7·8/98

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CHIMIA

Euroanalysis 10 Abstract Book

NEUE SCHWEIZERISCHE CHEMISCHE GESELLSCHAFT
NOUVELLE SOCIETE SUISSE DE CHIMIE
NEW SWISS CHEMICAL SOCIETY

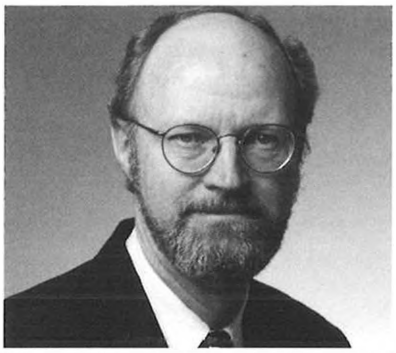
VERLAG HELVETICA CHIMICA ACTA

Fluka Prize

Reagent of the Year 1998

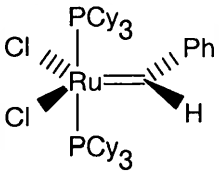
09587 Benzylidene-bis(tricyclohexylphosphine)dichlororuthenium, 1g / 5g

The Prize Winner 1998:
Robert H. Grubbs



Robert H. Grubbs was born near Possum Trot, KY, in 1942. He received his B.A. and M.S. degrees from the University of Florida working with M. Battiste and his Ph.D from Columbia University for work with Ron Breslow.
After a postdoctoral year with Jim Collman at Stanford he joined the Michigan State University (1969).
In 1978 he moved to The California Institute of Technology, where he is now the Victor and Elizabeth Atkins Professor of Chemistry.

The Reagent:
One of the most important reactions in organic synthesis is the formation of C-C bonds. A possible route to take is the transition metal catalyzed olefin-metathesis reaction.
Thanks to Robert H. Grubbs, olefin-metathesis has been taken a step further by the introduction of the Reagent of the Year 1998.



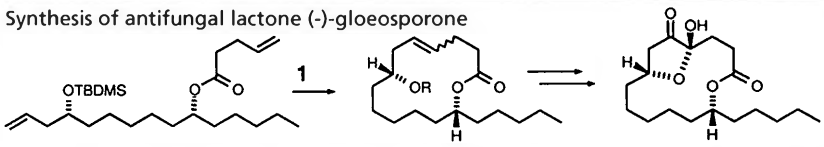
1
Fluka No. 09587

Different reaction types are catalyzed by the Grubbs catalyst
- Ring-closing metathesis of dienes
- Ring-opening cross metathesis of olefins
- Ring-opening metathesis polymerisation (ROMP)

Benefits of the Grubbs catalyst
- High activity in very small concentrations (10^{-4} mol%)
- Broad functional group tolerance
- Application in most solvents, including water
- Remarkable stability towards air and moisture

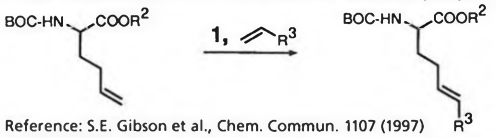
Application of the Grubbs catalyst in drug discovery and peptide synthesis

Synthesis of antifungal lactone (-)-gloeosporone



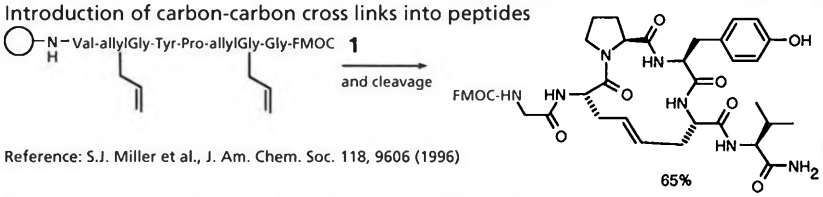
Reference: A. Fürstner, K. Langemann, J. Am. Chem. Soc. 119, 9130 (1997) 54%

Cross metathesis of the amino acid homoallylglycine



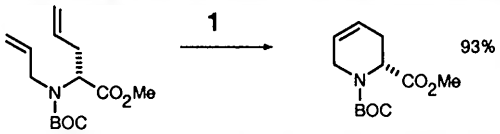
Reference: S.E. Gibson et al., Chem. Commun. 1107 (1997)

Introduction of carbon-carbon cross links into peptides



Reference: S.J. Miller et al., J. Am. Chem. Soc. 118, 9606 (1996)

Ring-closing olefin metathesis of non-natural α-amino acids



Reference: F.P.J.T. Rutjes, H.E. Schoemaker, Tetrahedron Lett. 38, 677 (1997)

The Fluka Prize:

The winner will be awarded the sum of sFr. 10 000.–. Nominations for the Fluka Prize «Reagent of the Year» should be submitted to the Fluka Prize Commitee c/o Fluka Chemie AG, CH-9471 Buchs/ Switzerland no later than September 30th. Full details regarding the Fluka Prize are available upon request.

Fluka

Fluka Chemie AG, Industriestrasse 25,
CH-9471 Buchs/Switzerland

For more information, please ask for our info sheet and see the Fluka Website http://www.Fluka.com/Fluka

E-mail: Fluka@sial.com

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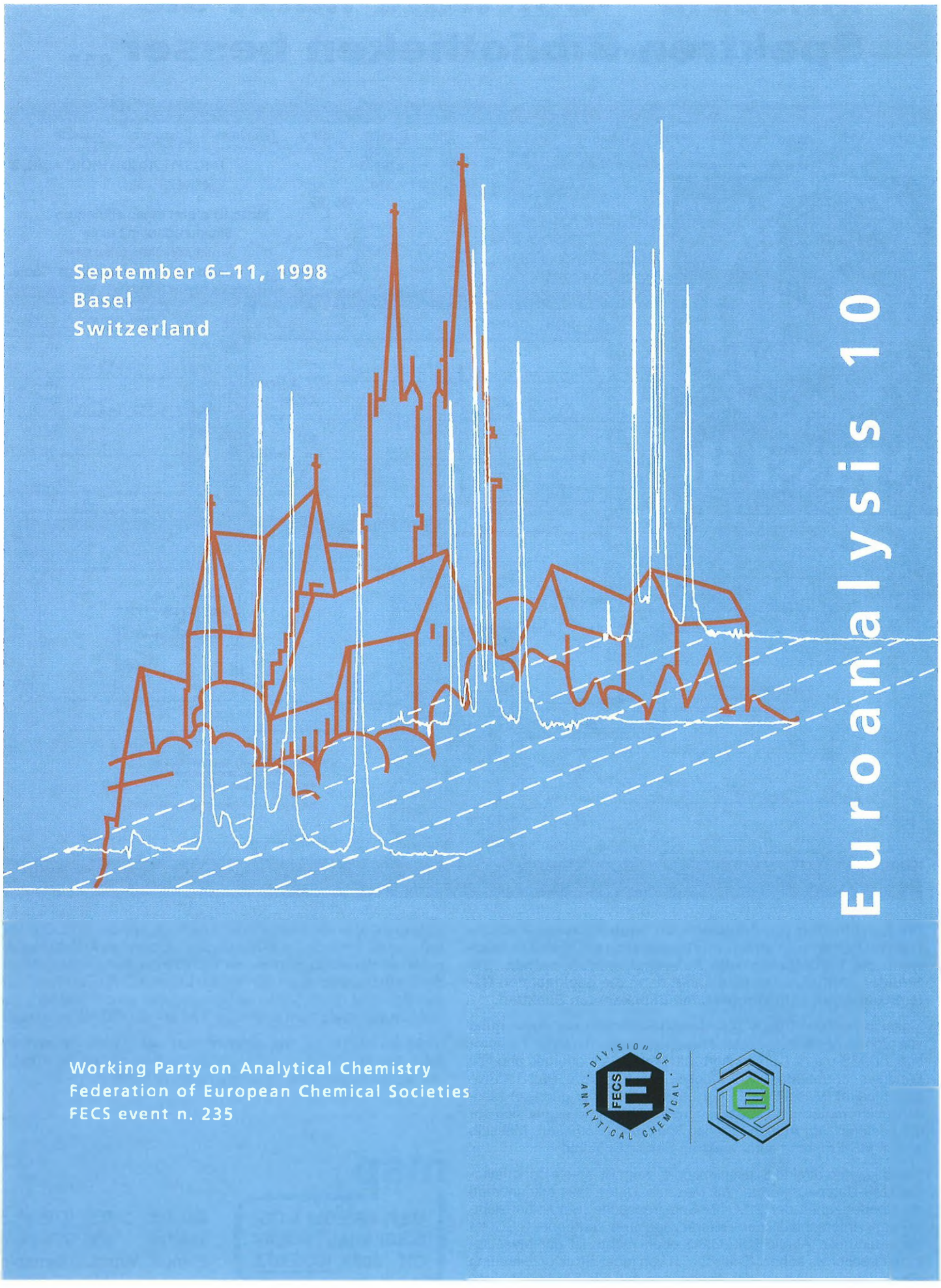

