DMTP), dibutylphthalate (DBP) and dioctylphthalate (DOP) in aqueous extract is based on their extraction with an organic solvent (hexane) and subsequent concentration using gas-liquid chromatography and an electron-absorbing detector. The detection limit is  $0.05 \text{ mg}/\text{dm}^3$  for DMTP and DBP, and  $0,01 \text{ mg}/\text{dm}^3$  for DOP.

Methyl metacrylates, alcohols, aromatic and aliphatic carbohydrates, acetic ester acids are detected using the vapour-phase method.

To detect rubber article accelerators and stabilizers, thin layer chromatography is used. 2,4-dichloroquinone-4-chlorimid is used as a reagent for developing thiuram, cymates, captax, altex, sulfamide, and vulcacide. Thin-layer chromatography is usually used to detect aniline and N-ethylaniline; however, the authors have developed a convenient and more universal gas-chromatography method.

# MICELLAR LIQUID CHROMATOGRAPHY IN PHARMACEUTICAL ANALYSIS

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Micellar liquid chromatography (MLC) is a new and intensively developing mode of reversed-phase chromatography. Recent reviews on MLC present its applications for separating organic and inorganic compounds, as well as for determination of distribution coefficients. Attractive to researchers are MLC advantages such as high reproducibility, unique selectivity of resolution, the possibility to divide and determine simultaneously various ionic and non-ionic components, low cost and safety, and the possibility to enhance or stabilise the fluorescence. MLC has found a wide application in pharmaceutical analysis and the analysis of biological fluids due to possibility to inject a sample directly, without preliminary protein precipitation or extraction.

The general drugs contain many active ingredients. To separate these active ingredients in a single HPLC run, the gradient mode must be employed because of their quite different hydrophobicities. The gradient elution, however, is not suitable for routine analysis as a quality control method because of relatively poor reproducibility and time-consuming analysis. Sometimes for the pharmaceutical analysis in reversed-phase HPLC mode any chromatographer should use special chromatographic column.

Also for analysis of some pharmaceutical substances a normal-phase mode of HPLC and a lot of organic solvents are needed, especially if it is used in routine analysis.

MLC enables to analyse drugs and active pharmaceutical substances without using special column and large quantity of organic solvents. So, from the point of view of pharmaceutical analysis ecology and “green chemistry” conception, assay with MLC using will be better than conventional reversed-phase chromatography.

We proposed using MLC for assay of azithromycin in tablets and capsules. As alternative conventional reversed-phase HPLC method MLC was used for analysis of Biseptol (sulfamethoxazole and trimethoprim) tablets and injection. The MLC was proposed to assay of triprolydine hydrochloride and pseudoephedrine hydrochloride in tablets as alternative normal-phase HPLC method described in USP pharmacopoeia.

# SPECTROFLUORIMETRIC DETERMINATION OF OXYTETRACYCLINE AND CITRATE ION USING TERNARY COMPLEX WITH EUROPIUM(III)

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A new ternary complex formed by Eu(III) ions with oxytetracycline and citrate has been investigated. The opportunity of use of the given ternary complex for definition of both organic ligands is shown. Oxytetracycline (OxTc) is an antibiotic of the tetracycline series which is permitted for human medication. It is a common antibiotic used against bacterial infections when growing animals such as cattle, pigs, sheep and poultry in agricultural production. Citric acid (Cit) is a very important compound in nature being an intermediate in the citric acid cycle. It is widely used as an additive in the pharmaceutical and food industry.

The triplet-state energy level of oxytetracycline, the excitation maximum (412 nm), lifetimes of Eu-OxTc (58  $\mu$ s) and Eu-OxTc-Cit (158  $\mu$ s), were determined. A 25-fold luminescence enhancement at 615 nm occurs upon addition of citrate within a short 5-min incubation time at neutral pH. It's accompanied by a threefold increase of the luminescence decay time. The optimal conditions for determination of OxTc are equal concentrations of Eu(III) and citrate ( $C = 1 \cdot 10^{-4} \text{ mol} \cdot \text{L}^{-1}$ ), pH 7.2. For determination of citrate, the optimal conditions concentrations of Eu(III) and OxTc are 1:0,5 ( $C_{\text{Eu}} = 1 \cdot 10^{-4} \text{ mol} \cdot \text{L}^{-1}$ ,  $C_{\text{OxTc}} = 5 \cdot 10^{-5} \text{ mol} \cdot \text{L}^{-1}$ ) at pH 7.2.

We determined the influence of oxy- and ketocarboxylic acids (succinate, fumarate, adipinate,  $\alpha$ -ketoglutarate, isocitrate, tartrate, L-malate) on the luminescence intensity of the Eu-OxTc complex. These substances interact as polydentate ligands similarly to citrate with the formation of ternary complexes with Eu-OxTc. As to succinate, fumarate, adipinate and  $\alpha$ -ketoglutarate this they cannot effectively coordinate with  $\text{Eu}^{3+}$  and significant fluorescence enhancement was not observed.

It was found that the effect of solvents and various surfactants: Triton X-100, Twin-80, Brij-35 sodium laurylsulfate, sodium cetylsulfate, cetylpyridinium chloride, cetyltrimethylammonium bromide on the luminescence intensity is insignificant.

The luminescence intensity is proportional to the concentration of OxTc in serum within the range 0,25 - 250  $\mu\text{g mL}^{-1}$  and to citrate in pharmaceutical formulations  $2,3 \cdot 10^{-6}$  -  $4 \cdot 10^{-5} \text{ mol} \cdot \text{L}^{-1}$  (0,5 - 8,0  $\mu\text{g mL}^{-1}$ ). The detection limit was 0,1  $\mu\text{g mL}^{-1}$  and  $1 \cdot 10^{-6} \text{ mol} \cdot \text{L}^{-1}$  (0,2  $\mu\text{g mL}^{-1}$ ) for OxTc and citrate, respectively.

# DETERMINATION OF 1-OCTANOL - WATER AND MICELLAR PSEUDOPHASE - WATER PARTITION COEFFICIENTS OF BENZODIAZEPINES

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By modeling the substance behavior at the interface of two liquid phases, in particular, stationary and mobile phases in liquid chromatography, 1-octanol – water partition coefficients ( $P_{o/w}$ ) or partition coefficients in biomimetic system: micellar pseudophase – water ( $P_{m/w}$ ) used as a hydrophobicity parameters.

The comparison of predicting capabilities of two kinds of hydrophobicity evaluations is of interest. For these purpose partition coefficients  $P_{o/w}$  and  $P_{m/w}$  for a number of benzodiazepines: gidazepam (I), medazepam (II), nitrazepam (III), oxazepam (IV), lorazepam (V) and diazepam (VI) were determined.

Distribution of benzodiazepines in 1-octanol – water system was investigated by a direct shake flask method at the presence of the compounds used in HPLC mobile phases: the phosphate buffer with pH 6,87 (substances (I) - (II)), acetic and phosphate buffer, perchloric acid at pH 3 (substances (III) - (VI)). Concentrations of substances in an aqueous phase after distribution controlled by HPLC (chromatograph Hewlett Packard, column Nucleosil 100-5 C<sub>18</sub>, mobile phase: acetonitrile - phosphate buffer solution with pH 2,5, 30:70 (v/v)).

Obtained  $P_{o/w}$  values for the description of benzodiazepine's retention in reversed-phase HPLC are used. The equation

$$\lg k' = (-0,5 \pm 0,1) + (0,73 \pm 0,04) \cdot \lg P_{o/w}, (R=0,999)$$

satisfactory describes the dependence of the retention factor ( $k'$ ) on hydrophobicity parameters of benzodiazepines, except gidazepam (I) and medazepam (II), that have the smallest retention times.

Distribution of benzodiazepines in system micellar pseudophase – water was investigated in micellar solutions of sodium dodecylsulfate. The protonization constants of benzodiazepines were determined by the UV-spectrophotometry. Values of protonization constants increase with increasing of sodium dodecylsulfate concentration. The binding constants of two protolytic forms of benzodiazepines with a micellar pseudo-phase and  $P_{m/w}$  values were evaluated from obtained dependence.



# VALIDATED HPTLC DETERMINATION AND CONTENT UNIFORMITY TEST FOR ALPRAZOLAM AND MELATONINE IN TABLET DOSAGE FORM

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A simple, rapid, precise and economical High Performance Thin Layer Chromatographic (HPTLC) method has been developed and validated for determination of Alprazolam and Melatonin in its pharmaceutical preparation. It was performed on silica gel 60 GF<sub>254</sub> Thin Layer Chromatographic plates as a stationary phase using mobile phase Toluene: acetone: ammonia (5:5:0.1v/v/v) and the detection was carried out in the absorbance at 226 nm showing R<sub>f</sub> value 0.31 for Alprazolam and 0.50 for Melatonin. The linear regression data curve shows good linear relationship in the concentration range 0.2-0.9 µg for Alprazolam and 3-10 µg for Melatonin. The content uniformity test was carried as per USP specification of the content uniformity test of 85-115%. The percent drug estimated from two different marketed formulations were found to be in the range 99.59-100.37 for both the drugs. The recovery of drugs was carried out by standard addition method were found to be 99.97 ± 0.94 and 100.05 ± 0.68 for Alprazolam and 99.73 ± 0.49 and 100.11 ± 0.35 for Melatonin by height and area respectively. The method was validated for accuracy, precision, specificity, linearity detector response and ruggedness. The proposed method provides a faster and cost effective quality control tool for routine analysis of content uniformity test for Alprazolam and Melatonin in tablet formulation.

# FLUORIMETRIC DETERMINATION OF KETOROLAC AND KETOPROFEN IN DOSAGE FORMS USING TERBIUM SENSITIZED LUMINESCENCE

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5-Benzoyl-2,3-dihydro-1H-pyrrolizine-1-carboxylic acid (ketorolac,  $L_1$ ) and 2-(3-benzoyl-phenyl)propionic acid (ketoprofen,  $L_2$ ) are biologically active ligands used in medicine as non-steroidal anti-inflammatory drugs.

$L_1$  and  $L_2$  have two absorption bands in ultraviolet spectral region at 247 nm and 319 nm; 207 nm and 262 nm, respectively, with high extinction coefficients. The triplet levels energy of ligands calculated from the phosphorescence spectra of their yttrium complexes at 77 K are  $20550 \text{ cm}^{-1}$  ( $L_1$ ) and  $20800 \text{ cm}^{-1}$  ( $L_2$ ), which are higher than the energy of  $^5D_0$  excited state of terbium(III) ( $20500 \text{ cm}^{-1}$ ). Transfer of excitation energy from ligands to the energy level of terbium is therefore possible.

The optimal conditions for the complexation were found. The luminescence of  $\text{Tb}^{3+}$  in  $L_1$  ( $L_2$ ) complex was established to be observed in a range of pH 2,0-11,0 with maximum at 7,0-7,5. The Tb (III) luminescence in complex with  $L_1$  ( $L_2$ ) also depends on amount of reagents, solvent nature, amount of surfactants and trioctylphosphine oxide (TOPO). It was shown that introduction into the system Tb- $L_1$  the 3-fold excess sodium dodecylsulfate (SDS) increases the luminescence intensity by 40 times and introduction into the system Tb- $L_2$  the 3-fold excess TOPO increases the luminescence intensity by 25 times by the order value connecting with the crowding out of water molecules from the inner sphere of complexes.

The luminescence properties of Tb (III) chelates were used in determination of ketorolac and ketoprofen in dosage forms. The luminescence intensity is proportional to the concentration of  $L_1$  within the range of  $0,05 - 20 \mu\text{g mL}^{-1}$  and to  $L_2$  within the range of  $0,1 - 10 \mu\text{g mL}^{-1}$ . The detection limits are  $0,025 \mu\text{g mL}^{-1}$  and  $0,05 \mu\text{g mL}^{-1}$  for  $L_1$  and  $L_2$ , respectively.

Accuracy and precision of the methods were checked by the «added-found» method and statistical treatment of the data of determinations (RSD ranged from 0.025 to 0.046).

# DETERMINATION OF CLARITHROMYCIN IN HUMAN PLASMA USING RP-LC WITH ELECTROCHEMICAL DETECTION

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A selective, sensitive and stability indicating reversed phase-HPLC method was developed for the determination of clarithromycin antibiotic in human plasma.

Liquid chromatography was performed on symmetry 5  $\mu\text{m}$  ( $100 \times 4.6$  mm i.d) column at  $40^\circ\text{C}$ . The mobile phase consisted of acetonitrile 0.043 M  $\text{H}_3\text{PO}_4$  (36:63, v/v) adjusted to pH 6.7 with 5 M NaOH and pumped at a flow rate of 1.2 ml/min. Detection of clarithromycin and azithromycin as an internal standard (I.S) was monitored on an electrochemical detector operated at a potential of 0.85 Volt. Each analysis required no longer than 14 min. Quantitation over the range of 0.05 – 5.0  $\mu\text{g/ml}$  was made by correlating peak area ratio of the drug to that of the I.S versus concentration. A linear relationship was verified as indicated by a correlation coefficient,  $r$ , better than 0.999.

The method was validated in accordance to the guidelines of the international conference on harmonization (ICH). Data with respect to accuracy, within- and between run precision, recovery, detection and quantitation limits were reported and found to be within the accepted international criteria. Neither endogeneous substances nor the commonly used drugs were found to interfere with the retention times of the analytes. Standard solutions of the drug and quality control preparations at high and low level concentrations were demonstrated to be stable at room temperature and/or  $-20^\circ\text{C}$  for long and short periods of time.

Eventually, the proposed method was successfully applied to quantify clarithromycin in spiked human plasma and real samples from healthy volunteers after oral administration of the drug indicating the utility of this method for clinical and bioavailability studies.

# DETERMINATION OF SOME PHYSIOLOGICAL ACTIVE COMPONENTS IN PHARMACEUTICAL PRODUCTS BASED ON BISHOFITE

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Bischofite contains near 65 elements of the Periodical Table, including magnesium, phosphorus, potassium, sodium, manganese, iron, calcium, copper, zinc, iodine, etc. The presence of physiological active macro- and microcomponents in bischofite causes its wide usage in medicine. It is necessary to notice, that during the conservation of technical bischofite rusty precipitate is formed, and that may lead to the removal of considerable part of microelements. Without those microelements the biological features and efficiency of brine is reduced. Therefore it is necessary to have the technologies of analytical supply of the control of biological impotent components in pharmaceutical products based on bischofite.

The main idea of research is application of accessible, simple and express methods that don't need expensive reagent techniques for analysis of pharmaceutical products based on bischofite. The determination of metal ions such as Mg, Zn, Cu, Fe by complex-formation titrations using a widely applicable chelating agent, EDTA, have been studied as a function of pH, complexing agents and indicators. The analysis consists of four parts:

- 1) Fe (III) is determined by direct titration with EDTA at pH 3 using sulfa salicylic acid as indicator;
- 2) total Mg, Cu and Zn is determined by direct titration with EDTA at pH 10 using eriochrome black T indicator after iron elimination with tartrate ions;
- 3) total Cu and Zn is determined by direct titration with EDTA at pH 5 using murexide indicator after iron elimination with acetate ions;
- 4) Zn is determined by direct titration with EDTA with xelenol indicator after iron elimination with acetate ions and copper – with sulfide ions.

This procedure was tested in the analysis of pharmaceutical products "Poltava's bischofite" (series "Elite" and "Profi") and a brine of bischofite with rusty precipitate. The data bear out the sufficient accuracy and reproducibility of the proposed procedure which allows to perform the determination magnesium, iron, copper and zinc ions at concentrations above  $10^{-3}$  M. It was found that the content of Mg ion in the studied brine decreases in comparison with "Poltava's bischofite". The Fe, Cu and Zn ions were not detected in the brine.