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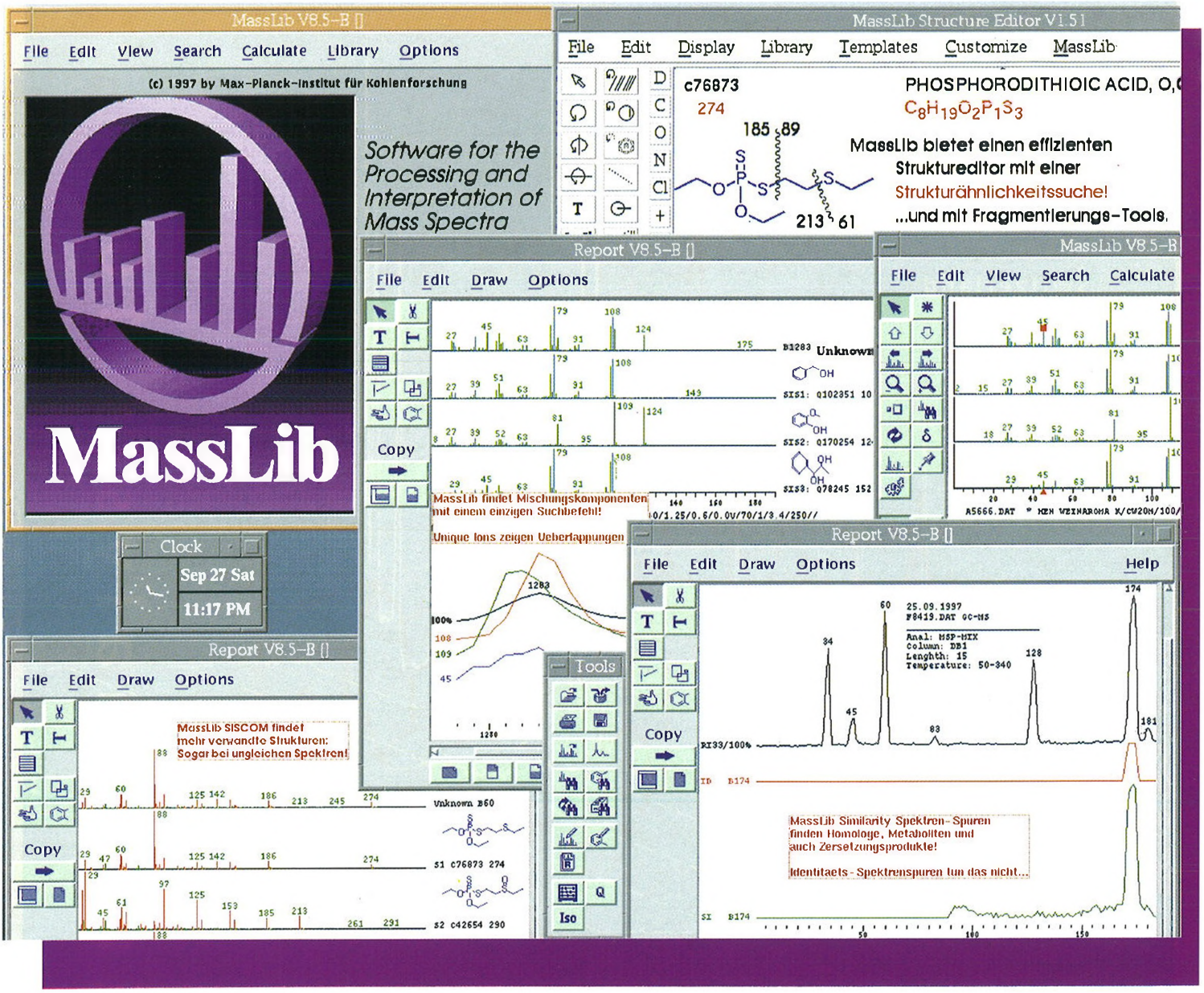

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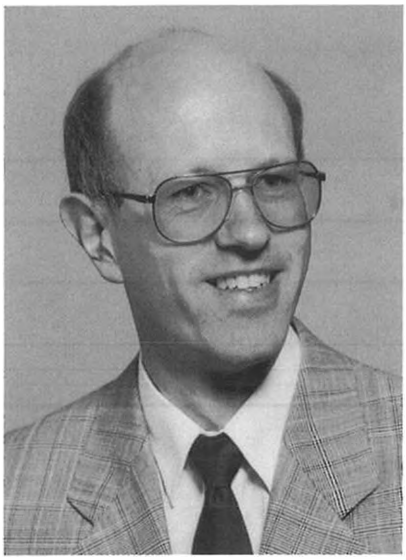
Invitation



Dear Colleagues

On behalf of the Division of Analytical Chemistry of the Federation of European Chemical Societies (FECS), the New Swiss Chemical Society (NSCS) and its Section Analytical Chemistry (SACh), I cordially invite you to the tenth European Conference on Analytical Chemistry, Euroanalysis 10 in Basel.

New research strategies in life sciences, an increasing concern about our environment and about the quality of our nutrition together with a fast progress in micro-engineering and molecular biology had a tremendous impact on the interdisciplinary science analytical chemistry. Analytical technologies are driven to reach the extreme numbers, just to give a few examples: Over 100'000 samples are processed per day in high-throughput screening labs, close to 100'000 recognition elements can be immobilized on a small, single-use chip, 100'000 theoretical plates per column allow for separations in a few seconds. On the other end of the scale, the detection of 1 molecule is no exotic task anymore and limits of detection below 0.000'000'000'000'000fl molar can be reached.

Despite the fact, that such novel approaches create exciting possibilities and the basis for future mainstream approaches, it shall not be underestimated, that established technologies carry the majority of the workload of analytical applications. As a consequence we have balanced the lectures to accommodate a wide spectrum of analytical activities and interests. **Plenary lectures** will cover aspects in Separation Sciences, Micro Fabrication, Quality Assurance and Spectroscopy. In the following three **parallel sessions**, the current state of the art in novel as well as established applications and technologies will be presented in short oral lectures.

In the last year, the European community of analytical chemists has lost two of their very active leading scientists, Prof. *H. Michael Widmer* and Prof. *Robert Kellner*. In honor of their achievements, **two memorial sessions** will be dedicated to their work.

The acceptance and rapid introduction of novel analytical technologies by the users require a constant and intense dialog between research groups, application experts, instrument manufacturers, and regulatory agencies. The **workshops**, newly introduced at Euroanalysis 10, will provide a forum for hopefully stimulating discussions.

Together with the scientific and the organizing committee it is a great pleasure for me to invite you to Euroanalysis 10 and I am looking forward to seeing you in September at this most exciting conference in Basel.

Markus Ehrat, Chairman Euroanalysis 10

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Welcome Address from the Government

On behalf of the people and the authorities of the Canton of Basel City I wish to extend a very warm welcome to all delegates and guests attending this European Conference on Analytical Chemistry.

We, the citizens of Basel, are proud that this gathering is taking place in our city, which was certainly not chosen merely by chance to be the host for this very important convention. Our city has a centuries-long tradition as a meeting place. Basel has always been one of Europe's busiest crossroads and a major commercial and political centre. Today, the city is still very much the gateway to Switzerland, as well as a key location for international communications.

Basel is a city devoted to art, culture and to science. The birth in 1460 of Switzerland's oldest university and the Reformation in 1529 attracted religious and intellectual refugees. And what may interest you: Basel was one of the first towns to manufacture paper. In the 15th century, the first papermill with the beautiful name 'To all winds' was here erected. The printing industry attracted at the same time famous scholars like *Erasmus of Rotterdam* and the *Holbein* family. Our city, our university profited greatly from men such as these.

Basel is unquestionably a city of chemistry. Every second inhabitant of the region lives directly or indirectly on the chemical and pharmaceutical industry. It is interesting to see that the silk-ribbon industry was responsible to a great extent for the emergence of the Basel Chemical Industry, above all the synthetic dyes. Today, the big companies *Ciba Speciality Chemicals*, *Clariant*, *Novartis* and *Hoffmann-La Roche* underpin the local economy.

From these few remarks several points emerge: without foreign impulse, foreign capital and merchants and scientists from other countries our city would not be what it is today. On the other hand, we may safely say that our town was always open-minded, open to foreigners and to new ideas. Thanks to this attitude, Basel was able to grow and thirdly: our economy was closely linked to science.

But your congress is not only a place to discuss Analytical Chemistry. It is at the same time an occasion to meet people from different countries and cultures, an occasion also to visit Basel. Basel is really charming, cheerful and sparkling, a unique mix of storybook architecture and modernism – a city just made for strolling, sight-seeing, shopping, with plenty of discoveries, both in and out of town.

I wish all of you a successful convention and a pleasant time during your stay in Basel.

Dr. Hans Martin Tschudi
Vice President of the Government

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Committees

Conference Praesidium

D.T. Burns, Belfast
M.F. Camões, Lisbon
M. Ehrat, Basel
G. Zambonin, Bari

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H. Vogel, Lausanne
R. Zenobi, Zurich

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Tentative Schedule

Time	Sunday, Sept. 6	Monday, Sept. 7		Tuesday, Sept. 8		
09.00		Opening Ceremony		**PL1**: Fused Silica Capillaries: The Fulcrum of Modern Analytical Separation Techniques **Csaba Horváth**		
10.15 13.00				Symp. 1 Analytical Chemistry in Life Sciences	Symp. 2 Flow Analysis/Separation	**Memorial Session R. Kellner**
		Lunch Break				
14.00		**Poster Sessions** H: Data Analysis and Chemometrics M: Sample Preparation for Trace Analysis O: Electrochemistry		**Poster Sessions** A: Analytical Chemistry in Life Sciences B: Flow Analysis C: Separation Techniques		
		Workshops				
16.00	Registration	**WS1** **Analytics in Combinatorial Chemistry** Chair: Ernst Gassmann	**WS2** **Antifficial Noses** Chair: Milena Koudelka-Hep	**WS3** **Drug Discovery by High-Throughput Screening** Chair: Siegfried Neumann	**WS4** **Chemical Sensors, Limits and Trends** Chair: Ernö Pretsch	**WS5** **Memorial Session R. Kellner Education in Analytical Chemistry** Chair: Filomena M. Camoes
18.00 19.00	Informal Get-Together					

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Euroanalysis 10, September 6–11, 1998

Wednesday, Sept. 9			Thursday, Sept. 10			Friday, Sept. 11		
PL2: Microfabricated and Miniaturized Systems in Analysis and Synthesis **D. Jed Harrison**			**PL3**: Are GC and LC Methods Process- or Performance-Based? **Thomas P. Layloff**			Symp. 10 Nutritional Analytical Chemistry	Symp. 11 Spectroscopy	Symp. 12 Novel Detection Concepts
EURACHEM Workshop	Symp. 5 Environmental Analytical Chemistry	**Memorial Session H.M. Widmer** Advanced Analytical Methods – Applications and Implications	Symp. 7 Chemical and Biochemical Sensors	**Analytica Chimica Acta** Emerging Techniques in Environmental Analysis	Symp. 9 Quality Assurance	12.00 Closing Ceremony		
Poster Sessions D: Mass Spectrometry E: Environmental Analysis G: Sensors I: Quality Assurance			**Poster Sessions** K: Nutritional Analytical Chemistry L: Spectroscopy ACA: Emerging Techniques in Environmental Analysis					
EURACHEM Workshop	**WS6** **The Role of Modern Mass Spectrometry in Biology** Chair: Peter James	**WS7** **Memorial Session H.M. Widmer Potential of Micro TAS** Chair: Elisabeth Verpoorte	**WS8** **Biosensors and Bioarrays** Chair: Ursula Spichiger	**WS9** **Analytical Aspects of Genetically Modified Food** Chair: Reto Battaglia	**WS10** **Quality Assurance in Daily Practice** Chair: Bauke te Nijenhuis			

Exhibition
Monday
to Wednesday
10.00–18.00

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Program at a Glance, September 6–11, 1998

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Wednesday, Sept. 9	Microfabricated and Miniaturized Systems in Analysis and Synthesis		PL2	311
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	2 Flow Analysis/Separation		2.1–2.7	314
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	WS4 Chemical Sensors, Limit and Trends		–	
	WS5 Memorial Session *Robert Kellner*: Education in Analytical Chemistry		–	
Wednesday, Sept. 9	WS6 The Role of Modern Mass Spectrometry in Biology		–	
	WS7 Memorial Session *H. Michael Widmer*: Potential of μ Tas		–	
Thursday, Sept. 10	WS8 Biosensors and Bioarrays in Cooperation with the Biovalley Initiative		–	
	WS9 Analytical Aspects of Genetically Modified Food: A Contribution of the Division of Food Chemistry of the FECS		WS9.1–WS9.3	329
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	Posters			
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	Analytica Chimica Acta	Emerging Techniques in Environmental Analysis	ACA P1–ACA P6	418

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EUROANALYSIS 10

September 6–11, 1998, Basel, Switzerland

ABSTRACTS OF ORAL PRESENTATIONS

Plenary Lectures

Tuesday, Sept. 8	Fused Silica Capillaries: The Fulcrum of Modern Analytical Separation Techniques	PL1
Wednesday, Sept. 9	Microfabricated and Miniaturized Systems in Analysis and Synthesis	PL2
Thursday, Sept. 10	Are GC and LC Methods Process- or Performance-Based?	PL3