# HETEROGENEOUS CATALYMETRY IN THE ANALYSIS OF METALLOIDS IN PHARMACEUTICALS

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Control of metalloid content in natural objects, foodstuff and pharmaceuticals is an important task for modern analytical chemistry. Determination of elements such as Arsenic is necessary for evaluation of object toxicity, since their content in environment may exceed MCL (maximum contaminant level), posing hazard to human health. Elements such as Selenium in definite doses are healthy, but in greater quantities they produce toxic effect.

For modern analysis, high sensitivity and selectivity of methods for the determination of these elements are important parameters. Catalytic methods of analysis possess such characteristics. Using of heterogeneous catalytic reactions on the interface also permits to reduce determination time.

In the present work, heterophase catalytic method was shown to be suitable for metalloid determination using Selenium as an example.

It is known that Selenium catalyzes reaction of some dye reduction by Sulphide. On this basis spectrophotometric and test-techniques for Selenium determination are developed. Inefficient reproducibility and low sensitivity are their deficiencies. In the present work, solid-phase reagent on silica gel modified first with quaternary ammonium salt and then by Indigocarmine was proposed for Selenium(IV) test-determination. Optimal conditions for the Selenium determination by method of fixed concentration were found. The detection limit of Se(IV) is 10  $\mu\text{g/L}$  ( $C_{\min} = 2 \text{ ng/sample}$ ). Calibration curve is linear in the range 50-400  $\mu\text{g/L}$  of Se(IV). The proposed method is successfully applied to the Selenium determination in multivitamins and bioadditions.

# **HISTORY OF ANALYTICAL CHEMISTRY**

*Keynote lectures*

# **ANALYTICAL CHEMISTRY: A WALK THROUGH TIME**

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Qualitative and quantitative chemical measurements can be traced to pre-biblical times, and have been important throughout the history of humans. The evolution of measurement techniques and tools from the first century to the twenty first century will be illustrated, along with the examples of early textbooks on analytical chemistry. The perceived value of gold and silver was the first incentive to acquire analytical information. The chemical balance is referred to in the earliest documents found, and has been an important tool throughout history. The chemical knowledge created by the Alchemists in the Middle Ages formed the basis for precise and accurate quantitative measurements. Gravimetry and titrimetry, along with stoichiometric concepts, evolved over the 17<sup>th</sup> to 19<sup>th</sup> centuries, and chemical instrumentation grew rapidly in the 20<sup>th</sup> century. Quantitative analysis textbooks, and hence the teaching of analytical chemistry as a discipline, appeared in the 19<sup>th</sup> century. These incredible advances in analytical science will be illustrated with some of the pioneers through the eons up to modern day.

## **90 ANNIVERSARY OF HETEROCYCLIC AZO COMPOUNDS**

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The historical aspects of synthesis, study and application of heterocyclic azocompounds (HAC) pyridinic of a line in analytical chemistry are considered. Works of A.E. Chicibabin on diazotation of 2-aminopyridine and its azocoupling with resorcinol (PAR) and 2-naphthol (PAN-2).

HAC as reagents in photometry and complexometric indicators, their advantage before known reagents. Modern aspects of application HAC in spectroscopic (photometric, extractive-photometric, fluorimetric, kinetic methods, solid-phase spectrophotometry, flow-injection, atomic absorption, roentgen-fluorescent analysis, thermo lens spectroscopy, colourmetry) and electrochemical (volt-amperometry, amperometry, ion selective electrodes, etc) methods of the analysis, division and enrichment (extraction, sorption, extraction chromatography, high pressure liquid chromatography, capillary electrophoresis thin layer chromatography). HAC in tests - methods of the chemical analysis. The reasons of high reactivity ability HAC.

The bibliography on application HAC is presented. Schools of the chemists - analysts on study and application HAC are discussed.

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# HOW THE EUROBACHELOR AND THE ECHEMTEST CAN HELP THE STUDENT MOBILITY IN THE EUROPEAN REFORM CONTEXT

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The European Chemistry Thematic Network (ECTN) and the ECTN Association ([www.ectn-assoc.org](http://www.ectn-assoc.org)) represents over 130 major university chemistry departments, from 30 countries. Each ECTN member is involved in various fields of investigation dealing with the European chemistry education in the European Higher Education Area.

At the conference we will enlighten two of the main projects carried out by the ECTN Association.

The Eurobachelor ([www.eurobachelor.net](http://www.eurobachelor.net)) is a product of the project “Tuning Educational Structures in Europe” and was approved by the EuCheMS in 2003. The diploma label will ensure reciprocal recognition to students all over Europe between accredited institutions. The Eurobachelor Label Committee is funded by the European Commission and supported by the EuCheMS.

The EChemTest ([www.echemtest.net](http://www.echemtest.net)) is an electronic evaluation platform in Chemistry based on a common core chemistry curricula agreed within the European Union countries. Dedicated originally to the academic public and to the student exchanges, it will enable Universities and Candidates to have a clear evaluation of the student’s knowledge level, and a clear understanding of the University’s pre-requisite level. The potential value of the common core approach is to give a ruling on the equivalency of levels between both the host and guest. Not intended to replace national examinations or diploma, one of the issues of EChemTest is the use and the dissemination of the Chemistry Eurobachelor according to the recommendation of the Bologna declaration.

During the conference the EChemTest demo version will be provided with free access to all attendees.

For any further details on the activities of the ECTN Network and Association, please visit our websites.



*Oral presentations*

# PROBLEMS OF DIRECTED FUNCTIONALIZATION OF ORGANIC ANALYTICAL REAGENTS

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The problems arising at directed functionalization of analytical reagents (OR) are considered, meaning both introduction of desirable functional groups and change of functions of a reagent in analytical system.

Any modern method of the analysis, irrespective of the nature and a way of registration of an analytical signal, provides application OR. In each case of the requirement to analytical properties of reagents approaches to forecasting systems (both structures OR are specific, and conditions of their application) should differ.

Formalization on the basis of the concept functional-active (FAG) and analytico-active (AAG) groups is obsolete. A number of difficultly taken into account circumstances is established. Beforehand to predict a way of coordination of metal by a reagent, dependent on others ligands, present in a complex, not always probably, even for the same reagents and the central ion the opportunity of change of stereochemistry of coordination unit, rigid division into the FAG s and AAG is unjustified, reagents with rigid structure («molecular prints») are capable to connect selectively organic molecules not only with the certain chemical properties, but also with corresponding spatial structure. Analytical systems are supermolecular: determined ions or compounds, as itself OR and other components of system, are solvates. OR takes part also in collateral processes, for example thautomerization, association, etc., as a rule influencing analytical characteristics. Therefore to predict follows analytical properties of all system with the purpose of updating initial supermolecula in optimum, resulting to re-capture of the best analytical signal. The information on structure supersystems with participation OR, the substances organizing system, and molecules of solvent is obviously insufficient. Therefore the full forecast of optimum structure supersystems while is rather complicated also a task it is necessary to solve in parts, since directed optimization of central unit of system - conditionally existing binary complex «connection (an ion of metal, anion) - a reagent», complicating it in process of accumulation of the necessary information.

The algorithm directed functionalization OR is given.

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# CHEMILUMINESCENT ANALYSIS BASED ON THE LUMINOL OXIDATION REACTION IN SPECIFIC REGIMES

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There exists a large number of methodics for the determination of various compounds which act as the oxidants of luminol or its analogues, catalysts of redox reactions, inhibitors and activating agents. In the development of such methodics one has usually to solve also the problems concerning the simplicity of their implementation and preliminary isolation or selective generation of the analytical form of the compound to be determined. Drawing attention to the positive features of some reactions which take place in the specific regimes, we present here some examples of corresponding methodics.

Using the luminol photochemiluminescence it is possible to determine not only the nitrates (as reported by us earlier), but also the nitrites. The urotropin is added to the water sample, and the solution obtained is illuminated by the Hg lamp. The chemiluminescence is measured after the addition of basic luminol solution to the illuminated solution. The detection limit is  $2 \cdot 10^{-9}$  M. The nitrates contained in the drinking water do not interfere at tenfold excess.

We have shown that known reaction of luminol with peroxydisulphate at low luminol concentrations takes place in the regime of controlled generation of  $\text{SO}_4^-$  ion-radicals at spontaneous destruction of peroxydisulphate. The detection limit for various types of antioxidants in water using this reaction is varied from  $10^{-5}$  to  $10^{-10}$  M. It is possible also to determine some polluting admixtures present in the atmosphere. The reagent used is the mixture of the luminol, base and  $\text{K}_2\text{S}_2\text{O}_8$ , which, once prepared, could be used during a working day.

We have also shown that in the aqueous strong basic medium the dissolved oxygen reacts with phthalic hydrazides at an appreciable rate, and with some hydrazides – also with high light yield. The methodics is developed for the determination of oxygen in gases in the concentration range of 21% (air) to  $1 \cdot 10^{-6}\%$  (high purity gases). The reagent used is the solution of 3oxyphthalic hydrazide in 7 M KOH, which, once prepared, could be used during a working day.

# THE MODIFIED BY THE DYE POLIMERIC IONITES IN THE HYBRID SPECTROSCOPIC METHODS OF ANALYSIS

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One of the most important tasks in Analytical chemistry is the effective and express microquantity determination of toxic metals and biologically active organic materials in different objects of environment, raw materials and products of food technology and biotechnology.

It is impossible to resolve these problems without the use of the contemporary analytical inspection methods.

Among the many, such combination method, which allows to combine the sorption concentration and the subsequent photometrical determination in solid phase, as solid-phase spectrophotometry (SPS), proves to be very effective in the analysis.

The results of the complexation study of Cu(II), Pb(II), Zn(II), Fe(III), Hg(II), Cd(II), Sn(IV), Zr(IV), Ti(IV) with arsenazo III, sulfonazo III, SPADNS, Eriochrome T, Acid Chrome Dark Blue, Xylenol Orange, Methyl Thymol Blue, Pyrocatechol Violet, Chrome Azurol S, Eriochrome Cyanin R, Basic Blue K, Methyl Violet, Brilliant Green, Rhodamine C and Astraphoxin in solid phase. The obtained data are used for the working out of a new method of metal determination.

Ultrasound Sample Preparation method was used for the analysis of food products.

Solid-phase basic dyes are also used for the study of their interaction with medical products: nicotinic, aminocaproic, acetylsalicylic and ascorbic acids and for the establishing of the new methods of SPS determination in known medical products.

Solid-phase acidic dyes are also used in the study of the ternary systems with pyrazolone derivatives. In addition, the colorless complex of the investigated metals with pyrazolone derivatives has been studied by means of the metal-indicator method.

The obtained results demonstrated that in a number of cases the solid-phase multiligand systems, and in other cases - pyrazolone derivatives, improve the extraction of metal from the analyzable solution, but at that, the multiligand systems are not produced in solid phase.

# **$\beta$ -DIKETONATES OF METALS AS POSSIBLE STANDARD MIXTURE MODELS FOR ATOMIC-SPECTRUM AND PHYSICOCHEMICAL METHODS OF ANALYSIS**

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Whilst solving some ecological problems of metals micro quantity determination in food products and water physicochemical and physical methods of analysis are employed. Standard mixture models (CO) are necessary for their implementation. The most interesting COs are the ones suitable for graduation and accuracy control in several analysis methods. Therefore the formation of poly functional COs is one of the most contemporary problems of modern analytical chemistry. The organic metal complexes are the most prospective class of CO-based initial substances where  $\beta$ -diketonates are the most appealing.

$\beta$ -Diketonates of some metals have been successfully synthesized and refined. The mass percent of  $\beta$ -diketonates in synthesized samples were verified by cryometric method on "Kaskad-04" installation and it is not less than 99,99 %. The error evaluation of tetrimetrical metal detection in compounds is not over 0,3 %. Using atomic emission spectrometry with inductively binded plasma, atomic absorption spectrometry and one factor dispersion analysis it was demonstrated that  $\beta$ -diketonates of metals are stable in hard state for over 5 years and their diluted solutions are stable during 4 months. The samples are proved to be homogeneous. The methodology of atomic absorption and extraction atomic absorption metal determination in water, food products, initial materials with the use of  $\beta$ -diketonates of metals as COs has been developed. The sufficient dissolvability of samples in organic solvents allows to cut down the time of analysis realization, the reagent assortment; to reduce the lower limit of determined substances and amounts and to raise the accuracy of extraction atomic absorption determination of metals micro quantity. The use of  $\beta$ -diketonates of metals makes it possible to increase the time of atoms withholding in elements under research. The synthesized samples have been tested during the determination of toxic elements in oil products using the ICP-AES method; in sails - by X-ray-fluorescent and emission spectrum methods. The advantages of new COs have been established.  $\beta$ -diketonate metals – based standard samples intended for graduation of analytical device and accuracy control of analysis results have been manufactured for several enterprises.

# ACADEMICIAN ANATOLY K. BABKO ARCHIV AS A SOURCE FOR MONITORING OF UKRAINIAN CHEMICAL SCIENCE DEVELOPMENT

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Today chemistry is one of leading branches of scientific knowledge in the world. It is a part of ordinary life of each person now. Last years scientists, who are study history of a science, try to fill informatively many existing gaps in history of development of a domestic chemical science. Documents and materials of chemical establishments are included to these researches. Unfortunately, there are poorly investigated archival funds of a personal origin of scientists-chemists. Documents of these funds frequently are a unique source that true to throw light on deep questions of development of branch of chemistry in which the scientist worked, ways of his scientific search, etc.

The largest storehouse of personal origin documents of outstanding scientists of Ukraine (about 350 funds, including more than 40 - scientists-chemists) is the Archivist Institute of National library of Ukraine. Among them the archival fund of academician of Academy of Sciences of Ukraine Anatoly Kirillovich Babko, the honored worker of a science, professor, founder of the Kyiv school of chemists-analysts. He is the author of 420 scientific works and several monographs and textbooks.

Family of the scientist has presented documentary materials to Academy of sciences in June 1974. Among them, the most important are manuscripts, typewritten copies about 100 scientific works of the scientist and working materials to them. Its includes articles, reports, monographs, the textbooks written by A.K. Babko during last 25 years; working writing-books with extracts, marks on various questions, abstracts of chemical literature; responses and reviews on thesis of Ph.D. and doctor's degrees, on articles, books, textbooks. For example, early works: "Product of solubility", "To a technique of definition of strontium in minerals" (1940-s), many unpublished works in 1940-1960, etc.

There are many documents of biographic character in fund: the certificate of the professor, the diploma, materials about A.K. Babko's participation in conferences, symposiums, in IUPAC; photos of the scientist during the various periods of a life; correspondence with large scientists of the world concerning development of analytical chemistry as a whole, and in Ukraine.