Symposia

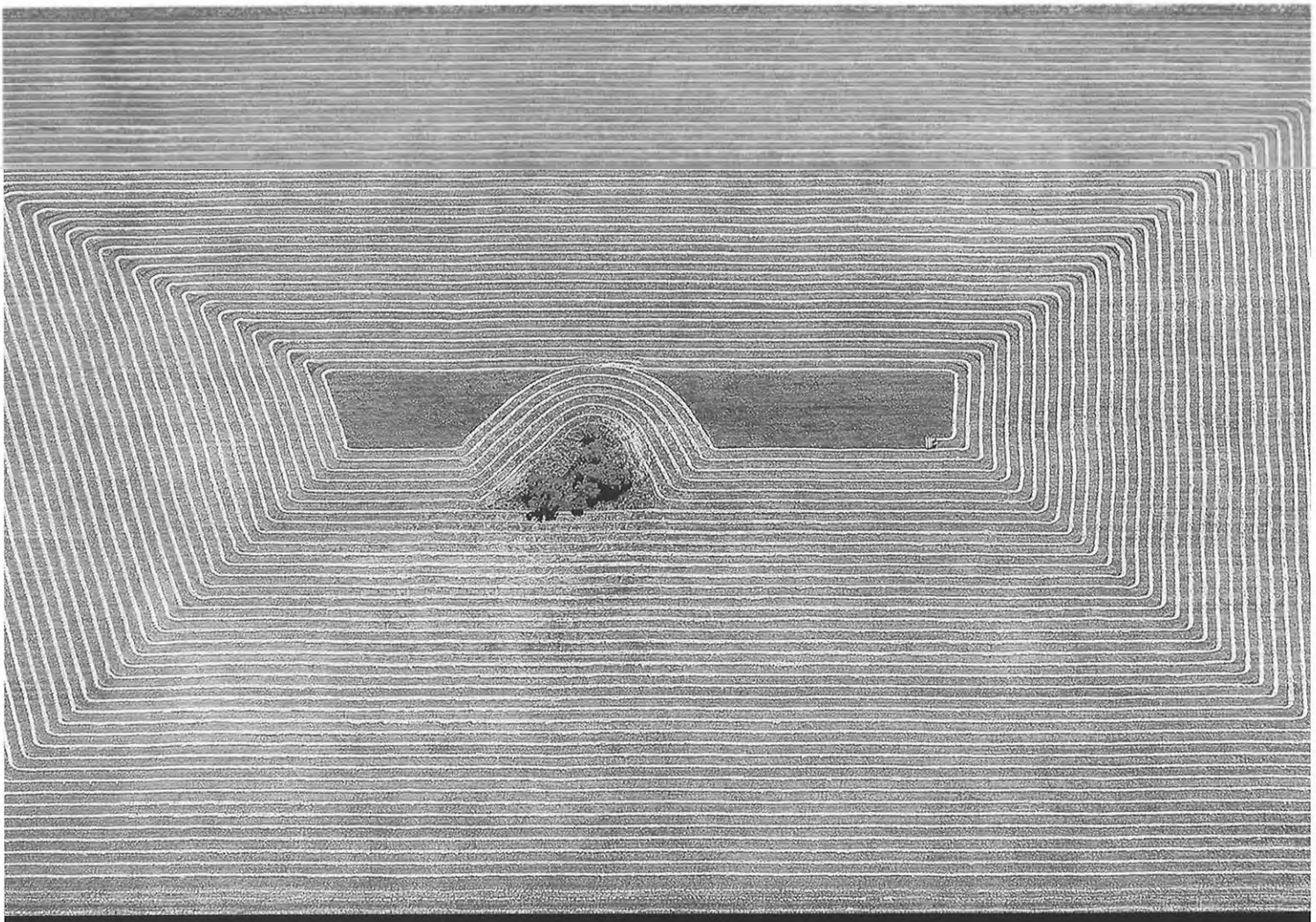
Tuesday, Sept. 8	Analytical Chemistry in Life Sciences	1.1–1.7
	Flow Analysis/Separation	2.1–2.7
Wednesday, Sept. 9	Environmental Analytical Chemistry	5.1–5.7
Thursday, Sept. 10	Chemical and Biochemical Sensors	7.1–7.7
	Quality Assurance	9.1–9.7
Friday, Sept. 11	Nutritional Analytical Chemistry	10.1–10.7
	Spectroscopy	11.1–11.8
	Novel Detection Concepts	12.1–12.7

Workshops

Monday, Sept. 7	Analytics in Combinatorial Chemistry	WS1.1–WS1.4
Thursday, Sept. 10	Analytical Aspects of Genetically Modified Food: A Contribution of the Division of Food Chemistry of the FECS	WS9.1–WS9.3

Special Sessions

Tuesday, Sept. 8	Memorial Session *Robert Kellner*	RK3–RK8
Wednesday, Sept. 9	EURACHEM Workshop	EURA1–EURA5
Thursday, Sept. 10	Analytica Chimica Acta: Emerging Techniques in Environmental Analysis	ACA L1–ACA L9



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PL1

Fused Silica Capillaries: The Fulcrum of Modern Analytical Separation Techniques

Professor Csaba Horváth
Department of Chemical Engineering
Yale University

Advances over the last twelve years with fused silica capillary (FSC) columns in gas as well as in liquid chromatography, electrophoresis and most recently in capillary electrochromatography have profoundly changed analytical separation technologies that conform to the differential migration process paradigm. With all the progress achieved by the various individual techniques in terms of resolution, speed of separation as well as sensitivity and sophistication of detection, the introduction of fused silica capillaries stands out as the most important milestone in this development.

After a brief review of the role of FSC columns in high resolution gas chromatography and micro-HPLC, the pertinent features of electrically driven separation techniques employing FSC columns are discussed. Capillary zone electrophoresis (CZE) and micro-HPLC are compared and the advantages and disadvantages of FSC columns are examined. In the ensuing treatment capillary electrochromatography (CEC) will receive close inspection. CEC can be viewed as an analytical separation technique that is brought about by merging capillary electrophoresis with micro-HPLC into a *bona fide* chromatographic technique distinguished by its electrophoretic platform. After establishing the genealogy of CEC, its theoretical foundation and operational features will be compared to those of CE and micro-HPLC. The present develpment state of CEC will be delineated and some of the expectations from the new technique are examined. Particular attention is paid to the need for novel stationary phases and for a better theoretical understanding of the interplay of electrosmotic transport phenomena and chromatographic retention in FSC columns packed with particulate or monolithic stationary phases.

PL2

Microfabricated and Miniaturized Systems in Analysis and Synthesis

D. Jed Harrison
Department of Chemistry
University of Alberta
Edmonton, Alberta, Canada, T6G 2G2

Micromachining technology has provided a means of fabricating miniaturized, three dimensional structures capable of manipulating chemicals, biochemicals and biological entities such as cells for a variety of purposes, including diagnostic assays. This technology offers promise in developing new, miniaturized instrumentation with a high level of automation and rapid analysis times for the performance of clinical assays, genetic analysis, drug screening, and chemical analysis, amongst other applications.

A number of miniaturization methodologies are being explored, including micro-spritzers and high density titre plates, microfluidic devices, array techniques, utilizing either pressure, displacement or electrokinetic pumping methods to name a few. This lecture will briefly examine a number of these competing technologies, in an effort to provide perspective on the present state of the art. Focus will then be given to work in the author's laboratory on the use of microfluidic devices that utilize pressurized or electrokinetically driven flow to develop micro-Total Analysis Systems and other microfluidic devices.

The use of such devices for organic synthesis, automated performance of immunoassays or DNA assays, and the evaluation of cell response to agonists and antagonists will be described. Some of the barriers to ultimately achieving integrated, automated fluidic devices that perform sophisticated analysis, synthesis or screening will be discussed, as will the likely avenues that could lead to success.

PL3

"Are LC/GC Methods Process- or Performance-Based?"

Thomas P. Layloff
U.S. FDA/Div. Of Testing and
Applied Analytical Development
1114 Market Street
St. Louis, MO 63101

The traditional implementation of regulatory analysis is to perform methods exactly as written. This concept carries with it the implicit assumption that the method is robust and reproducible, i.e., among laboratory analyses show low variance. Because of this requirement regulatory methods are frequently established using tried and true technologies since the reproducibility of state-of-the-art (SOTA) procedures generally has not been established. In the 1950s the regulatory methods focused on titrimetry, gravimetry and spectrophotometric measurement. Gradually the SOTA technique of Gas Chromatography became more commonplace with established reproducibility. More recently LC methods have begun to move from SOTA to regulatory applications. In both chromatographic techniques there are large numbers of different columns commercially available. In addition the chromatographic properties of the columns may change with continuing use. The large number of chromatographic columns and changes in their partitioning characteristics poses a significant regulatory challenge. These challenges with be discussed from the process-based and performance-based method description perspectives.

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1.1

HUMORAL IMMUNE RESPONSES IN CEREBROSPINAL FLUID DURING INFLAMMATORY DISEASES OF THE HUMAN NERVOUS SYSTEM

T.O. Kleine
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Objective: Humoral immune responses in central nervous system (CNS) have to be discriminated from systemic responses during inflammatory CNS diseases which cause disturbances of the blood-brain-barrier (bbb) function. Here, they are determined by the qualitative detection of oligoclonal bands (OBs) comparing equal amounts of immunoglobulins (Ig) in pairs of CSF and serum samples as well as by calculation of an intrathecal Ig production with formulae considering the amount of serum albumin which passes the disturbed bbb from blood into CSF. Material and Methods: The semi-automated PhastSystem ™ (Pharmacia LKB) was applied to isoelectric focusing (IEF) on self-made PAG microgels (43 x 50 x 0.4 mm) expanding pH gradient to an Ig relevant range (pH 3-10) using a self-made sample applicator for 4 µl native human CSF containing e.g. ≥8 mg/l IgG [1]. Immunofixation was done with antisera against human τ chain and its Fc fragment as well as against kappa and lambda light chains. Ig quantification was done with immunonephelometric assays. Results and discussion: The high resolution of the IEF technique applied here detects at least 5 patterns of immuno reactions: Type 1: a normal background pattern of IgGs in CSF and corresponding serum samples. Type 2: additional IgG subclasses in CSF indicated by OBs, demonstrate local IgG synthesis; they varied interindividually as well as during the disease process. Detection of both light chains and no τ chain only in CSF points to the appearance of other Ig (sub)classes (e.g. of IgA or IgM) besides free light chains in CSF. Type 4: additional Ig bands in CSF and serum samples standing out against the normal polyclonal background of the gel, indicate a systemic immune activation; it may be confirmed by elevated Ig levels in blood serum and by protein electrophoresis on CAF sheets. Type 3: a mixed type showing the presence of bands of types 2 and 4. Type 5: paraprotein pattern in CSF and serum samples was confirmed by immunofixation of serum Igs. Conclusion: Different immune responses in CSF of patients with inflammatory CNS diseases, detected by IEF, point to an Ig heterogeneity changing during the disease process. IEF proves to be more sensitive and accurate to detect an intrathecal Ig production than its calculation with formulae which may be disturbed by bbb alterations.

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1.2

PARALLEL AFFINITY SENSOR ARRAY (PASA) BASED ON CHEMILUMINESCENCE DETECTION

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Due to their cross-reactivity, immunoassays lack the ability to distinguish strictly between structurally related compounds. If many different compounds have to be determined in a sample or the compounds to be determined are not known *a priori*, immunoassays or normal immunosensors are not very useful.

We have set up a parallel affinity sensor, which is based on chemiluminescence detection in an array configuration. The affinity array is located on a glass-plate of a flow-cell; the immunological reagents are immobilized on this plate by means of hydrophobic interactions or covalent coupling. To achieve maximum sensitivity, we use enzyme-enhanced chemiluminescence with a peroxidase/luminol system. In addition, a very sensitive CCD-chip is used as a detector, which puts hundreds of thousands of independent measurement channels to one's disposal.

For applications in environmental analysis it is very important that the EC maximum admissible concentration for drinking water (0.1 µg/L) can be reached, e.g., for the herbicide terbuthylazine. The sensitivity depends largely on the affinity of the used antibodies and is similar to the sensitivity obtained in common immunoassays [1]. This parallel affinity sensor array (PASA) can be applied for the identification and quantification of multiple analytes with chemometric methods [2]. It is well suited to be extended to any analyte, which can be measured with immunological or similar affinity-based methods.

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[2] R.J. Schneider et al. Fresenius J. Anal. Chem. **343** (1992) 145-146.

1.3

CHARACTERISATION OF DUGONG LIVER FERRITIN

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Dugongs are herbivorous sea mammals that feed virtually exclusively on seagrass. They are mainly found in tropical areas that support extensive seagrass beds. Dugong liver contains very high levels of iron (up to 137,000 µg/g dry wt). Generally, iron is stored in the protein ferritin. Histological studies indicated dense deposit of iron in the tissue, without evidence of the tissue damage normally associated with very high iron levels[1]. Purification of ferritin using a modification of the method of Page et al., 1980 from dugong liver was carried out in order to precisely determine the form of iron present. The speciation studies on iron were carried out by Mössbauer spectroscopy. The size distribution and iron core crystallinity of the ferritin were also determined using transmission electron microscope.

Mössbauer spectra of purified ferritin at 78K indicated the presence of ferrihydrite ($5Fe_2O_3 9H_2O$) rather than geothite-like (α-FeOOH) iron oxide. The Mössbauer spectra of a sample of dugong liver tissue indicated the presence of a goethite-like iron phase related to that found in transfused human thalassemic patients[2]. This iron phase is not normally found in tissues of mammals whose iron is absorbed from the diet. The iron core study indicated that purified dugong ferritin had a limited crystallinity. The characteristics of purified dugong ferritin are similar to other mammalian ferritins, based on amino acids determination of the ferritin protein cage.
The naturally high level of iron in its food is reflected in the high liver iron values. The ability of the liver tissue to withstand the high concentration of iron in the tissue without apparently damaging the tissue deserves further study.

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[2] St Pierre et al., Biochim. Biophys. Acta, 1987

1.4

SEPARATION OF *TRANS*-DIHYDRODIOL ENANTIOMERS OF CARCINOGENIC POLYCYCLIC AROMATIC HYDROCARBONS BY CSP-HPLC

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Polycyclic aromatic hydrocarbons (PAH) require metabolic activation in order to exert their mutagenic and/or carcinogenic activity. Bay- or fjord-region dihydrodiol epoxides are thought to be the most important, biologically active PAH metabolites. They are formed by cytochrome P450-mediated oxidation of intermediate *trans*-dihydrodiols. The stereoselectivity involved in the enzymatic formation of *trans*-dihydrodiols and their subsequent oxidation is an important factor determining the biological activity of the parent PAH. Investigations of the stereoselectivity of PAH activation usually require both enantiomerically pure reference materials and chiral discriminating techniques for metabolite analysis. The techniques available comprise either chromatographic separations of diastereomeric esters of the dihydrodiols or their direct chiral separation by electrokinetic micellar capillary chromatography or by HPLC using type I chiral stationary phases. In the present study cellulose-tris-(*N*-3,5-dimethylphenyl-carbamate), a type II chiral stationary phase, has been found to be highly efficient in the separation of *trans*-dihydrodiol enantiomers. For the seven dihydrodiols tested including benzo[*c*]phenanthrene-3,4-dihydrodiol 1, dibenzo[*a,l*]pyrene-11,12-dihydrodiol 2, benzo[*c*]chrysene-9,10-dihydrodiol 3, benzo[*g*]chrysene-11,12-dihydrodiol 4, naphtho[*1,2-a*]pyrene-9,10-dihydrodiol 5, naphtho[*1,2-e*]-pyrene-11,12-dihydrodiol 6 and benzo[*a*]pyrene-7,8-dihydrodiol 7 a baseline separation of the enantiomers was achieved (Rs ≥ 1.5). Peaks were almost symmetrical (ratio of peak width at 10% peak hight ≤ 2) and capacity factors (between 2 and 7) usually increased with the number of carbon atoms. The elution order of the enantiomers of compounds 1, 2, 3, 4 and 7 was confirmed by co-chromatography with the available optical pure (-)-dihydrodiols. The enantiomers of 1, 2, 3, 5, and 7 follow an uniform elution order in that the (-)-*R,R*-enantiomers eluted earlier than their optical antipodes except those of dihydrodiols 4 and 6 which show the opposite elution order. Circular dichroism (CD) spectra of eluting enantiomeres were taken and used for further characterization of the compounds. Whereas CD spectra of dihydrodiol enantiomersof 2, 5 and 6 were hitherto unknown, the CD spectra of optically active 1, 3, 4 and 7 were in good accordance to those published. Based on the available data, the *R,R*-configuration was tentatively assigned to the (-)-enantiomers of 5 and 6. The chromatographic system described here offers a powerful tool for the elucidation of stereoselectivities observed in PAH metabolism. Moreover, it appears to be suitable for scale-up applications and thus for the preparative separation of dihydrodiol enantiomers from racemates.