**9<sup>th</sup> Analytical  
Russian-German-Ukrainian  
Symposium  
(ARGUS-9)**

**Kyiv, Ukraine  
September 14-17, 2005**

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*Keynote lectures*

## **SITE OF ANALYTICAL CHEMISTRY IN LINE OF NATURAL SCIENCES**

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Features of analytical chemistry as parts of chemistry, «discipline laying between chemistry and metrology» (K. Doerffel) who in essence is «chemical metrology» (N.P. Komar), close connections of analytical chemistry with many fields of physics and biology are considered (As is well known physical and biological methods of obtaining and measurement of analytical signals are used in increasing frequency). The applied aspect of analytical chemistry is caused by that all branches of an economy are interested in the data on chemical composition of various objects as well as natural and engineering sciences, environmental protection, pharmacy, medicine, archeology, criminalistics and even astronautics. It is shown by the example of function materials, that tasks of analytical chemistry are not reduced to development of techniques of the analysis and the control of the material composition according to the requirements of other sciences and branches of technics. Finding of new laws that allow understanding features of a researched material and to optimize its parameters can be as the result of interaction of analysts and specialists in the field of material science. Methods of sample preparation and separation of components realizable at the analysis can serve as model of technology of fine cleaning of substances, obtaining of new materials and researching their properties. At last, chemical analysis of function materials in some cases becomes a part of technology of obtaining of materials with the adjusted properties.

# CHEMICAL AND PHYSICAL CHARACTERIZATION OF LAYERED SAMPLES

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Multilayered structures play an important role in the production of, e.g., biomaterials, catalysts, corrosion protectors, detectors/diodes, gas and humidity sensors, integral circuits, optical parts, solar cells, and wear protection materials. One of the most sophisticated developments is a head-up-display (HUD) for cars, consisting of a polycarbonate substrate and a series of the layers Cr (25 nm), Al (150 nm), SiO<sub>2</sub> (55 nm), TiO<sub>2</sub> (31 nm), and SiO<sub>2</sub> (8 nm). Such systems should be characterized by non-destructive analytical methods.

Nearly all of the important chemical (identification of elements, purity, homogeneity, speciation) and physical (roughness, thickness, serie of the layers) parameters of such a structure can be determined non-destructively by X-ray methods (e.g., EDXRS, WDXRS, TXRS, SYXRS,  $\mu$ -XRS, NEXAFS).

For construction of suitable samples molecular beam epitaxy was selected, the method of choice for the production of complicated epitaxial layer systems with different materials. As substrates Si wafer material (about 20×20 mm<sup>2</sup>, thickness 1 mm) and SiO<sub>2</sub> discs (diameter 30 mm, thickness 3 mm) were used. Eight layered structures (one, two and three layers) were built up with Al, Co, and Ni, with an indicated thickness of 70 nm, each.

These samples were measured non-destructively by energy-dispersive XRF with synchrotron radiation excitation (SYXRS), by  $\mu$ -XRF, by wavelength-dispersive XRF (WDXRS), and by Rutherford back scattering (RBS), by X-ray reflectometry (XRR) and by destructive secondary ion mass spectrometry (SIMS) as well (both last methods were used for independant comparison).

Not all of the parameters mentioned above could be determined with each method. In some cases informations had to be introduced as an assumption for the evaluation of the spectra.

The evaluation of the various XRF measurements will be discussed for different effects: in EDXRS the spectra evaluation is performed by different programs with varying assumptions, partially different mass attenuation coefficients are used, the calibration procedures are principally different (e.g., thin foils with given thickness, or, infinitely thick samples), measurement under atmospheric pressure or in vacuum, secondary excitation (enhancement) mainly of Al by Si radiation.

The comparison of the results of very different methods has to be judged very precisely, as, e.g., the given thickness of a layer is a function of the limit of detection (LOD) of a method. Additionally, the detected areas vary from about 0.01 up to about 400 mm<sup>2</sup>. Therefore, the methods with a low level of detection and with a high sensitivity (high slope of the calibration function) give a higher value for the layer thickness. Furthermore, the layers are broadened with time by diffusion.

# ATOMIC SPECTROSCOPY AS A TOOL FOR MICROELECTRONICS TECHNOLOGICAL PROCESSES MONITORING

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Atomic spectroscopic methods may be used as a tool for the investigation “*in situ*” of sputter etching in reactive gas atmosphere and deposition technique in thin-films processes, for instance, superconductor’s technology. Comparative simultaneous (atomic-emission and laser excited atomic fluorescence) investigation of gas phase has been carried out by sputtering of yttrium, zirconium and yttrium-zirconium alloy samples at varying oxygen partial pressure in the range of 0 -  $5 \cdot 10^{-3}$  bar. The advantages of such elaborated combined method for online monitoring of processes have been demonstrated. The correlation in behavior between emission and fluorescence spectra in wavelength range 590-620 nm has been established. The model of the analytical emission and fluorescence signal forming mechanism of metals and their oxides in gas phase at sputtering in glow discharge and laser excitation of fluorescence has been proposed.

Fluorescent spectra of yttrium oxide in pulsed glow discharge were investigated under different conditions. A few series of lines have been identified as YO lines: 613.21, 614.84, 616.51, 617.91 nm; 647.06 648.65, 650.25 nm; 584.19, 585.88, 587.35 nm. All these lines belong to transitions between oscillation levels ( $v'$ ) of main ground state  $^2\Sigma$  and oscillation levels ( $v''$ ) of first excited state  $^2\Pi$ . The lines show different dependence on laser delay time. The explanation is as following: while glow discharge is running, part of YO molecules are in excited oscillation states, so that in fluorescence spectrum are present lines, corresponding to transitions with all oscillating quantum numbers  $v'$ ,  $v'' = 0, 1, 2, 3 \dots$ . After glow discharge quenching the population of excited levels with  $v' = 1, 2, 3 \dots$  decrease, the higher is excited level the faster is decreasing. The intensities of corresponding fluorescence lines fall down. From the other hand the population of main ground state with  $v' = 0$  increases due to relaxation of molecules from excited levels. The intensity of corresponding fluorescence line grows.

Fluorescence spectra were measured at wavelength scanning of tunable dye-laser. In spite of the monochromic excitation the fluorescence spectrum has quite complex composition. Such variety of wavelengths allows to optimize fluorescence excitation and registration for any technological conditions.

# SOLID-PHASE EXTRACTION IN DETERMINATION OF ORGANIC COMPOUNDS IN WATER BY GC-MS

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Application of chlorination and oxidation agents for preparation of drinking water from natural water leads to production of chlorinated and oxidized volatile, semivolatile and nonvolatile organic compounds in low concentrations from pg/l, ng/l to µg/l. This depends on various factors: total content of organic compounds in natural water and presence among those of light oxidized / light chlorinated part of organic compounds, on type of oxidation agent, its doze, temperature of water etc.

Preparative isolation of nonvolatile and semivolatile organic compounds fractions (hydrophobic weak acids, hydrophobic weak bases, hydrophobic neutrals, humic and fulvic acids) from natural and drinking waters in optimal conditions was systematically investigated by solid-phase extraction method with porous polymer sorbents followed by isolation from general concentrate of antropogenic and/or toxic semivolatile compounds produced in chlorination and ozonation processes.

More than 60 classes of semivolatile organic compounds were identified by GC-MS including highest normal and isomeric alkanes, normal and isomeric aliphatic mono- and dicarboxylic acids, highest normal aliphatic monocarboxylic acids ethyl esters, unsaturated aliphatic monocarboxylic acids with one, two and three double bonds, unsaturated aliphatic dicarboxylic acids, branched (methylene attached) unsaturated aliphatic dicarboxylic acids, oxo- and hydroxyderivatives of the aliphatic mono- and dicarboxylic acids, aliphatic tricarboxylic acids, aliphatic dichlorocarboxylic acids, aromatic mono-, di- and tricarboxylic acids, phthalic acid alkyl esters, phenolcarboxylic acids, steroids, highest aliphatic alcohols, aliphatic carbonyl compounds, alkyl-, cycloalkyl- and alkenylbenzenes, alkylphenols, alkylarylureas, aryl sulfones, sulfur heterocycles, nitrogen and phosphorus compounds, surfactants etc.

Determination of C<sub>1</sub>-C<sub>6</sub> carbonyl compounds, phthalic acid alkyl esters, mutagen MX and its geometric isomer E-MX, chlorophenols, organochlorine pesticides (OCPs) – α-, β-, γ-, δ-HCH, DDE, DDD, DDT, total isomeric-specific content of polychlorinated byphenyls (PCBs) (tri-, tetra-, penta-, hexa-, hepta-, octachloroisomers) in SCAN and SIM mode was carried out. MDL of procedure for OCPs makes up 0.01-0.1 and PCBs – 0.17-0.38 ng/l at enrichment factor K = (1.50-4.00)·10<sup>5</sup>.

# ACTING MECHANISM OF INORGANIC CHEMICALS MODIFIERS IN ELECTROTHERMAL ATOMIC ABSORPTION SPECTROMETRY

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We have examined proposed earlier acting mechanisms of inorganic chemical modifiers in the electrothermal atomic absorption spectrometry. It is well noted that there exists inconsistencies and impossibility of quantitative description and prediction of chemical modifiers actions. We propose [1] acting mechanism of inorganic chemical modifiers, which is based on the formation of individual chemical compounds and diluted condensed solutions. In this method we have simultaneously examined the interaction among analyte, chemical modifier and matrix of the sample during the stages of sample drying, pyrolysis and atomization of elements.

The quantitative computations were conducted using equilibrium thermodynamic model. The proposed model for thermochemical processes divides layer of the sample into contacting and non-contacting zones with the material of the atomizer. The correlation of all initial components in thermodynamic system has been validated. Principles of results comparison with numerous experimental data to confirm the correctness of proposed mechanism have been validated as well.

Using As, Pb, S, Se and Te we have theoretically studied acting of palladium, magnesium and combined (Pd + Mg) chemical modifiers in clean solutions and samples with different matrices (nitrate, sulfuric, chloral). We have shown the possibility of quantitative description of acting mechanism of chemical modifiers and exposure of basic characteristics, which were established earlier only experimental: influence of modifier composition and its thermochemical properties, modifier/analyte ratio, molecular mass of modifier, sample matrix. The computations allow predicting plots of pyrolysis curves and atomization of elements and quantitatively compare effectiveness of acting of chemical modifiers among themselves.

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# MODERN STATE AND PROSPECTS OF THE DEVELOPMENT OF X-RAY FLUORESCENCE ANALYSIS IN RUSSIA

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The report gives consideration to the contribution of the scientists from Russia to the development of XRF analysis in the period from 1999 to nowadays. The state of XRF in the earlier period was discussed in the reviews<sup>1-3</sup>. Presented in detail are only the most important advances connected to the special features of XRF method. The reviews and the monographs, published in this period, the Conferences on XRF problems, held in Russia, the defended dissertations are separately discussed (~380 papers, 5 monographs and 17 dissertations). The statistical analysis of the publications on XRF is presented (the distribution in the Russian and foreign journals and in the towns: Moscow, Irkutsk, Novosibirsk, St. Petersburg and others).

The progress in the development of the theory and practical application of XRF is appreciated (an estimate of the spectral X-radiation distribution of common-used X-ray tubes of different constructions; changes in this distribution when polarizers are used; the estimates of some physical process contributions to the fluorescence intensity, which are substantial for light elements; the quantitative contribution estimates of some X-ray background components and others; procedures for concentration calculations using measured intensities).

The state of the instrumental base of Russian laboratories is discussed. The progress in the development of the capillary optics is noted. A number of new models of XRF spectrometers are designed, in which polycapillary lenses are used. This is very important in case of the application in vivo of XRF determination of some elements in bones and tissues and also forensic researches. One pays attention to the problem of a sample preparation and an output of new CRMs and to the XRF application to the study of geological and ecological samples. The investigations on the creation of the methodical maintenance are highlighted for the comprehensive study of the pollution of soils, plants, waters, aerosols, and biological tissues by XRF. It is noted a small number of papers, connected to the XRF application to the industry.

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# GENERAL STRATEGY FOR IDENTIFICATION OF TOXIC CHEMICALS IN ENVIRONMENTAL SAMPLES

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Identification of structures of toxic chemicals in environmental samples requires to use modern analytical methods, such as gas chromatography (GC) with element selective detectors (NPD, FPD, AED), capillary electrophoresis (CE) for screening purposes, gas chromatography/mass-spectrometry (GC/MS), gas chromatography / Fourier transform infra red spectrometry (GC/FTIR), nuclear magnetic resonance (NMR), etc.

For organic toxic chemicals and their degradation products the number of possibilities is very high. The environmental samples composition usually is very complicated. Unambiguous identification needs serial-parallel strategy of analysis with many-stage crosschecking of data.

In this cause main steps of identification are:

- Collecting and judgment of information received from sampling and sample preparation;
- Screening of the samples for the presence of compounds of interest by different element selective detectors, preliminary identification of heteroatom compounds;
- Execute “pure” spectrum and library identification;
- In case of absence library spectrum and chromatographic characteristics to find out a chemical structure the following methods should be used:
  - a) determination of molecular fragments,
  - b) determination of molecular mass and brutto formula,
  - c) identification of isomers,
  - d) confirmation of whole structure of compound by means of comparison of all analytical data.

The analytical strategy accepted in the laboratory designated by the Organization for Prohibition of Chemical Weapons will be discussed.



# ORGANIZED LIQUID MEDIA AND PRINCIPLES OF SUPRAMOLECULAR CHEMISTRY IN CHEMICAL ANALYSIS

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Analytical chemistry having an interdisciplinary character cannot set aside the attractive power and advances of supramolecular chemistry – “the chemistry beyond the molecule” or “the chemistry of molecular assemblies and of intermolecular bonds” as defined by Jean-Marie Lehn, who won the Nobel Prize in 1987. Recognition, reactivity, and transport, as well as self-assembly, self-organization and self-replication are the basic functional features of supramolecular species and chemistry.

The main supramolecular self-assembled species involved in analytical chemistry are micelles (direct and reversed), microemulsions (oil/water and water/oil), liposomes, and vesicles, Langmuir-Blodgett films composed of diphilic surfactant molecules or ions. They can form in aqueous, nonaqueous liquid media and on the surface. The other species involved in supramolecular analytical chemistry are molecules-receptors such as calixarenes, cyclodextrins, cyclophanes, cyclopeptides, crown ethers etc. Furthermore, new supramolecular host-guest systems arise due to analytical reaction or process.

In order to bind the analyte, a host must have binding sites that are of the correct electronic character, i.e. polarity, donor/acceptor ability, H-bond, overall hardness or softness of the host, to complement those of the analyte (guest). The preorganisation (or extent of reorganisation) and complementarity determine the free energy of binding and analytical effect. Strong but selective binding is the basis of molecular recognition and *selectivity* of analysis.

The next important phenomena that the result of supramolecular effect are the concentration and proximity effects concerning the components of analytical reaction, even through they are considerably different in hydrophobicity, charge of the species, complexing or collisional type of interaction. The concentration and proximity effects determine the equilibrium of analytical reaction, the efficiencies of intramolecular or intermolecular electronic energy or electron transfer and as a result the *sensitivity* of analytical reactions.

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# NMR MIXTURE ANALYSIS USING HYPHENATION TECHNIQUES AND SOFTWARE

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NMR over many years has developed into the main tool for structure elucidation in chemistry. Higher magnetic field strengths, one- and multidimensional Fourier Spectroscopy have significantly increased the sensitivity and the field of applications. New methods of sample handling and automation shortened the measuring time and increased the sample throughput. Magic angle spinning and cross-polarization extended structural NMR investigations to the solid state. The computer controlled use of magnetic field gradients established magnetic resonance imaging as an easy-to-use tool in material science, biomedical science and medical diagnostics.

For the chemist using NMR the main task always was to determine the molecular structure of single carefully isolated pure compound. Mixture analysis by NMR needs a completely different approach. In a mixture each component has its own NMR spectrum which overlaps into a mixture spectrum containing more than thousand NMR lines. There are two ways of analysing those mixtures by NMR.

*The first is the combination of HPLC with NMR (LCNMR) or even with NMR and MS (LCNMRMS). Over the last ten years these methods have been significantly improved. NMR in itself is has a rather low sensitivity as compared to optical and MS methods, but is very structure-specific. Thus the first task was to increase sensitivity. Special coupling devices and flow-through microprobeheads have been developed. Stop flow and solid phase extraction lead to a sensitivity increase of almost two orders of magnitude and allow to use all the informative and sensitive methods of multi-dimensional NMR Fourier spectroscopy. With high magnetic fields and cryoprobeheads the range of picograms becomes accessible for low molecular compounds. The ozonolysis of  $\alpha$ -pinene and metabolism of paracetamol will be shown as an example.*

*The second method for mixture analysis is the use of specialized software together with spectral databases. We have developed a mixture analysis program AMIX for one- and multidimensional spectra. The most important present applications are the field of combinatorial chemistry and toxicity screening of medical preparations in the pharmaceutical industry. An important medical application is screening of newborn infants for inborn metabolic errors.*

*Oral presentations*

# ESTIMATION OF SOME CHARACTERISTICS OF THE CHERNOBYL'S INCIDENT ON ELEMENT DISTRIBUTIONS IN SAMPLES TAKEN FROM REACTOR CONCRETE CASING

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Distribution of the contents of isotopes Ti, Ni, Zr, Cs and U in the cores, which was taken from the concrete casing surrounding Chernobyl reactor before accident, was studied. Measurements were carried out by gamma-activation analysis with help of the bremsstrahlung gamma-beam from the high-current electron accelerator\*. The top energy of the irradiation spectrum was 20.2 MeV, the absorbed doze was  $2 \cdot 10^6$  Gr.

For the analysis heat and mass transfer in concrete samples at high temperatures, the numerical model has been developed. It describes concrete, as a porous multiphase system which at local level is in thermodynamic balance with body interstice, filled by liquid water and gas phase. The model allows researching the dynamic characteristics of diffusion in view of concrete matrix phase transitions, which was usually described by means of experiments.

Comparison of the measured isotope distributions with simulation data is carried out within the framework of the models corresponding to various developments, accompanied accident of 1986. Estimations of characteristics of physical influence (temperature, etc.) to which ChAPS's concrete structure have been undergone are discussed.

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\* N.P. Dikiy, S.Yu.Sayenko, V.L. Uvarov, E.P. Shevyakova, The nuclear-physical methods application for a radionuclide transport in a granite rocks studies. *VANT, Nuclear-Physical Researches Series*, 2000. No. 2, p. 54-57.

# SELECTION AND USE OF INTENSIVE PARAMETERS OF ANALYTICAL SIGNAL ON MULTICOMPONENT ANALYSIS BY NON-SELECTIVE METHODS

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Multicomponent analysis by non-selective methods is based on the measurement of total analytical signal (AS) of mixture of components at several intensive parameters and on the construction of combined equations and the solving of it. The difference of partial sensitivity of components determined in common defines uncertainty.

All instrumental analytical methods can be analyzed as the spectrometry of zeroth, first, second and higher orders.

Multicomponent analysis using spectra of second order develops mainly in spectrofluorometry and chromatography.

According to the conception of the development of the system of spectra of additive properties stated by I.G. Per'kov the use of spectra of second order, represented by AS arrays, measured concerning two axes: the length of a wave and water phase pH in monophase, pseudomonophase (micellar solutions) and twophase systems is of great interest.

The measurement in twophase systems is discussed by the example of dithizonate of zinc, in pseudomonophase systems – by the example of zinc and cadmium complexes with 1-(2-pyridylazo)-2-naphthol, lanthanoid ion complexes with 1-(2-pyridylazo)-resorcin.

The perspective of using consecutive reactions is grounded on the example of the analysis of isomeric mono-nitrophenols and anion surface-active substances. The variants of systematic analysis of mixtures of tri-, di- and mono-nitrophenols, anion surface-active substances, based on the combination of measurements of consecutively received extracts at different pH values are discussed.

The use of change of the balanced composition of the mixture depending from the reductive-oxidative potential is shown on the example of coulometric determination of iodides and bromides and spectrophotometric determination of iodides in the presence of bromides at electrochemical oxidation.

The algorithms of solving the task of creating an optimal schedule of measurement are discussed. In addition, they are realized in the software package OPTIMIZM.

# ACID-BASED SURFACTANT CLOUD POINT EXTRACTION AND PRECONCENTRATION OF POLYCYCLIC AROMATIC HYDROCARBONS PRIOR TO FLUORESCENCE DETERMINATION

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In recent decades the development of preconcentration steps to be implemented prior to analytical determinations of trace level compounds has been explored in considerable depth. With a view to eliminating or at least minimising the use of organic solvents used in conventional liquid–liquid extraction, other methodologies have been developed, such as membrane extraction, solid-phase extraction, solid-phase microextraction, etc.

The aqueous micellar solutions of some surfactants exhibit the cloud point, or turbidity, phenomenon when the solution is heated or cooled above or below a certain temperature. Then the phase separation into two isotropic liquid phases occurs: a concentrated phase containing most of the surfactant and an aqueous phase containing a surfactant concentration close to the critical micellar concentration. The anionic surfactant solutions show this phenomenon in acid media without any temperature modifications. The aim of the present work is to explore the analytical possibilities of acid-induced cloud point extraction in the extraction and preconcentration of polycyclic aromatic hydrocarbons (PAHs) from water solutions. The combination of extraction, preconcentration and luminescence detection of PAHs in one step under their trace determination in objects mentioned allows to exclude the use of large volumes of expensive, high-purity and toxic organic solvents and replace the known time and solvent consuming procedures by more simple and convenient methods.

Sodium dodecylsulphate was selected as an anionic surfactant. Factors affecting acid-induced cloud point extraction including surfactant, hydrochloric acid, PAHs, and electrolyte concentration, centrifugation have been examined. Finally, we applied the optimized acid-induced CPE system for combination of the extraction and preconcentration steps with fluorimetric determination of some representatives of PAHs. Suggested means was used for PAHs determination in tap water.

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## HIGH EFFECTIVE METHOD OF IMPURITY PRECONCENTRATION BY MICRODROP EXTRACTION

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Liquid extraction is still the most reliable method of preconcentration of high boiling polar substances. We have shown an opportunity of further increase in efficiency of preconcentration by this method. The increase in a ratio of volumes of a water phase and organic solvent allows to raise the concentration coefficient of impurity and to approach it to coefficient of distribution. Besides, the significant economy of rare high purity solvents is possible. The complicating aspect in realization of this approach in extraction preconcentration is difficulty in the control of small volumes of solvents and their losses in extraction process. Volumes of solvents at the level of milliliters [1] are usually used. We develop a simple variant of preconcentration by solvent volume  $(1-2) \cdot 10^{-3}$  ml. The developed method is organically combined with gas chromatographic analysis. Reliability of the suggested method is shown at microextraction preconcentration of carbon disulfide, halogenorganic and aromatic substances from water by high purity carbon tetrachloride. The analysis of extracts was carried out with the use of gas chromatographs Shimadzu 14B, Tsvet-800 with capillary columns, photoionization and flame-ionization detectors, and GC-MS method with mass-selective detector MSD 5973N. The achieved values of concentration coefficient are 30-120 and are very close to distribution coefficient. Russian and SUPELCO standard samples were used for calibration. Researches of stabilization of process microdrop extraction have been carried out: microadditives of solvent and salting out effect were used. Reproducibility of microextraction preconcentration is characterized by size of relative standard deviation  $S_r=0.08-0.15$ . Limits of detection of impurities in water are  $10^{-8}-10^{-9}$  %. Results of the analysis of water samples of various origin are shown.

## **ABOUT COMBINED USE SEVERAL METHODS OF THE ANALYSIS ON ION OF BEAM**

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Development and research of new materials demands perfection existing or creation of new analytical technologies. To analytical methods more and more rigid requirements are put forward: much element analysis, low limits of the detection, not destroying character of the analysis (it is desirable the object without sampling); carrying out of the analysis without standard samples: an opportunity of carrying out of the local analysis and definition of structures on depth of object: small time of the analysis, etc. Any of modern methods does not meet to the full to all these requirements.

Perspective the methods based on an irradiation of analyzed object by proton of beam and registration of characteristic x-ray radiation (method PIXE), the gamma-radiation, the charged particles (PIGE, NRA), backscattering protons (RBS) are represented. It three methods are allocated from group of nuclear-physical methods on ion of beam. Each of them possesses the certain opportunities and restrictions, but as they appreciably supplement each other, their joint use considerably expands a circle of problems solved by them.

Processes of interaction ion of beam with the substance, put in a basis of each of methods are considered. Conditions of possible simultaneous use of two or three methods are determined.

The information on prevalence of these techniques in a world practice and examples of use of various combinations of methods is resulted at the decision of specific tasks.



# APPLICATION OF LASER BASED MASS-SPECTROMETRIC METHODS FOR TRACE ANALYSIS OF SYNTHETIC AND NATURAL CRYSTALS

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It is well known that trace elements content at sub-ppm level significantly influence on physical properties of single crystals which are used in micro- and opto-electronics. A study of dependence of conductivity, scintillation characteristics, energy resolution, radiation resistance, etc on chemical composition of materials and a development of single crystals growing technology are based on results of trace elements determination obtained by different analytical methods. On the other hand, determination of trace elements in natural crystals and chemical composition of micro-inclusions lets to obtain the unique information about their geological origin.

Laser based mass spectrometric methods, such as: laser ionization (LIMS) and laser ablation in combination with inductively coupled plasma mass spectrometry (LA-ICP-MS) are powerful analytical techniques for survey analysis of solid substances. To realize the analytical performances methods for the direct trace analysis of synthetic and natural crystals modification of a traditional analytical technique was necessary and suitable standard reference materials (SRM) were required. Recent developments allowed extending the range of analytical applications of LIMS and LA-ICP-MS will be presented and discussed. For example:

- To increase the radiation absorption and ionization efficiency of IR YAG-Nd laser (wave length - 1064 nm) used in for analysis of synthetic oxide single crystals:  $\text{Bi}_4\text{Ge}_3\text{O}_{12}$ ,  $\text{Li}_2\text{MoO}_4$ ,  $\text{LiB}_3\text{O}_2$  the samples were grounded and pills of  $\varnothing 10$  mm were pressed and analyzed by LIMS "EMAL-2" (Ukraine);
- LA techniques using UV YAG-Nd laser (wave length - 266 nm) for trace analysis of natural and artificial diamonds and for determination of chemical composition of micro-inclusions ( $5 - 50 \mu\text{m}^3$ ) in natural quartzites were developed by ICP-MS "ELEMENT" (Germany).

The set of Glass Standard Reference Material NIST SRM 610 – 614 was used for quantification of amount up to 45 trace elements in the synthetic oxide single crystals and natural quartzites.

# **SIMULATION OF XRF METHODS AND PROCESSES BY MEANS OF X-ENERGO TOOL-KIT**

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Efficient application of XRFA is impossible without use of specialized software. By means of this type of programs in XRFA is realized not only the analysis itself, but also the design of new methods and optimization of spectrometers.

Most efficiently realization of software of that type may be realized in case if solution of different problems is realized on the base of some universal set of data on the atomic constants and tools for operation with them and other data necessary for setting samples composition, terms of determination, etc.

The paper presents the experience of development of the tool box of the analyzed type, which was called by authors X-Energo.

The tool box includes four main groups of programs:

1. References – enabling access to atomic constants used by X-Energo users.
2. Methods, those include theoretical corrections, fundamental parameters, regression in different modification.
3. Analysis – a wide set of programs for the analysis of x-ray generation and interaction with stuff of the arbitrary composition. Among these are the programs for simulation of spectrometers of different types with determination of there analytical characteristics for certain type of analysis.
4. Services – including programs for spectra processing and editing, manipulation with different types of data like samples compositions, terms of determination, analytical lines intensities.
5. Educational programs – set of programs enabling the illustration of some specific features of x-ray and in particular XRFA.

The toolbox has demonstrated high efficiency and enables a flexible adjusting to user needs.

# INFLUENCE OF SALT COMPOSITION ON THE CONCENTRATING IMPURITIES BY MEANS OF LOW TEMPERATURE DIRECTED CRYSTALLIZATION

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Growing scintillation, optical or acoustic single crystals needs the control of pureness of a feed stock, and also the account of distribution of trace contaminants over obtained ingots is necessary. In order to provide such control one uses preliminary concentrating of impurities. Low-temperature directed crystallization (LTDC) of water solutions with salt content in a wide range is one of efficient methods of analytical concentrating. The given work is devoted to studying of regularities of distribution of impurities during LTDC of water-salt liquids of pre-eutectic and eutectic composition.

The directed crystallization was carried out, from a seed, by means of Bridgeman-Stockbarger method. Behaviour of impurities was defined on change of values of a characteristic distribution coefficient  $k_L$ . Dye arsenazo-1 served as a model impurity, allowing to visualize process of LTDC. We investigated the water solutions containing ingredients of natural and waste waters (CsI, NaCl,  $KNO_3$ ,  $KH_2PO_4$ ,  $Na_2CO_3$ ,  $MgSO_4$ ,  $Na_2SO_4$ ) in different concentrations, up to eutectic one. It is shown, that values of distribution coefficients of trace contaminants are influenced by both speed of crystallization, and concentration of salt-macrocomponent. It was established, that dependence of  $k_L$  for impurities from concentration of a macrocomponent has linear character in the beginning. The further increase of concentration of salt does not cause essential change of  $k_L$  during crystallization of solutions of investigated salts (except for CsI), and a plateau appears on the dependence, but in case of CsI the curve has a maximum.

The found regularities are explained in view of features of crystallization of ice, mechanism of entrance of impurity in a solid phase during LTDC of water solutions, and of dependence of structure of a water-salt eutectic by nature of salt-macrocomponent.

## THE USE OF BIOSENSORS ON THE BASE OF *E.coli* FOR ARSENIC DETECTION IN ENVIRONMENT

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It is well known that arsenic is one of the most dangerous elements in terms of its potential impacts to both to human and ecosystem health. Therefore the problem of As detection at ppb level remains very important from the point of environmental hazard investigation. The goal of the present work is the developing of very simple and inexpensive assay for arsenite and arsenate determination in environmental samples using whole-cell bacterial biosensors.

The principle of biosensor is based on the ArsR repressor protein interaction with specific DNA region and its ability to react with arsenite [1]. The artificial coupling between DNA fragment containing the binding site for ArsR and a DNA fragment with the gene for the enzyme *beta-galactosidase* has been created. Both pieces of DNA were connected to so-called plasmid. By means of genetic engineering *E.coli* bacterium with the plasmid an arsenite test has been created resulting in synthesis of beta-galactosidase, which is proportional to the arsenite content.

The bacterial plasmid presumably responds to arsenite (As(III)), but the fact of reducing the arsenate to arsenite has been established, reflecting in slower plasmid respond. It permits us to make arsenic speciation using simple and rapid assay.

Procedures of the beta-galactosidase activity measuring using colour reaction with ONPG and X-Gal without cells permeabilization were developed and the detection limit at the level of 4 ppb has been achieved. The influence of the foreign ions (phosphate, sulphate, carbonate et. al) was studied.

The developed assay was successfully applied for the arsenite and arsenate determination in contaminated waters of the gold recovery plant and in snow covers of the industrial anthropogenic sources vicinities as well. The data produced are in a good agreement with the results of independent methods: atomic absorption and atomic emission spectrometry and capillary electrophoresis.