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1.6

BIOAFFINITY SCREENING WITH CAPILLARY ELECTROCHROMATOGRAPHY

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Screening methods are in demand for compounds with binding activity to biological recognition elements such as cellular receptors. For screening of e.g. combinatorial libraries it is important that such a method allows to discriminate between different molecules with binding activity.

We describe a method which combines the selectivity of bioaffinity recognition with the high resolving power of capillary electrochromatography (CEC). The method not only allows for screening of molecules with binding affinity but also holds information about cross reactivities of the compounds of interest.

Using 30 minutes on-column preconcentration on a C4 reversed phase and standard UV detection we separated four cardiac glycosides from other steroids in nanomolar concentrations with efficiencies of up to 200000 plates/m and good repeatability. Upon addition of immobilized Anti-digoxigenin Fab fragments prior to injection, cardiac glycosides were bound to various degrees as indirectly determined by comparison of the two electropherograms measured before and after addition of the affinity particles.

1.7

ELUCIDATION OF THE T CELL RECEPTOR COMPLEX AND FUNCTION IN EARLY T CELL SIGNALING

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The TCR is an oligomeric membrane protein complex consisting of a mainly extracellular αβ-dimer noncovalently, and with unknown stoichiometry, bound to CD3-subunits γ, δ, ε and a ζ-dimer. It is the intracellular domains of the latter proteins which transduce the extracellular signal received by the αβ-dimer into an appropriate intracellular signaling cascade. Thus a fine-tuned communication between proteins closely associated with the TCR is needed to enable a T cell to respond differently when receiving altered signals, e.g., leading cells to proliferation, cell death, or anergy. Today, only little is known about the entire composition of the TCR signaling machinery because the low abundance of cellular signaling proteins and the restricted number of available antibodies against such proteins have so far hampered the direct biochemical analysis of signaling complexes in living cells. Technical advances in the area of capillary-based peptide separation and peptide analysis by electron spray mass spectrometry (ESI-MS) have dramatically increased the sensitivity of peptide analysis. We set out to study the T cell receptor (TCR) protein composition under different stimuli with this emerging technology.

The protein pool of CD11.3 cells was radiolabeled with L-[^{35}S]-methionine. TCR immunoprecipitates were prepared from unstimulated cells and cells stimulated by TCR crosslinking with 145-2C11 antibody. Immunoprecipitated proteins were separated by high-resolving 2-D gel electrophoresis and detected by silver-staining and autoradiography. A complex composition of TCR-associated proteins could be revealed by this approach. Preliminary results on the characterization of some proteins using capillary LC ESI-MS/MS of in-gel digested proteins will be shown, presenting for the first time the direct biochemical analysis of a biologically relevant receptor signaling complex.

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2.1

FLOW AND SEQUENTIAL INJECTION SYSTEMS:- THE STATUS, ACHIEVEMENTS AND CHALLENGES TOWARDS PROCESS CONTROL, MONITORING AND MINIATURIZATION.

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Flow injection analysis (FIA) coined by Růžička and Hansen 21 years ago (1976) is a well established technique that became the fastest growing concept in Analytical Chemistry. The introduction of sequential injection analysis (SIA) in 1990 broadened the scope of flow analysis. Although the injection and propulsion components used in SIA are quite different to FIA, the underlying principles remain the same: well-defined sample and reagent zones are injected and merged with reproducible operational timing control, the reaction products are formed within well-defined areas of composite concentration gradients, and the transient signal yields reproducible analytical results. FIA is based on the injection of a liquid sample by an injection valve into a moving, non-segmented continuous flow carrier stream of a suitable liquid. The injected sample forms a zone, that is processed in a manifold system to a suitable product zone, which is then transported to a detector that continuously records a physical property of the product zone. In SIA the sample and reagent zone(s) are aspirated through a multiposition selection valve to create a stack of well-defined zones adjacent to each other in a holding coil. After the selection valve has been selected to the detector position, the flow in the carrier stream is reversed and the zones mutually disperse and penetrate each other to form a composite product zone as they passed through a reaction coil to the detector. In the talk various aspects of FIA and SIA will be discussed, comparing FIA and SIA as analytical tools according to the **present status** and **achievements** of the two techniques. The **prospects** and **challenges** of both concepts towards **process control**, **monitoring** and **miniaturization** will be highlighted.

2.2

BISEGMENTED FLOW SYSTEM FOR DETERMINATION OF LOW CONCENTRATION OF GASEOUS CONSTITUENTS

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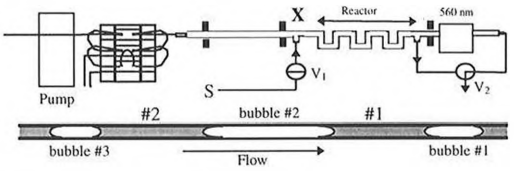
The determination of gaseous analytes through the use of Monosegmented Flow Analysis been proposed recently. However, segmented flow systems have not been yet investigated to be used in the determination of low concentration gaseous analytes of environmental interest. These specimens are present in very low concentration (ppbv) and usually some kind of pre-concentration need to be performed before some classical method can be employed in the determination. This work proposes the investigation of a bisegmented system for determination of gaseous specimens. The flow system is depicted in Fig. 1 along with the flow pattern it produces. The system is computer controled and when the bubble #2 of the flow pattern reaches the point "x", the carrier flow is stopped and valves 1 and 2 are turned on to allow the intake of the gaseous sample. The sample (S) is pumped through the reaction glass tube that was previously wetted with an absorbing reagent contained in the liquid segment #1. The gaseous analyte is absorbed by the reagent layer and after this pre-concentration step the valves are set off and the carrier flow is re-established. The liquid segment #2 does contain an appropriate reagent to collect the retained analyte and to produce a coloured compound detected in the spectrophotometric flow cell. The system has been applied to the determination of NO_2 by absorbing the analyte in triethanolamine and collecting it in to Greiss reagent. The system is capable of determine this specimen in air in the range 25 to500 ppbv. (**FAPESP**).

Fig. 1



2.3

THE USE OF AN ELECTRO-DIALYSER/FLOW SYSTEM FOR ZINC ASSAYS IN PHARMACEUTICAL SAMPLES

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Electro-dialyser/FIA systems have been successfully employed as cleanup and dilution tools. The use of a passive membrane in such an electro-dialyser is still a fairly new concept. With this technique the high dilution factor of samples in normal dialysers fitted with passive membranes were reduced to a minimum and as a result the detection limit also decreased. The main disadvantage of the electro-dialyser / FIA system, however, was the formation of gaseous products at the electrodes in the electro-dialyser (causing serious problems during the detection of the analyte) and the high dispersion in the dialyser unit itself leading to higher detection limits and relatively high RSD values. In previous work done by the authors, the detection limit was decreased to values of less than 1.5 mg/l by means of a preconcentration step. This preconcentration step, however, also increased the experimental time. In the latest innovation the injection mode of the sample was changed from the previous method in such a way that the dispersion in the dialyser was decreased to such an extend that preconcentration of the analyte was not necessary. This not only decreased the experimental time, but also lowered the detection limit to a lower value than obtained with preconcentration.

The electro-dialyser used, consisted of a passive membrane sandwiched between two electrodes which were used to introduce an electrical field across the membrane. The electric field introduced, increased the mass-transfer of ions across the passive membrane with the result that the percentage dialysis (depending on the applied potential) increased to more than than 90 %. The number of runs was improved from 14 runs.h^{-1} (in the previous system) to 24 runs.h^{-1}. Since no preconcentration is involvedt and the dispersion was reduced to a minimum in the dialyser unit, the RSD of the new system showed a vast improvement in comparison to the previous system used.