[1] Sylvia Danert, Gary Barrett, Jessika S. Feliciano et al. / Chem. Rev., 2000, 100, P. 2705-2738

# PARAMAGNETIC CENTRES OF DISPERSE SORBENTS IN ANALYTICAL DETERMINATION OF ECOTOXICANTS

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The development of highly selective sorbents for medicine, chemistry, ecology, biotechnology is impossible without usage of methods of analytical chemistry. Among various approaches directed on increase of sensitivity of analytical methods of traces elements determination, for example, in water solutions sorption methods play an important role. The nature of sorption centers are of great importance at synthesis of sorbents with multifunctional properties.

In the work the results of regular study of role of paramagnetic centers as centers of selective sorption of ecotoxigats of various natures from water medium are presented.

It was found, that the defects of structure of disperse materials - paramagnetic centers, are highly selective centers of sorption, which results in display of abnormal properties in process of extraction of ecotoxigants from composite solutions. It was shown, that such properties are characteristic for paramagnetic centers of different nature - namely, paramagnetic centers with unpaired electron on carbon materials, atoms of biometals ( $Al^{+3}$ ,  $Cu^{+2}$ ), defects of structure of inorganic sorbents and etc.

The laws of formation of paramagnetic centers on disperse materials of various nature are investigated, the interrelation between quantity of paramagnetic centers and sorption ability of disperse materials is revealed.

The methods of formation of disperse materials with given type of paramagnetic centers are offered, depending on concrete purpose of material at analytical concentrating of ecotoxigants.

Is was established, that abnormal high (more than 98 %) sorption ability of disperse materials caused by presence of paramagnetic centers in them allows to recommend materials of such type for deep purification of water solutions from wide spectrum of ecotoxigants, that is confirmed by the carried out experimental researches by the example of petroleum, ions of heavy metals, radionuclides, pathogenic microflora, high harmful viruses.

The concrete examples of selective binding ecotoxigants of different nature are considered with participation of paramagnetic centers. The questions of creation on the base of this materials sensitive sensor and materials - concentrators for analytical determination of ecotoxigants traces in water medium are discussed.

The mechanisms of sorption, proceeding with participation of paramagnetic centers, and possibilities of synthesis of materials of new generation for analytical chemistry are analyzed.

## EXAMINATION OF THE CHEMICAL ELEMENTS RATIOS IN HUMAN NAILS (SRXRF)

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The role of nails in human metabolism is still the unexplored field. Nowadays, on the literature sources, there is no information about elemental content of each nail of individual human. There is a little information about how the elements to get into the nail structure. Weather it is possible the exogenous elements to enter the nail or no? How the elements to distribute in different nails of the same individual? How the elements to distribute on the total area of nail? Weather the changes in elemental composition in time take place.

The goal of our research was the comparison of the elemental content in cut part of nail and the part of nail, which contacts with the soft tissues of finger, the determination of elemental concentrations in 20 nails of individual, the determination of the elemental distribution as a dynamic mechanism.

The sampling of nails was performed from the all fingers of hands and foots of healthy people both sexes at the age of 20-30 years old. We elaborated the method for removing the exogenous contaminations from the nail samples.

The analysis was performed by XRF method with SR. SRXRF is an instrumental, multielemental, non-destructive analytical method using synchrotron radiation as primary excitation source. The fluorescence radiation was measured on the XRF beam-line of VEPP-3 (E=2 GeV, I=100 mA), Institute of Nuclear Physics, Novosibirsk, Russia. For quality control were used international reference standards.

There were obtained all metrological characteristics, namely precision, accuracy and lower limits of detections. For this purpose the different types of International Certified Reference Materials were used.

The results obtained show, that absolute meanings of elemental concentrations in the nails of each human are individual. The change of the elemental content with time in nails of a donor is individually dominated. These data allow drawing a conclusion, that the application of nails in non-invasive diagnostic is correct.

# VARIABLE TEMPERATURE FTIR SPECTROSCOPY IN THE STUDIES OF SURFACE PHENOMENA

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The lecture deals with the advantages of IR spectroscopy at low or variable temperatures in the studies of molecule-surface interactions, lateral interactions between the adsorbed molecules and catalysis.

Spectral studies at low temperatures enable us to broaden the number of test molecules for surface acidic sites and besides ammonia pyridine and nitriles, to use CO, NO and H<sub>2</sub> that do not adsorb at 300 K.

Low-temperature adsorption of weak CH proton-donating molecules such as CHF<sub>3</sub>, acetylene and its derivatives or HCN, enables one to characterize the basicity of surface electron-donating sites.

Lateral interactions between the adsorbed molecules can affect dramatically the strength of surface sites. Coadsorption of weak acids with basic test molecules reveal the effect of induced Bronsted acidity, when in the presence of SO<sub>2</sub> or NO<sub>2</sub>, protonation of such bases as NH<sub>3</sub>, pyridine or 2,6-dimethylpyridine occurs on silanol groups that never manifest any Bronsted acidity. This suggests explanation of promotive action of gaseous acids in the reactions catalyzed by Bronsted sites. Just the same, presence of adsorbed bases leads to the increase of surface basicity, which can be detected by adsorption of CHF<sub>3</sub>.

At low temperatures unstable adsorption products or reaction intermediates could be trapped. Thus, 'carbonite' CO<sub>2</sub><sup>2-</sup> ions arise on CO interaction with basic oxygen ions which account for catalytic reaction of isotopic scrambling of CO or thiophene on activated CaO.

Spectroscopy at variable temperatures enables us to reveal linkage isomerism of adsorption, when certain molecule form with the same site two or more complexes with different geometry and chemical properties. The most studied so far is the case of CO in zeolites, when besides the usual C-bonded complexes with the cations or OH-groups, energetically unfavorable O-bonded complexes are formed.

Low-temperature spectroscopy is indispensable for the studies of processes on the ice surface, illustrated by ozone adsorption and ethylene ozonolysis. Such results are important to clarify the mechanism of atmospheric pollutant elimination and air purification in the nature.

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## VERBA-XRF AS A NOVEL CONCEPTION OF X-RAY FLUORESCENCE ANALYSIS

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I propose novel developed conception named VERBA-XRF to calculate the content of chemical elements in the process of X-ray fluorescence analysis. For device specified and samples of certain composition, one constructs intensity correction system for analytical lines accounting for the influence of any chemical element's content in the specimen varying from zero to 100%. Correction system coefficients do not depend on specimen element content. In addition, these coefficients determine the influence of physical processes forming analytical line intensity and that of constructive parameters of X-ray spectrometer.

All the calculations for every analytical line use its own AC-10 virtual unified sample material containing 10% of chemical element analyzed. In practice, instead of AC-10 specimen, one can use certified sample material named Benchmark Reference Material (BRM). One must know complete chemical content of BRM. Having measured analytical line intensity of the specimen, one can determine the intensity from AC-10 by correction system. Anyone certified sample material can be used as BRM for a few elements. Quantitative composition of BRM does not depend on the range of varying chemical elements' content in samples analyzed substantially facilitating a selection and change of these BRM.

Principal difference of VERBA-XRF conception from all existing methods of X-ray fluorescence analysis is that intensity-content graphs for materials analyzed are no more needed. One can analyze all types of materials with unique system of corrections guaranteeing the absence of uncontrolled systematic error.

VERBA-XRF conception efficiency shows itself in numeral methods analyzing ferrous alloys and powder-like materials like raw materials for cement industry, slag, electrolysis precipitations in non-ferrous metallurgy.



# DIRECT ATOMIC ABSORPTION ANALYSIS OF SILICA BASED MATERIALS AND SOME OF ITS PECULIARITIES

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Direct atomic absorption spectrometry (AAS) analysis of increasing ( $e \approx 0,10$  g) mass of solid samples is the great practical interest since in a number of cases it allows to eliminate a long-time and labor consuming pretreatment dissolution procedure of materials and preconcentration of elements to be determined. Nevertheless at prevalent analytical practice  $SiO_2$ -based materials direct AAS are not practically used.

Main particularities of direct electrothermal (ETA) AAS determination  $\geq 0,05$  ppm of *As*, *Bi*, *Sb* and *Sn* in high-purity  $SiO_2$  and corresponding composites using furnace-flame atomizer and solid sample technique (SoST) are described. Operation parameters its atomizer were studied according contribution into their values the mass-transporting processes listed elements from solid  $SiO_2$  into gaseous phase and including temperature program of furnace heating according that mixtures to be studied are necessary performed:

- a) the stability of evaporation process, ensured by the preservation samples of analyte in an infused state;
- b) high values of coefficient extraction of elements:  $q = Q/100$ , where  $Q$  - the yield of an element from material analyzing (mass %) in gas phase;
- c) minimum time of element evaporation ( $t$ ) the value of that is conditioned by corresponding its thermochemical transformations.

It was established that at direct AAS analysis of  $SiO_2$ -based materials with SoST on account of agglomeration process and low rate evaporation trace amounts of *As*, *Bi*, *Sb* and *Sn* into zone of analytical signal formation the range of so-called effective temperature heating ( $T_{eff}$ ) has arranged by not effective then  $\geq 1600$  K. To eliminate or partially reduced some of difficulties at the *As*, *Bi*, *Sb* and *Sn* transporting from increasing analytical mass ( $\geq 0,1$  g) of  $SiO_2$  into gas phase some of high-temperature modifiers has been used.

The results obtained has been used at the development of effective direct AAS method determination of 0,05–1,0 ppm *As*, *Bi*, *Sb* and *Sn* in  $SiO_2$ -based materials. At these values of relative standard deviation ( $S_r$ ) does not exceed 0,25.

*Poster presentations*

# **SOURCE OF COLLIMATED THERMAL NEUTRON BEAM BASED ON A NEUTRON GENERATOR FOR NONDESTRUCTIVE EVALUATION OF MATERIALS AND PRODUCTS**

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This paper presents calculation and experimental studies of a moderator with a thermal neutron extraction channel, based on an NG-400 pumped neutron generator produced by the All-Russia Automation Research Institute. The neutron generator provides a maximum 14-MeV neutron flux density of  $5 \cdot 10^{10}$  n/cm<sup>2</sup>·s on the outer surface of the target chamber.

The moderator material and optimum sizes, the extraction channel configuration, as well as the converter and reflector material and sizes, were determined using the MCNP-4B code and the steepest descent method to attain a maximum flux density of thermal neutrons at the position of an object to be studied. The calculated data were experimentally verified, which showed good agreement.

It is supposed to apply this neutron source to nondestructive evaluation of products using neutron radiography and elemental analysis of materials by detection of capture gamma rays.

# TRACE ELEMENTS MILLIPROBE XRF ANALYSIS OF SINGLE ACCESSORY MINERAL GRAINES AS A TOOL FOR THEIR TOTAL Pb AGE DATING

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This paper presents an application of the “total lead” method of accessory minerals age dating. Analytical problem of the method is precision measurement of U, Th and Pb concentration in single micro crystal of zircon and monazite. Traditionally this is solved by utilizing the EMPA method, which demands a significantly labour-consuming sample preparation. Micro XRF method designed by Cheburkin [Scherrer, etc. 2002] has advantage for detection limit, but is more problematic during sample preparation (micro-drilling of petrographic thin section and following mounting of a sample). Represented version of single mineral grains XRF analysis (the instrument is described [Savenok, 2005]) is free of this disadvantage. Here grains are simply placed on thin substrate and irradiated by an X-ray from the tube. Since the method is absolutely non-destructive, small grain can be repeatedly measured for improved statistics (and improved age precision), thus providing a possibility of analysis by other method.

This work describes a method of concentration calculation and dependence of final dating precision from grain size, U, Th and Pb concentration and analysis time.

# HEAT RESISTANT NICKEL-BASE ALLOYS AND THE PRODUCTS OF THEIR CORROSION COMPOSITION DETERMINATION

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Heat resistance and gas corrosion resistance depends on chemical, phase compositions and structure of an alloy. The local corrosion destruction (LCD) of heat resisting alloys (HRS), especially a cast condition, probably, is determined by sweat of alloying elements.

The molybdenum, tungsten and tantalum concentration influence on LCD nickel-ferrous HRS resistance, used for gas turbine installations parts is investigated. The tests were carried out on modeling compositions. Samples were molded on the basis of an alloy of the ZMI-3C. The concentration of tantalum varied from 0 up to 5% with a step of 0,5%. The contents of elements were determined by a spectral method.

Samples were tested on in a melt of salts (75%  $\text{Na}_2\text{SO}_4$ , 25% NaCl) at 950°C in an air atmosphere for 24 hours. Micro X-rays spectrum by the analysis found that the chemical composition of carbides of an alloy of the ZMI-3C and test alloys differs noticeably. In the monocarbide of phase composition of an alloy of the ZMI-3C there increased concentration of titanium and tungsten is observed in comparison with test alloys containing chemical composition tantalum. The concentration of more than 2% of tantalum in test alloys has allowed mostly to deduce tungsten from a mono carbide phase (MC) into solid solution. Thus resistance of test alloys LCD has been increased essentially, as carbide phase is mostly sensitive aggressive environments influence. The critical value of total molybdenum and tungsten concentration in MC should not exceed 15%.

The further research of HTC-resistance of alloys was carried out by putting synthetic ashes simulating fluid gas turbine fuel combustion products on sample surfaces. Corrosion kinetics of corrosion was investigated in an interval of temperatures 800-950°C, the duration of samples endurance made 500 hours. Having removal the corrosion products, the samples were investigated by weight, metallography and X-ray diffraction phases analyses methods. The positive influence of tantalum on HTC-resistance is found to be seen at higher test temperature (950°C). The higher tantalum concentration in alloys the lower a superficial zone by chrome, that complicates nickel-sulfur interruption. The concentration of nickel in scale has decreased in 2-2,5 times. In alloys containing 2% and more of tantalum density of a formed oxide film has increased and its phase composition will change.

# INVESTIGATION OF INDIVIDUAL PARTICLES OF ZEOLITE POWDER BY X-RAY ELECTRON PROBE MICROANALYSIS

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The powders of zeolites of various trademarks are used to produce petroleum-refining catalysts. In this connection, it is very important to have complete information concerning not only chemical composition and distribution of impurity elements, but also shape, surface, structure and sizes of particles. It allows a more detailed analysis of the physical-chemical characteristics of catalysts, affecting their activity at different stages of technological process. One prospective for solving these tasks is X-ray microanalysis with an electron probe (EPMA).

The EPMA technique is developed for individual particles of fine-dispersed zeolite powder of various trademarks: ZSM-5, ZSM-12, MOR, BEA. The phase and chemical composition of zeolite powder, the surface, shape of particles, structure and their distribution in terms of the size were studied using Superprobe-733 device.

The results of phase analysis showed, that particles of different shape and various size were found in all samples of zeolites. The particles of flaky, orbicular, rounded and oval shape with size of 10  $\mu\text{m}$  are distinguished in zeolite sample ZSM-12. The particles of faceted shape as square, parallelepiped, rectangle with size of 5-10  $\mu\text{m}$  are observed in zeolite samples MOR and BEA. Larger particles of rounded, square, rectangular, rhombic, trapeziform, triangular shape with size of 5-20  $\mu\text{m}$  are separated in zeolite sample ZSM-5, while finer-dispersed fraction of particles with size of 3-10  $\mu\text{m}$  are observed in this sample after aging of gel (during 9 and 24 hours). The data on zeolite powder chemical composition showed the heterogeneous distribution of silicon. The increased contents of silicon are evident towards edges of particles that connected with aggregation and adhesion properties of particles.