2.4

A COMPARATIVE STUDY OF SPME AND LLE OF PESTICIDES FOR HRGC DETERMINATION

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Solid Phase Micro Extraction, SPME, is a recently developed technique which is based on the use of a fused silica fibre coated with a stationary phase. Depending on the type of coating, the fibre has the ability to extract the analites from aqueous or gaseous samples. The analites are then thermally desorbed in the injection port and analysed by gas chromatography. Being a solvent-free technique, thus non toxic to the environment and to the operator, it has clear advantage towards liquid-liquid extraction, LLE. In this work we present the results of a comparative study between both methods regarding performance, precision, cost and time consumption, on the determination of pesticides in water samples.

The precision of the extraction step was obtained through the detailed knowledge of the instrumental interpolation uncertainty, the volumetric step uncertainty and the final experimental dispersion calculated from replicate analysis. The estimation of all uncertainties but one (extraction) and of the experimental dispersion (simulated by the combination of step uncertainty estimations) allows the estimation of the unknown by difference. Therefore it is possible to calculate that important source of uncertainty, hence based on experimental evidence instead of subjective judgement.

The assumptions developed for this treatment were the gaussian distribution of the extraction efficiencies, its independence on the analite concentration and equivalent sensitivity of the instrument for samples and standards. The deviations of the recoveries from 100% are, therefore, attributed to extraction efficiencies instead of matrix effects.

The results were corrected by application of recovery factors.

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2.5

FIELD-PORTABLE CAPILLARY ELECTROPHORESIS INSTRUMENT WITH POTENTIOMETRIC AND AMPEROMETRIC DETECTION

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A portable capillary electrophoresis instrument with potentiometric and amperometric detection has been designed and built, which includes lead acid batteries as independent power source, a 30 kV high voltage power supply and the detection electronics. With a size of 340 mm x 175 mm x 175 mm and a weight of 7.5 kg it is easily movable by one person.

Electrodes were constructed by inserting a wire of the desired electrode material into an piece of glass capillary as electrode body. A simple capillary-electrode holder cell allows an exact alignment of the electrode and the separation capillary without using a microscope and a micromanipulator.

To achieve the required robustness of the potentiometric detector, coated-wire electrodes were constructed by coating the tip of a platinum electrode with a ion-selective PVC-matrix membrane. These electrodes were used for the detection of monovalent inorganic anions and alkali and alkaline earth metal cations. They show a detection performance similar to the previously applied micropipette ion-selective electrodes but they have a higher mechanical robustness and a longer lifetime. By adding a crown ether to the background electrolyte not only the separation of alkali and alkaline earth metals could be improved but also the sensitivity of the ion-selective electrode towards some of these ions was considerably enhanced. These electrodes have also been applied to the detection of different classes of organic cations and anions.

A metallic copper electrode was also used as potentiometric detector for native amino acids.

For the amperometric detection mode, we designed a new potentiostat circuitry, which makes use of the electrophoretic system as reference and requires besides the working electrode only a single counter electrode in the detection cell.

2.6

HPLC OF AMINO ACIDS AND PEPTIDES WITH TETRAPHENYLPORPHYRIN STATIONARY PHASES

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Covalent attachment of porphyrins to silica gel provides stationary phases exhibiting hydrophobic interactions with analytes and additionally showing $\pi-\pi$ interactions with analytes of aromatic properties, which was satisfactory utilised earlier by other authors especially for HPLC of fullerens and polycyclic aromatic hydrocarbons.

In this study retention of 18 common amino acids and several di- and tripeptides was examined on tetraphenylporphyrine (TPP) stationary phase unmetallated and metallated with Cu(II) and Zn(II). HPLC measurements were carried out with UV detection at 210 nm mostly in isocratic system with phosphate eluents in concentration range from 5 to 50 mM at pH in the range from 3.0 to 7.0. As retention of these solutes is partly based on interaction between aromatic systems of analytes and stationary phase and partly on coordination interactions with metallic centres of porphyrins a satisfactory resolution was observed for aromatic and basic amino acids The use of acetonitrile as organic modifier of mobile phase reduces significantly $\pi-\pi$ interactions for all examined amino acids except l-cysteine and L-tryptophan.

TPP columns are more selective towards peptides, than amino acids, and especially towards peptides with aromatic amino acids. Effect of metallic centre in stationary phase is more pronounced for TPP metallated with Cu(II) than Zn(II). Both columns were successfully employed for separation of C-peptide from bovine insulin, both in isocratic and gradient elution.

2.7

SEPARATION AND DIVISION INTO FRACTIONS OF NON-IONIC SURFACTANTS AND THEIR METABOLITES FROM THE WATER MATRIX

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Separation of non-ionic surfactants (NS) from the water matrix is necessary prior to further procedures because of: i) the complexity of the matrix, ii) minute concentrations. In currently used gas-stripping separation only ethoxylates having 5-30 oxyethylene subunits (EO) are separated, while the other NS are lost. The aim of this work is to develop separation schemes for the separation of total NS plus metabolites from the water matrix and their division into fractions to broaden relevant information.

Preliminary separation of NS and poly(ethylene glycols) (PEG) from sewage and water samples is done by extraction with chloroform while that from tap water by solid phase extraction. Two separation schemes for the division of NS and PEG's into fractions are developed and compared. One combines liquid-liquid extraction with precipitation. The total mixture is successively extracted with ethyl acetate and chloroform. The ethyl acetate fraction contains ethoxylates having 1 - 30 EO, non-ethoxylate NS and free fatty alcohol (FFA) while the chloroform fraction, PEG's and ethoxylates having over 30 EO. Both fractions are divided into subfractions by a precipitation of ethoxylates and PEG having over 5 EO with modified Dragendorff reagent. The alternative scheme consists of four successive extraction steps: the fraction of n-hexane containing short-chained ethoxylates, non-ethoxylate NS and FFA; the fraction of ethyl acetate containing ethoxylates having 10 - 30 EO, the dichloromethane fraction consisting of ethoxylates having over 30 EO and long-chained PEG's and the chloroform fraction containing short-chained PEG's. Distinguishing ethoxylates having over 30 EO and long-chained PEG's is possible using the two-monitor indirect tensammetric technique. Each scheme provides valuable information concerning residual NS, long- and short-chained PEG's as well as some other metabolites in raw and treated sewage and surface water.

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5.1

ANTHROPOGENIC INFLUENCE FROM NORTHERN EUROPE OVER COASTAL AREAS OF PORTUGAL – SULFATE AEROSOL MEASUREMENTS –

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Project ACE-2 aims at the determination and understanding of the properties and controlling factors of the anthropogenically modified atmosphere of the North Atlantic, in order to assess their relevance for radiative forcing. It has been running for two years, with long-term measurements and an intensive campaign in June/July 1997. Monitoring stations have been set-up in four locations, Azores (P), Madeira (P), Tenerife(S) and Sagres (P). These stations are equipped each with meteorological sensors, a cloud condensation nuclei counter and a high-volume sampler (PM10 (particulate matter 10 μm) inlet, Whatman-41 filters and air flow 0.5 m^3 min^{-1}). Sampling conditions were computer controlled for wind sector and wind velocity. During the intensive campaign na experimental additional station has been set-up at Cabo Raso, in Lisbon coastal area, for comparison purposes with the more southern stations. Sampling of aerosol particles was done with two stage filter packs (PM10 inlet, Nucleopore and Whatman-41 filters and air flow 0.016 m^3 min^{-1}). The cut-off of the filter packs was determined between 1-2 μm. Samples have been analysed for major water soluble inorganic species Na^+, and organic acids by ion chromatography. The results show a coarse fraction mainly constituted by sea-salt particles and a fine fraction with non-sea-salt (nss) sulfate, with comparable results for Cabo Raso and Sagres. Two main pollution episodes (6-11/7 and 21-23/7) have been confirmed by the increase of nss-sulfate concentration back trajectories showing that polluted air masses come from the North of Europe. Background concentration levels in Sagres are apparently higher than those at Cabo da Roca, which may be related to input from urban and industrial areas along the South West coast of Portugal.