The detailed study of chemical composition, structure, surface, shape and sizes of particles of fine-dispersed zeolite powder by EPMA will provide useful recommendations to improve the technology of producing alkanes and alkyl benzenes catalysts.

# **MATHEMATICAL BASIS AND SOFTWARE FOR SINGLE GRAIN MILLIPROBE XRF TRACE ELEMENT ANALYSIS (XRF-MP/SG) OF ACCESSORY MINERALS**

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The new promising method - single grain milliprobe X-ray fluorescence analysis (XRF-MP/SG) - was applied for the zircon single grain trace element concentrations measurement. The application of the method raised up several problems has to be solved. They are modeling and consideration of the mineral grain form, size and orientation influence on fluorescence intensity. The calculation of the fluorescence intensity for the different types of the grain forms has been carried out to solve the above-stated problems. Also the software for the element concentrations calculation with consideration of the above-stated factors has been developed. The software was applied to obtain concentrations of trace elements in zircon single grains. The current results of the work allowed formulating the perspectives of the future XRF-MP/SG method improvement.

## ORGANOALUMOSILICA SORBENTS FOR CONCENTRATION OF HEAVY METALS IN SOLUTIONS

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The sorption concentration of heavy metals became one of the basic methods of analytical preparation of tests owing to the high efficiency and simplicity of apparatus design. Among various natural and synthetic sorbents for concentration the sorption materials on the base of silica gel and its modified forms by various function groups, including hydrophobic, are used widely. Organosilica sorbents which contain in their composition both hydrophilic (silica gel) and hydrophobic (polymethylsiloxane) component can be perspective for concentration of inorganic ecotoxicants – heavy metals from water solutions. This is supported by: the presence of inorganic component, which increase mechanical and thermal stability, hardness of polymeric matrix excluding the necessity of preliminary preparation of sorbent, alternating surface hydrophilic and hydrophobic groups, ion-exchange properties, which increased at modification of sorbents by ions of metals, high kinetic and sorption characteristics.

Influence of the various factors in static conditions (concentration of heavy metals, both time of contact and ratio of solid and liquid phase, pH of medium) on sorption of Pb(II), Cu(II), Cd(II) and Zn(II) from water solutions is studied and the optimal conditions of their extraction by organosilica sorbents modified by ions of Al(III) and Cu(II) are found.

It was shown that most effective sorbents for concentration of heavy metals in water were silica-polyalumomethylsiloxane and its modified forms possessing increased capacity and the improved kinetic characteristics (sorption equilibrium was attained within 5-10 min. for Pb(II) and Cd(II), 2-3 hours for Cu(II) and Zn(II), respectively). It was established that at joint presence of heavy metals in solutions over interval of concentrations 0,05-0,3 g/dm<sup>3</sup>, possible at industrial accident and terrorist acts, the extraction of heavy metals by organoalumosiloxanes and their forms modified by Cu(II) in water solutions accounted for 98,6-100 %.



## **CONTENTS OF ELEMENTS IN DRIED GRAPE RAW, MEASURED BY GAMMA-ACTIVATION ANALYSIS**

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During development of drying circuits for the rests of primary processing grapes, the element content of received raw material components was studied. The initial material was processed in vacuum drying installation at the fixed temperatures in a range 40-60°C. The gamma-activation analysis with help of the high-current electron accelerator was applied to measurements\*. The content of elements Ca, Mn, Ni, Zn, Rb, Zr, Mo, I and U in skins and seeds of white grapes "Aligote" and of red grapes "Moldova" was determined.

The essential differences under the element contents of are found out in the different grape sorts. There was higher concentration of the measured elements in skins of "Aligote" grapes and in seeds of "Moldova" grapes observed. It is necessary to note, that used modes of drying were specially selected to minimize loss of biologically important elements and to keep initial biochemical qualities of a grape material.

The received results can be used at a choice of a drying mode for optimization of power expenses, at operation of drying installation, and correction of mineral structure.

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\* N.P. Dikiy, A.N. Dovbnaya, N.A. Skakun, V.L. Uvarov, M.A. Khazhmuradov, B.I. Shramenko, Use of accelerators in geology, medicine, isotopes production and atomic power energetic, Problems of Atomic Science and Technology (PAST), Nuclear Physics Investigation Series, 2001, No. 1, pp. 26-35.

# INTERELEMENT INFLUENCE CORRECTION IN THE XRFA USING INTENSITIES RATIO

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The usage of the ratio of characteristic lines as analytical parameter in the process of formation of the calibration curve provides a significant decrease of the residual error. In Realization of this method simultaneously with the decrease of the matrix effects causes some decrease or even full compensation of the form and condition of the measured surface.

In the experiment was determined that for linear calibration curve for CrKa in GSO PG24-PG31 the standard error was 0.045%. The application of theoretical corrections method enables a decrease of that value to the level of 0.013%. In case when for the analytical parameter is taken the ratio  $I_{CrKa}/I_{FeKa}$  the standard deviation decreases to 0.002%.

Such significant increase of accuracy may be explained on the base of analysis of the numerical values of the theoretical correction coefficients  $K_{Cr}$  and  $K_{Cr/Fe}$ , calculated for  $I_{CrKa}$  and for analytical parameter  $I_{CrKa}/I_{FeKa}$ . Changing from lines intensities for the ratios of analytical element line intensity to the intensity of the line most effecting the result of analytical element (chromium in this case) measurement enables the decreases of the error 5 or even 10 times practically to the level of statistics of the count rate. In case of chromium the influencing elements will be titanium, tungsten or molybdenum.

The same results were gained for Cr analysis in high alloyed steels. The error of linear calibration in this case is 0.28%. The application of theoretical corrections decreases this error to 0.07%. The standard error of the linear calibration on the base of the analytical parameter  $I_{CrKa}/I_{FeKb}$  is 0.23% and the application of the theoretical corrections in this case gives error 0.04%.

Other example of the application of described method may give analysis of copper in brass. It is well known that for the analytical line of copper CuKa the strong absorption takes place in Fe, Mn, Sn, Pb. These elements have the similar effect on ZnKa. It is possible to suppose that the ratio  $I_{CuKb}/I_{ZnKa}$  will less effected by the named elements. The analysis that was realized has confirmed that the variation of the named above ratio is about 25 less then variation of  $I_{CuKa}$ .

Presented approach enables an efficient approach to the choice of the proper calibration curve, having two terms. Method was tested on big amount of standards of brass, bronze and aluminium alloys.

# X-RAY FLUORESCENCE ANALYSIS OF COAL CONCENTRATES USING QUASI-SOLID SPECIMENS

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Among other methods the X-ray fluorescence analysis (XRF) has some advantages, namely: rapidity, selectivity, accuracy and an opportunity of automation. Accuracy of the analysis is caused by quality of the specimen obtained from analyzed sample.

The direct analysis of liquid samples is the most simple but the least acceptable. Using solid specimens for XRF is preferable. It is shown, that quasi-solid specimens on a basis gel-forming agent (gelatine) and polymeric films on the basis of the water-soluble polymer (polyvinyl alcohol) are most suitable for the analysis of aqueous medium. Using of prior concentrating on sorbent (charcoal) allows to reduce essentially the limits of detection of elements. It was established, that the carbonic concentrate (sorbate) can be used for preparation of gel and film specimens.

Simple, convenient and cheap techniques of obtaining of quality specimens in a combination with prior sorption concentration of impurities on absorbent charcoal (as complexes with 8-oxyquinoline) are presented. It is shown, that it is necessary to standardize conditions of separation of sorbate from an analyzed solution for obtaining of reproducible results ( $S_r=0,07-0,10$ ). There are found optimum conditions for obtaining the film specimens containing carbonic sorbate and polyvinyl alcohol. It is supposed to use the gel specimens containing sorbate, which are made simply and quickly, for a preliminary estimation of impurity level. Film specimens can be used for obtaining of more exact and reproducible results.

# THE USE OF INTENSITY OF COHERENT AND NON-COHERENT SCATTERED RADIATION OF THE X-RAY TUBE FOR THE COMPENSATION OF MATRIX EFFECTS AT THE ANALYSIS OF SOLUTIONS BY X-RAY FLUORESCENCE

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The general approach of quantitative determination of metals in organic and water-organic media by X-Ray fluorescence was developed. For the intensity of string lines of the corresponding series of characteristic X-ray radiation virtually does not depend on the form of presence of an element detected, the reducing of primary and fluorescent radiation by the probe substance becomes the main matrix effect studied. To compensate this effect we propose to use as an analytical signal the ratio of intensity of the strong line of characteristic radiation of the studied element to the intensity of coherent and non-coherent scattered radiation of the X-ray tube anode.

For water, organic and water-organic metal salts mixtures the dependence of integral and spectral intensities of coherent and non-coherent scattered radiation on the atomic number ( $Z$ ), density, oscillator layer thickness, chemical composition, and the conditions of the registering of analytical signals (voltage and tube current, tube anode material, crystal-analyzer) was investigated. The dependence obtained was compared to that for the solid probes (metals, alloys, pressed powder probes).

As a result we propose the technique of Mo, W, and Re determination in production cycle solutions with the use of peak of non-coherent scattered primary radiation in order to take into account the matrix influence on the analytical signal. The accuracy of the results was checked by the "input-found" technique.

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# FIELDFLOW FRACTIONATION OF MICROPARTICLES USING ROTATING COILED COLUMNS

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Field-flow fractionation (FFF) is a set of high resolution liquid chromatography-like elution methods used for sizing and separation of a wide range of particulate, colloidal and macromolecular materials. Recently the authors have shown that rotating coiled columns (RCC) traditionally applied to separation of different solutes by countercurrent chromatography can be used in FFF methods. A column of a certain configuration rotates around its axis and simultaneously revolves around the central axis of the planetary centrifuge. The asymmetrical centrifugal force field, acting on the RCC, provides different migration speeds of particles in one carrier fluid. As compared to the conventional sedimentation FFF (the separation is performed in a one narrow channel) the restriction for particle mass in the sample is avoided in RCC because column volume can be varied through varying the number of turns and layers of the coil. Planetary centrifuge design parameters have a great influence on the fractionation process; this can be used for optimization of separation conditions. It has been shown, that fractionation of suspended sample components can be achieved mainly by successive changing fluid pumping rate at a constant value of column rotation speed. The behavior of particles in RCC was studied by the examples of latex, silica gels and natural quartz sand particles of irregular shape. A theoretical model, describing the separation process according to design, operation parameters of RCC, and properties of particles has been proposed. On the basis of experimentally studied dependences of fractionation and retention of different particles and theoretical model, optimal conditions of soil samples separation into silt, clay and sand fractions have been selected. RCC can be also applied to the dynamic fractionation of trace elements in each fraction that may help to obtain detailed information about distribution of toxic elements in environmental samples. It may be concluded that the use of RCC for studies on the mobility of heavy metals in soils and sediments provides the basis for a new comprehensive approach to the speciation analysis of environmental samples.

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# **GAS CHROMATOGRAPHIC – MASS SPECTROMETRIC DETERMINATION OF INORGANIC HYDRIDES, PERMANENT GASES AND HYDROCARBONS IN HIGH PURITY SILANE**

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Silane is the primary source of silicon for the deposition of silicon thin films and its compounds and is used in the fabrication of photovoltaic cells, photocopier drums, silicon carbide and integrated circuits. At present high-isotopic enriched silane is the starting substance for production of high purity monoisotopic silicon  $^{28}\text{Si}$ ,  $^{29}\text{Si}$ ,  $^{30}\text{Si}$  single crystals. These devices require silane of extreme purity. The total contents of impurity in silane should not exceed  $1 \cdot 10^{-4}$ , and separate –  $10^{-5}$ - $10^{-9}$  %. Analytical methodology must be developed to keep pace with the technological advances in the design and fabrication of silicon devices. The most suitable method for the determination of gaseous impurities in silane is gas chromatography–mass-spectrometry. The silane analysis has been carried out on GC/MS Agilent 6890/MSD 5973N quadrupole gas analyzer. Impurities separation was performed in the capillary PLOT columns Porapak Q ( $l = 30$  m,  $d = 0,32$  mm) and GasPro ( $l=60$  m,  $d=0,32$  mm). The ultra pure helium has been used as carrier gas at 1.4 - 2 mL/min. Temperatures of ion source was 105°C, quadrupole mass filter - 150°C, columns - 30-120°C (programmed at 10°C/min). The injection of silane sample was carried out using two positions Valco EH2C6WEZPH-CER5 valve. The injection volume of silane was 50  $\mu\text{L}$  under pressure 10 - 760 torr. The factors are studied that limit the possibilities of gas chromatographic analysis of high purity silane. The stages of sampling, gas chromatographic separation and processing of the obtained data are examined. The presence of carbon dioxide, disilane, methylsilane, arsine, nitrogen, oxygen, methane, ethane, ethylene in silane has been shown. The calibration mixtures based on silane and helium for all determined impurities in concentration range  $10^{-2}$ - $10^{-4}\%$  has been prepared by manometric method and calibration curves have been plotted. Synthetic mixtures preparation error has not exceeded 1-5%. The stability of impurities in silane was investigated. The detection limits of impurities by MS-GC method are  $10^{-5}$ - $10^{-7}\%$ .

# METHOD OF BINARY PHASES OF VARIABLE CAPACITY FOR GAS CHROMATOGRAPHIC ANALYSIS OF HIGH PURITY VOLATILE SUBSTANCES

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Gas chromatographic determination of small concentration of impurities in high purity substances has a number of features, one of which connected with significant band tailing of the basic component, overlapping chromatographic zones of impurities, eluting from a column after the basic component. We investigate an opportunity of impurities determination by the method of binary phases of variable capacity. In this method the main component plays the role of an additional stationary liquid phase and possibility of large injection volume of sample is appeared. The model object of research was a high purity carbon tetrachloride. The experimental part of research was carried out with mass-spectrometric (Agilent 6890/5973N), photoionisation and flameionisation detectors (Shimadzu 14B, Tsvet-800). The important condition of formation of binary phase of variable capacity is the necessity in concave distribution isotherm of the matrix substance. The temperature range of formation of concave distribution isotherm of the carbon tetrachloride was determined. It is established, that the injection volume of the sample influences for the retention time of impurity: the more the injection volume, the more is the increase in retention time of impurity, and time shift of peaks of impurity and they are closer to the basic component. For substances, eluting at once after the main substance ( $\alpha=1.1-1.5$ ), the efficiency of the column has appeared to be by 2-3 times higher than in case of linear distribution isotherm of the main substance and with a sample being introduced in smaller quantities (by  $10^2-10^3$  times lower). A comparison of the tail part of chromatographic band of the basic components, observed on capillary and packed columns, was carried out. The slowed down decrease of the main substance concentration for packed columns is characteristic of concentration by 1-2 orders higher than for capillary ones and is connected with residual porosity of the solid supporter. For this reason the achieved limits of detection of “heavy” impurities of aromatic and chlororganic substances are  $10^{-7} - 10^{-9}$  wt. %, that is by 4-15 times better than those for the packed columns.

# VARIETY OF CHEMICAL ELEMENTS IN THE ENVIRONMENTAL SYSTEMS

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Highly sensitive methods of determination of natural objects structure lead to a large amount of data on the content of elements in different natural objects, such as rocks, soils, minerals, natural water, alive organisms, meteorites etc.

These results let V.I. Vernadsky to discover a very important geo-chemical phenomenon: that every natural object contains all chemical elements. i.e. all elements are spread in the nature [1].

According to V.M. Goldschmidt and Ya.I. Fersman the spread of chemical elements is determined by their nuclear characteristics.

In this thesis we suggest a model of the formation of elements, which allows us to make the connection between the spread of elements and their nuclear charge. We've got a function of distribution for the state close to the final period of active formation of elements and for the state, corresponding to the period of forming of condensed bodies [2, 3].

For description of possible ways of formation of charges we use a binomial spread [2, 3] i.e. a normalized differential function of the spread.

$$\rho_0(r) = C_n^r p^r (1-p)^{n-r}, \quad (1)$$

where  $p$  – possibility of the existence of a proton in the forming charge;

$q=1-p$  – possibility of the existence of a neutron in the forming charge.

Final expression for a description of the spread in the objects of the environment:

$$\lg K_r = A^0 r_0(r) + B \quad (2)$$

where  $K_r$  – spread of elements;  $A$  and  $B$  – some coefficients.

This hypothesis was used for descriptions of 30 natural objects. We can see a good agreement of the hypotheses with the experimental data.

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# NEW NANOCOMPOSITES OF BIOMEDICAL PURPOSE

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The problem of creation of new types of medical preparations and progressive technologies based on complex of physico-chemical as well as on medico-biological properties of nanosized ferromagnetics remains urgent for biology and medicine. Application of iron as nanosized powders may be various for creation of magnetic medicinal preparations. Usage of ferromagnetic nanoparticles with given properties and structure in biology and medicine constitutes the basis for design of medicines of a new generation which would be efficient, harmless, hypoallergic and without side reactions. Complex of requirements to such powders realized simultaneously is following: powders must be not pyrophoric, stable to corrosion, hydrophilic; must possess the high magnetic features; must not contain harmful admixtures and possess adsorption, catalytic and bactericidic characteristics.

Magnetite and carbonyl iron powders used in biomedical purposes are not consistent with above-mentioned requirements.

Technology of obtaining nanosized ferromagnetic powders and on their basis with metals-admixtures of Ag, Pt, Au, Cu, Zn was developed for the first time [1].

An attempt was made to create new efficient nanocomposites of biomedical purpose. For oncology, neurooncology and surgery: suspensions; magnetic liquids; containers containing ferromagnetic powders on basis of physiological solution, blood substitutes, medicinal preparations. For surgery and festering surgery: activated carbon material (ABBM Dnipro MP); the unguent-emulsion "Magnolia"; sprinklings; films-adsorbents; membranes-adsorbents; application-dressing materials. For endocrinology, therapeutics and oncology: capsules (magnetic containers for directed transport of medicines into key organ).

Mechanism of action of nanosized (0.005 – 0.02  $\mu\text{m}$ ) powders of ferromagnetics on biological systems is based on effect of magnetic fields created by ferromagnetic microcrystal assemblies and on specific action of every metal added which determined the field of practical application.

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# AN X-RAY PHOTOELECTRON SPECTROSCOPIC EXAMINATION OF PHOSPHORUS CONTAINING MATERIALS: OVERVIEW ON METHODS ADVANCES AND ABILITIES

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Diphosphate tungsten bronzes (DTB)  $\text{Cs}_{1-x}\text{Hg}_y(\text{P}_2\text{O}_4)_4(\text{WO}_3)_8$  are charge-density wave (CDW) conductors. The framework of  $\text{Cs}_{1-x}\text{Hg}_y(\text{P}_2\text{O}_4)_4(\text{WO}_3)_8$  contains columns of corner-sharing  $\text{WO}_6$  octahedra internked through  $\text{P}_2\text{O}_7$  group. Properties of  $\text{Cs}_{1-x}\text{Hg}_y(\text{P}_2\text{O}_4)_4(\text{WO}_3)_8$  can be tuned via out-of-framework cations content for adaptation in the CDW memory devices.

For DTB films obtained by CVT inhomogenous distribution of out-of-framework cations and admixture capture are observed. The aim of the present work is to use imaging X-ray photoelectron spectroscopy (*i*-XPS) for chemical state mapping which enable future optimization of the CVT technology. The P, O and Hg content in the DTB may be varied during the CVT.

The image analysis procedure shows that the oxygen content in the films practically does not change after heat treatment. In the investigated temperature range, all applied heat treatments enhance the P/W ratio as compared to the value corresponding to the untreated ones. The *i*-XPS analysis of these samples indicates the occurrence of Hg in  $\text{Hg}_2^{2+}$  (*i.e.* in the bronze) and Hg, HgO crystallites, which also denotes changes in the valence state of Hg ions during the applied heat treatment. The sample obtained at 1073 K has Cs/Hg = 0.31 and it contains the highest  $\text{Hg}_2^{2+}$ -ion concentration in the thin surface layers investigated and no crystallites. The analysis showed all of the treated samples exhibit increased concentrations of P and Hg. The P:O ratio is only slightly greater than 1:5 in most cases, suggesting that the majority of the P detected is  $\text{P}_2\text{O}_7$ , not  $\text{P}_2\text{O}_5$  contamination. Low levels of ionic iodine species are also present on the surface, indicating a direct reaction between the bronze surface and the transport agent. Since the bronze elements are readily detectable in all cases, the bronze form a continuous layer less than ~8 nm thick. The *i*-XPS analysis demonstrate the advantages of technique (analysis of first few atomic layers at the sample surface within 10% accuracy and with a detection limit of about 1% at.), and monitored results of CVT procedures, which efficient to produce good quality films with an acceptable purity for electro-physical properties examination.

# EXTENDING SURFACE ANALYSIS OF NEW MOSFETS BASED ON NANO AND MKM SCALED CDW PHOSPHATE AND OXIDE BRONZES

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Application of extending surface analysis using imaging X-ray photoelectron spectroscopy (*i*-XPS) combining with electron dispersion X-ray microanalysis and image treatment software allows one to extract the spectra of characteristic areas and to reconstruct an image of the chemical state of interest by means of a chemical state mapping. In this way, it is possible to transform the images such that they are useful for monitoring of cation transport in a thin film so chemically meaningful. The object of implementation of the techniques focused on chemical mapping is a new MOSFETs assembly based on an artificially grown layers of  $Cs_xWO_3$  and diphosphate tungsten bronzes (DTB)  $Cs_{1-x}Ti_y(P_2O_4)_4(WO_3)_8$  which are charge-density wave (CDW) conductors at 10, 50, 80 and 200 K. The framework of  $Cs_{1-x}Ti_y(P_2O_4)_4(WO_3)_8$  contains columns of corner-sharing  $WO_6$  octahedra interlinked through  $P_2O_7$  group. Properties of  $Cs_{1-x}Ti_y(P_2O_4)_4(WO_3)_8$  can be tuned via out-of-framework cations ( $Cs^+$  and  $Tl^+$ ) content for adaptation in the CDW memory devices. The present research is directed on developing analytical methods that allow quantitative information to be extracted from images. Extending surface analysis was performed using wavelength and energy dispersive X-ray analysis (WDX-EDX) probe and Cs fluctuation at the intra and inter layers of the  $Cs_xWO_3$  and DTB. It was shown that sensitive WDX analysis enables a much better energy resolution, preventing peak overlap errors encountered in EDX and lower background noise, but exhibits a higher time consumption, greater sample damage due to the high beam currents. It has been shown that for small  $x$  a ordering of the Cs occurs inside and between the octagonal DTB channels. This ordering process has a dramatic effect on the charge transport properties of the DTB due to the 1D character of the electron gas of the DTB. This is the first observed charge localization-delocalization phenomena of the Anderson type in the thin films of quasi-1D compounds. Application of the modern analytic techniques allows to analyzed transport process in the CDW films. Respectively the CDW conductors thin film remains a productive field for examination of transport process in surface interface and its effect on the electro physical characteristics of thin films assemblies for the nearest future.

# **X-RAY FLUORESCENCE ANALYSIS OF ORGANIC COMPOUNDS CONTAINING BROMINE USING QUASI-SOLID SPECIMENS**

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Halogenated organic compounds, in particular, brominated ones are frequently serve as intermediate or final products in organic synthesis. X-ray fluorescence analysis (XRF), which differs by selectivity, universality and high accuracy, is one of the most suitable methods for the control of the contents of bromine but is rather rarely used for the given purpose. The purpose of research work was to develop simple and universal techniques of obtaining the specimens for XRF of halogenated organic compounds, which are distinguished by high quality of work-surface.

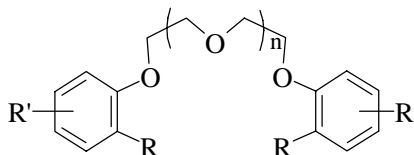
A number of quasi-solid specimens are offered and techniques of determination of bromine in various bromine-containing compounds are developed. It is possible to choose the most suitable specimen depending on an aggregate state of analyzed object. It is shown, that caramel specimens are the best ones for the analysis of alkaline solutions of halogenated organic compounds, and caramels or film specimens are the best ones for the analysis of powders. It is necessary to prepare organogel specimens in case of the analysis of liquid organic samples having liquid state under normal conditions. It is important to note, that the developed methods of obtaining of caramel specimens and film specimens are universal for determination of other halogens in halogenated organic compounds. Their realization depends only on opportunities of an X-Ray spectrometer, in particular, on the opportunity of carrying out of measurements in vacuum that is necessary for detection of soft  $Cl K\alpha$  or  $IL\alpha$  radiations.

# THE DETERMINATION OF COPPER MICROAMOUNTS ON THE TERBIUM LUMINESCENCE SENSITIZED BY IT IN HETEROBINUCLEAR COMPLEX

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The atom-fluorescence method was mainly used for the determination of copper microamounts. The luminescence determination of copper in the complex with pyridine and halogen-ions, with macrocyclic and other ligands is known. On the other hand, copper ions are the quenchers of lanthanide luminescence in complexes with different ligands – organic and inorganic. Since in f-d heterobinuclear complexes any d-metals (Zn, Cd) were able to increase the f-luminescence it was interesting to investigate copper ions influence on the Tb luminescence in the heterobinuclear complexes with podands - bis[2R-4(5)R'-phenyl]-ethers of oligoethyleneglycoles of general formula:



where  $n = 0$ :  $R = \text{COOH}, \text{CONH}_2, \text{CONHNH}_2$ ;  
 $n = 1$ :  $R = \text{NH}_2, \text{COOH}, \text{CONH}_2, \text{CONHNH}_2, \text{OCH}_2\text{CONHNH}_2, \text{OH}$ ;  
 $R' = \text{H}, \text{C}(\text{CH}_3)_3$

For the first time the sensitization of Tb luminescence by Cu ions has been detected in solution of Tb·Cu complex with 1,5-bis(2-hydrazino-carbophenoxy)-3-oxapentane (L).

The ratio of components in heterobinuclear complex is Tb:Cu:L=1:1:1. Maximum of Tb luminescence was recorded at  $\lambda_{\text{max}} = 545 \text{ nm}$  and Cu luminescence - at  $\lambda_{\text{max}} = 440 \text{ nm}$ . Since the increase of the Tb luminescence depends of the concentration of Cu in solution it was possible to determine Cu microamounts on Tb luminescence sensitized by it in heterobinuclear complex.

The method of Cu determination in which ligand is monometal Tb·L complex was used in analysis of standard samples of Zn and Ni alloys.

Experimental detection limit for copper is  $0.01 \mu\text{g/mL}$ .

## DETERMINATION OF TRACE ELEMENTS IN GEOLOGICAL SAMPLES BY MAGNETIC SECTOR ICP-MS

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Inductively coupled plasma-mass spectrometry (ICP-MS) is a multi-element analytical method with detection limits which are, for many trace elements, including the rare earth elements, better than those of most conventional techniques. With increasing availability of ICP-MS instruments in geological laboratories this method has been established as the most prominent technique for the determination of a large number of minor and trace elements in geological samples.

In 2001 a highly sensitive analytical technique with magnetic sector: ELEMENT2 (Finnigan MAT, Bremen, Germany) was installed in our Institute. This is an ICP-MS instrument employing a double focusing mass analyzer which allows to register the signal in three different resolution: low (LR)-300, average (MR)-4000 and high (HR)-10000 M/ $\Delta$ M.

In this work we present the estimations of accuracy, precision, detection limits and confidence intervals of ICP-MS results obtained in the last few years for reference samples of different composition, which are frequently analyzed with batches of research samples. We describe the technique to determine abundances of thirty nine elements from Sc to U in geological samples covering a wide range of mineralogical compositions: ultramafics, basalts, gabbros, andesites, phylolites, granites and shales. The isotopes of mostly common elements and operation modes (LR and/or MR) of registration for different isotopes were selected regarding a possible effect of interferences with isobar and molecular ions of other elements.

Three different techniques of chemical sample preparation were used:

- 1) an open acid digestion using the HF, HNO<sub>3</sub> and HClO<sub>4</sub> mixture (5:1:0.5);
- 2) an autoclave dissolution using mixed 5 ml HF and 1 ml HNO<sub>3</sub> during four hours at 220°C;
- 3) a fusion decomposition with LiBO<sub>2</sub> in glass carbon crucibles in high frequency furnace at 1100 °C for 4 minutes.

Internal standard of Rh with 2 ppb concentration was added to all the solutions. Three certified Multi-element solutions (CLMS-1,-2,-4, SPEX, USA) were employed for constructing calibration graphs.

The elements for which the results can be underestimated because of an incomplete digestion of refractory accessory minerals such as zircon and garnet, and/or formation of insoluble fluoride complexes have been distinguished. Recommendations on the choice of the decomposition procedure for such samples are given.

# ELECTRON PROBE MICROANALYSIS OF THE METALLIC WARE OF THE BRONZE AGE

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In the Baikal region the metal of the Bronze Age are displayed only by metallic ware finding accidentally. The outstanding importance and undoubted value of the archaeological finds demand preservation of real godsend. The X-ray electron probe microanalysis (EPMA) is a perspective method for investigation the archaeological finds. EPMA is non-destructive analytical method and we can study the composition of the sample from  $10^{-13}$  of gramme of substance.

The EPMA technique is elaborated for the finding Fe, Ni, Sn and Zn in the copper ware from archaeological finds for the microprobe Superprobe-733 (JEOL Ltd, Japan). Specimen preparation for the analyses involved removing small pieces of material with a micro drill. These pieces were then stuck onto scotch tape and cast in epoxy resin. After solidification of the epoxy the specimens were mechanically polished with diamond pastes to achieve a high-quality surface. The layer of carbon was evaporated onto the surface for providing the conductivity.

The change of the detection limits in accordance with the accelerating voltage, probe current and counting time was chosen as the criterion to select optimum conditions for analysis of these elements: accelerating voltage of 20 kV, probe current of 30 nA and counting time of 30 s. Analyzed values were corrected for matrix effects using the PAP method by applying the MARCHELL program adapted for the Superprobe-733 operating system. The background was calculated. The absorption factors were calculated using the Marenkov's formulae.

The EPMA accuracy dependence on the homogeneity of reference samples was mathematically demonstrated. We substantiated that separate standard samples of copper-rich alloys made for optical and chemical analysis can be used as reference samples for EPMA.

The metrological testing the elaborated technique was carried out. The relative standard deviations for each element did not exceed the admissible relative standard deviations. The quality of results obtained corresponds to the category 2. The chemical compositions were obtained for the archaeological finds, discovered on the lakeside of Baikal.

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# THE POTENTIAL OF TOTAL REFLECTION X-RAY SPECTROMETRY FOR STUDY OF THE BLOOD SERUM

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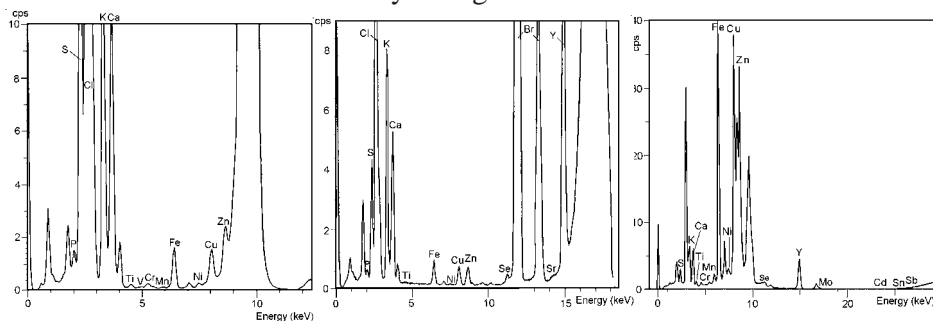
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At present time the investigations of microelement composition of biological objects are focus of interest. Among these are plant, sea organisms extracts, and biological liquids like blood serum, whole blood, urine, etc. It is well known that vitally important functions such as work of heart, brain activity, the normal functioning of nervous and reproductive systems are in direct dependence on the concentration of specific elements. Therefore, the qualitative and quantitative analysis of element composition of biological liquids allows to determine, in particular, the influence of pollution of the environment on the vital activity of organisms.



a) blood serum of the human, WLβ, 500 s

b) blood serum of the rat, MoKα, 500 s

c) model solution, WBr32, 500 s

The Far East medical clinics conduct the investigation of limited number of elements (Fe, K, Ca, Mg, Na, P, Cu). The multielement express analysis of human (a), rat (b) blood serum and model solution (c) were carried out using TXRF method. The results were obtained by means of spectrometer TXRF 8030C (FEI Company, Germany). The device allows to conduct the study in different ranges of the energy: i) 0–8.5 KeV, WLβ; ii) 0 – 15 KeV, MoKα; iii) 0 – 30 KeV, WBr32 that considerably increases both the number of detected elements and the accuracy of experiments.



# X-RAY FLUORESCENCE DETERMINATION OF MINOR AND TRACE ELEMENTS IN VARIOUS TYPES OF ROCKS, SOILS AND SEDIMENTS BY PIONEER SPECTROMETER

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Over the last seventeen years the Analytical center at our Institute amassed the actual material on the application of XRF method to the quantitative determination of some major (Mg, Al, P, S, Cl, K, Ti, Mn, Fe) and trace (V, Cr, Co, Ni, Zn, Rb, Sr, Y, Zr, Nb, Mo, Ba, La, Ce, Pb, Th, U) element contents [1, 2]. This paper presents the specific features of developed techniques for the determination of 25 element contents in different types of rocks using new Bruker Pioneer automated spectrometer connected to Intel Pentium IV. The special features of X-ray fluorescence analysis application to the determination of analyzed elements in various types of rocks are presented. The software of this new X-ray spectrometer allows to choose optimal calibration equations and the coefficients for accounting for line overlaps by **Fquant** program and to make a mathematic processing of the calibration array of CRMs measured by the **Loader** program.

In developing the techniques for the determination of analyzed elements in rocks the optimum measuring conditions were selected. One studied in detail the different variants for accounting for an X-ray background intensity such as a measurement of a radiation intensity at angular positions on a short and long wavelength side of an analytical line, use of a background intensity at a distant angular position, use of an intensity of scattered characteristic radiation from an X-ray tube. The examples and practical recommendations on some analytical problems are presented. The analyzed material (about 1 g) is pressed into pellets of an equal density. The boric acid is used as a pellet substrate. The ranges of analyzed contents were presented. The metrological characteristics of the developed technique were calculated.

For the samples of high C concentrations, obtained by a chemical enrichment of coaly shales, the technique was developed, which uses in addition the  $CK_{\alpha}$  analytical line intensity to correct interelement effects. The application of this correction allowed to reduce errors in determining the studied element concentrations up to an acceptable level. The carbon content was determined over the range 1 to 100 %.

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# INCREASING OF EFFICIENCY ROENTGENOFUORESCENT ANALYSIS AT A STAGE OF DESIGN OF EXPERIMENTS

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Roentgenofluorescent analysis (RFA) process can be divided into three stages: 1) design of experiment, 2) carrying out of measurements, 3) analysis of received results. Efficiency of process of the analysis, and also time of carrying out of measurements in many respects depend on process of design of experiments. Possibilities for increase of efficiency of RFA process of solids at the expense of selection of optimum parameters of carrying out of experiment from the preliminary information about the physical nature of substance and parameters of the measuring equipment are considered in present work.

Choice of spectral range for radiation recording and crystal-analyzer used in the measuring equipment is the important parameters at carrying out of the analysis of a qualitative and quantitative composition of substance and can have significant influence to measuring result, including the period of carrying out of experiment and volume of the useful information.

Optimum conditions of carrying out of experiment for expected composition of substance are offered to determine by methods of mathematical modeling. At build-up of mathematical model of radiation spectra the major factors influencing an observed data are taken into account: features of the measuring equipment, lines of the higher orders of diffraction, a profile of spectral lines and radiation absorption in a sample. Selection criterions of spectral range for carrying out of measurements are determined from the built mathematical model.

It is shown, that the offered approach allows to optimize a choice of a spectral range for carrying out of measurements and to recommend for a selected spectral range of value of the parameters of the equipment. It's permitting to implement measurements most efficiently.

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# ON-LINE COUPLING OF CONTINUOUS-FLOW FRACTIONATION OF HEAVY METALS IN ENVIRONMENTAL SOLIDS WITH ATOMIC EMISSION SPECTROMETRY

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The behavior of elements (toxicity, bioavailability, and distribution) in the environment depends strongly on their chemical forms and type of binding and cannot be reliably predicted on the basis of the total concentration. In order to assess the mobility and reactivity of heavy metal (HM) species in solid samples (soils and sediments), batch sequential extraction procedures are used. HM are fractionated into operationally defined forms under the action of selective leaching reagents.

Recently it has been shown that rotating coiled columns (RCC) can be successfully applied to the dynamic (flow-through) fractionation of HM in soils and sediments [1]. Since the flow rate of the extracting reagents in the RCC equipment is very similar to the sampling rate that is used in the pneumatic nebulization in inductively coupled plasma atomic emission spectrometer (ICP-AES), on-line coupling of these devices without any additional system seems to be possible.

In the present work it has been shown that on-line coupling of flow-through fractionation in RCC with ICP-EAS detection enables not only the fast and efficient fractionation of trace elements (TE) in environmental solids to be achieved but allows real-time studies on the leaching process be made. A novel five-step sequential extraction scheme was tested in on-line mode. The optimal conditions for the fractionation were chosen. Investigating elution curves provides important information on the efficiency of the reagents used, the leaching time needed for the separation of each fraction, and the potential mobility of HM forms.

The proposed method can be applied to the speciation analysis of environmental solids for risk assessment of their contaminants as well as to design of effective leaching schemes.

*The work was supported by the Russian Foundation of Basic Research (grant No. 04-03-32837)*

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# DETECTION OF CHROMATE DEFECTS IN Cr(III) CONTAINING DIPHOSPHATES BY LUMINESCENCE TECHNIQUE

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Complex oxides containing chromium ions are of interest as prospective active bodies for optical solid-state lasers. The Cr-doped  $A^1A1P_2O_7$  ( $A - Na, K$ ) were grown by spontaneous crystallisation from  $A^1_2O - Al_2O_3 - Cr_2O_3 - P_2O_5$  systems. The chromium content in the crystals was determined by a local X-ray analysis using Link ISIS system mounted on an Jeol 200 FX microscope. The basic units of the similar  $A^1A1P_2O_7$  frameworks are composed of  $AlO_6$  octahedron sharing two corners with diphosphate group. Partial substitution of Al positions in the  $A^1A1P_2O_7$  by  $Cr^{3+}$  ions was expected. Moreover, during the crystallisation red-ox reactions are possible, which result in incorporation of admixture centres different from  $Cr^{3+}$ . Such centres effect on the spectral properties significantly, therefore the  $A^1A1P_2O_7$  luminescence was investigated at 4.2, 77 and 300 K. The ILGI-501, LGN-503 and LG-22 lasers were used to excite the luminescence. The excitation spectra were detected after irradiation by DXeE1-1000 xenon lamp in 300–650 nm wavelength range. Spectrometers DFS-12 and DMR-4 were used for the spectra recording.

The luminescence spectra of the  $A^1A1P_2O_7$  consist of two main bands, that lies in the blue-green and in the red spectral regions, respectively. The maximum positions of the bands depend on the crystal composition and temperature, the intensities of the bands depend on the chromium content and the excitation wavelength. The red luminescence band and the narrow spectral lines (observed for the chromium-doped  $KA1P_2O_7$  only) were assigned to the electron transitions in the  $Cr^{3+}$  ions in distorted octahedral oxygen surround. The blue-green band consists at least of three components. A complex structure of these band results from a superposition of matrix intrinsic radiation and emission of the distorted  $CrO_4^{2-}$  groups. The only suitable position for location of chromium (VI) is substitution of phosphorus resulting in formation of mixed anion  $PO_3-O-CrO_3^{3-}$ , one oxygen vacancy per two chromate groups is necessary for the charge compensation.

The luminescence technique is valuable tool for the detection of chromate defects in dielectric complex oxides for a laser application in the presence of excess of the  $Cr^{3+}$  ions. Such technique enables detection of low contents of admixtures in a special state, which are undetectable by ordinary analytical routs.

## SRXRF ANALYSIS OF BIOSAMPLES FROM PAZYRYK EXCAVATIONS

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In the 90's of the last century members of the Archeological and Ethnographical Institute of the Siberian Branch of the Russian Academy of Sciences have excavated on the plateau Ukok in the Republic Mountain Altai several "frozen" graves.

Unlike the famous "royal" Pazyryk Kurgans, the ancient burials on the Ukok Plateau have been untouched by grave robbers: they were discovered in their original state. Among numerous unique finds, the most remarkable ones are well-preserved human hair and nails, tails and manes of the horses buried together with the people and also the ash from the censer.

The goal of present investigation is the continuation of the researches on the determination of elemental content in the specimens from Pazyryk graves and the comparison of the elemental interrelations between the all samples. In addition, it was performed the determination of elemental concentrations in hair and nails of contemporary people from Ukok Plateau.

The analysis was performed by XRF method with SR. SRXRF is an instrumental, multielemental, non-destructive analytical method using synchrotron radiation as primary excitation source. The fluorescence radiation was measured on the XRF beam-line of VEPP-3 (E=2 GeV, I=100 mA), Institute of Nuclear Physics, Novosibirsk, Russia. For quality control were used international reference standards.

The new data obtained on the elemental content of the ash from ritual censer confirm the hypothesis, which was postulated in earlier researches, about that possibility of the human copper-poisoning during the ritual narcotic inhalations.

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# **X-RAY FLUORESCENCE INTENSITY ELEMENTS OF MULTICOMPONENT POWDER MATERIAL WITH CONTINUOUS GRAIN SIZE DISTRIBUTION OF COMPONENTS**

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The effect of fluorescence intensity elemental analytical lines on grain size of components is one of the major reasons, which has an influence on the accuracy of x-ray analytical results of multicomponents powder materials. There are well-known methods for homogenization of powder materials, i.e. melting with flux and fine grinding. However, these methods are not suitable for technological polydisperse powder materials which contain metals and ferrous alloys powders. Therefore the development of theoretical methods taking into account grain size effect for x-ray analysis powder materials is actual problem.

The existing models for emitting x-ray fluorescence intensity of elemental analytical lines from heterogeneous samples are limited in practical applications, because in most publications the relations between the fluorescence intensity of analytical lines elements and the properties of powder materials were not completely studied. For example, particles distribution of components within narrow layer of irradiator which emitted x-ray fluorescence intensity of elements might be in disagreement with particles distribution of components within whole sample.

The relationship for x-ray fluorescence intensity radiation of analysing element of multicomponent heterogeneous powder materials is suggested. It is supposed that grain size distribution of components should continue. The formula for semi-infinite heterogeneous irradiator was deduced from the general principles. The final expression for x-ray fluorescence intensity of analytical line element A includes the fundamental constants, the volume parts of components of sample, and the density distribution functions of grain size for all the components in analysing sample. The size of components particles is described by equivalent diameter of spherical particles, which have the volume of irregular particles form. It is shown, that the fluorescence intensity of analytical line element A depended on autoadhesive properties caused by surface interaction of particles which determined physical-chemical and technological characteristics of materials. Obtained expression is described the enveloping effects connected by autoadhesive properties of material particles. The applications for some practical important cases of received relations are considered.

# STANDARD SAMPLES AND EXPERIMENTAL CHECKING OF COMPETENCE OF ANALYTICAL LABORATORIES

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Environmental analytical association «Ecoanalytica» produce standard samples during last 12 years. Two topics will be discussed. The first is the principles of development of structures and maintenance of quality of standard samples. The organization of manufacture and maintenance of their stability are considered too in the report. Besides them authors consider scientifically-methodical aspects of preparation of samples for experimental check of technical competence of analytical laboratories and also samples for interlaboratory tests.



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### Electronic Chemicals

Honeywell Electronic Materials is one of most basic manufacturers of high-purity process chemicals. We produce the broadest range of Ultra High Purity (UHP) <1 part-per-billion (PPB) chemistries required by our customers to enable them to meet industry technology roadmaps. By producing our chemicals from basic raw materials, we have better control of product quality and increased reliability of supply. We offer a full range of electronic chemical grades and are focused on ultra high-purity. Furthermore, we have developed expertise in the development of packaging technologies, providing a full range of container options, from bottles to isotainers.

Our Electronic Chemicals group is an industry leader in most basic manufacturing of Wet Process Chemistries, from UHP Straights (100 ppt qualities), Custom formulated Wet Etch, Solvents and Solvent Blends, and Cleaning Products.

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# Quality is the difference

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## ICP accessories

general and special designs of

- torches, bonnets, shields, purge tubes
- spray chambers, end caps, elbows
- nebulizers (CGN, X-flow, V-groove)
- coils, cones and multipliers for ICP-MS

## APEX Q (IR; HF) - System

for high sensitivity sample introduction

- increases signal intensity (factor 5-15)
- reduces oxide ratio (factor 10-100)
- fast rinse out and low memory
- fits easy to all ICP instruments



## TeflonPFA and Quartz ware

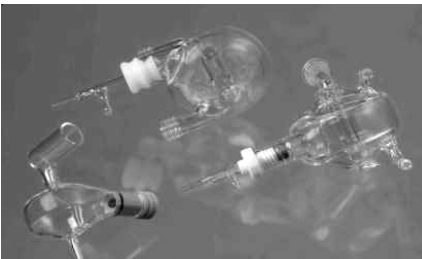
sample handling in ultra trace analysis

- sample cups, tubes, bottles, dishes,...
- subboiling acid/liquid purification
- element enrichment by subboiling
- autosampler probes and pump tubings

## HF resistant kits

made of ultra pure materials

- nebulizers (TeflonPFA, PEEK, PI, PP)
- spray chambers (cyclonic, Scott)
- semi and total demountable torches
- injectors of alumina, sapphire, platinum



## Spray chambers

made of quartz or borosilicate glass

- O-ring free nebulizer adaption
- optional jacketed for cooling
- chamber volumes 10 ...100 mL
- aerosol ports for all ICP instruments

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