5.2

See page 425

5.3

NEW LASER MULTIPHOTON IONIZATION METHODS FOR ENVIRONMENTAL ANALYSIS

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We report a first attempt to use the laser multiphoton ionization method for analysis of trace aromatic compounds on the surface of environmental (soils and aerosols) samples. A fast conductivity technique was developed for such on-line analysis and was applied to several (organic and inorganic) environmental samples. Matrix effects were investigated and compensation methods were suggested. Limits of detection in the ppb range are reported for polycyclic aromatic hydrocarbons (PAH) compounds.

Direct analysis of combustion by-product aerosols by laser multiphoton ionization coupled with a renewable liquid droplet technique is also addressed. PAH polluted aerosols were sampled by means of renewable water microdroplets and quantitative analysis was then performed using the multiphoton ionization technique. Two droplet contamination regimes were clearly observed. These are associated with either a volume uniform or a surface favored concentration. Detection limits as low as 1 pg were obtained for PAH contaminated such microdroplets.

A combination of laser multiphoton ionization and laser induced fluorescence is shown to provide both high sensitivity and selectivity. These combined techniques involve both single and two-photon processes, thus, provide unique analytical information. Multidimensional presentation of such data is shown to be useful for environmental analytical applications.

5.4

POLAROGRAPHIC AND VOLTAMMETRIC DETERMINATION OF NITRATED POLYCYCLIC AROMATIC HYDROCARBONS

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Nitrated polycyclic aromatic hydrocarbons are well known environmental carcinogens and there is an ever increasing demand for the determination of their trace amounts [1]. Modern polarographic and voltammetric techniques were shown to be sensitive enough for the determination of various types of chemical carcinogens [2]. Therefore, we have investigated the possibility to use differential pulse polarography, differential pulse voltammetry and adsorptive stripping voltammetry for the determination of trace amounts of 1-nitropyrene, 9-nitroanthracene, 2-nitrofluorene and 2,7-dinitrofluorene as model substances. The influence of pH and the composition of the base electrolyte on the polarographic and voltammetric behaviour of these substances was investigated and the optimum conditions for their determination in the concentration range of 1.10^{-4}-1.10^{-9} $mol.l^{-1}$ were found. Practical applicability of these methods was demonstrated on the determination of trace amounts of these chemical carcinogens in river water and on polarographic and voltammetric monitoring of the chemical destruction of the test substances.

Acknowledgement: This research was supported by Grant Agency of Czech Republic (Grant No. 203/98/1187).

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5.5

ANALYSIS OF SEDIMENT SAMPLES FROM THE ARCTIC SEAS TO ASSESS RADIOACTIVE CONTAMINATION

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The radioactive contamination of Arctic Seas is of particular concern, especially in countries with Arctic coastlines [1]. The major sources of radioactive contamination of these seas can be classified as: 1) Disposal of liquid and solid wastes into the Barents and Kara Seas. 2) Unsafe nuclear submarines and nuclear power plants which sank into the bays of Novaya Zemlya Island. 3) Global radioactive fall-out induced by atmospheric nuclear weapons tests and radioactive substances brought with river runoff.

The International Arctic Seas Assessment Project [2] was co-ordinated by the International Atomic Energy Agency (IAEA) and involved 14 countries. King's College Geography Department received 26 sediment samples. The samples were analyzed to understand the rate and mechanisms of sedimentation in seas and oceans and to assess its possible ecological implications.

Soft bottom sediments were recovered by a means of box corer (30x30 cm) at water depths ranging from 15 to 334 m. Subcore samples were taken in 10 cm diameter PVC tubes and were subsequently sectioned at 0.5, 1.0 and 2.0 cm intervals and stored frozen. The sediment core profile received by IAEA-MEL (IAEA Marine Environmental Laboratory) contained a dark brown surface layer of fine grey silt and clay. The samples wet sieved freeze dried and homogenized in IAEA-MEL. The analysis was carried out using University of London facilities. The geochemical composition was determined by a ICP-AES spectrometer and an X-ray fluorescence spectrometer. Sediment reaction pH and cation exchange properties were measured. Particle size analysis was carried out using a sedigraph 5100 particle size analysis system. Results from X-ray diffraction and scanning electron microscope photographs were used to help in the determination of whether or not the sediments and related radioactivity are more likely to come from rivers or from the adjacent island of Novaya Zemlya.

[1] Yu.A. Izrael, A.V. Tsyban, S.M. Vakulovskii, *Russian Meteorology and Hydrology*, **1994**, (10), 9-15.
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5.6

DETECTION OF AMBIENT AIR POLLUTANTS BY LONG PATH FT-IR GAS SPECTROSCOPY

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Fourier transform infrared (FT-IR) spectroscopy has the advantage, compared with other methods, that several gases can be detected simultaneously and the monitoring can be performed continuously.
A commercially available FT-IR instrument (Bio-Rad FTS-185), with 0.5 cm^{-1} resolution has been used. The system also includes a multipass gas cell with 360 m effective path length, an InSb and an MCT detector.
The performance and the detection limits of the two detectors have been compared, using MIR and NIR sources.
The most unhealthy and most frequently encountered gases have been selected for calibration, including the always present background gases CO_2 and H_2O.

CONCENTRATION AND DETECTION LIMITS OBTAINED OF INDOOR AIR POLLUTANTS*
(Smoky Room)

Compounds	*Concentration (ppm/v)*	*Detection limits (ppb/v)*
Acetaldehyde	0.54	3.0
Carbon-dioxide	390.00	0.2
Carbon-monoxide	6.64	1.0
Ethylene	0.51	0.5
Isoprene	0.46	0.8
Methane	3.50	0.7
Methyl alcohol	0.34	0.7
Nitrous oxide	0.28	0.5
Non-methane hydrocarbons	0.40	0.5

* Measured by MCT detector and MIR source

Acknowledgement
We would like to express our thanks to Bio-Rad Digilab Gmbh (Germany) for the supporting of this project.

5.7

QUANTIFYING UNCERTAINTY IN THE ANALYSIS OF ENVIRONMENTAL SAMPLES

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The total uncertainty of an analytical measurements can be expressed as the amount of sampling uncertainty and analytical measurement uncertainty. Measurement uncertainty can be controlled and evaluated by an appropriately selected QA program. Using certified reference materials the systematic error can be estimated and the analytical measurement and/or instrument can be calibrated.
Many environmental decisions are based on the results of quantitative chemical analysis of environmental samples. The evaluation of uncertainty requires a close look to all possible sources of uncertainty. In many cases, all that can be done is to develop an uncertainty "budget" and estimate the contribution of each component. In practice, a preliminary study will quickly identify the most significant sources of uncertainty and the value obtained for the total uncertainty may almost entirely be controlled by the major contributions. Consequently, a good estimate can be made by concentrating effort on the largest contributions.
In our work the measurement uncertainty of the determination of toxic metals of lake and river sediments has been calculated. Samples were collected in the Lake Balaton and the concentration of Pb, Cd, Hg, Cr, Mn, Ni, Fe, Al, As, Cu, and Zn was determined by atomic absorption method. The individual uncertainty components were evaluated for the experimental procedures. Blanks and uncertainties of the different steps such as sampling, transport, storage, reagent, homogenization, grinding, weighing, digestion, filling up the flasks to mark, calibration of measuring devices, dilution of sample solution, and preparation of calibration curves were estimated and the total uncertainty was calculated.

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7.1

LAB IN THE BAG

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"LAB IN THE BAG" is rather an analytical concept than an analytical technique. The goal of the development is to yield reagentless, continuous, and quantitative information on the chemical composition of various types of specimens. The analysis system integrates several sensing techniques providing orthogonal as well as interrelated information on specific analytes. Therefore we speak of a multidimensional system. The single sensing techniques and elements are implemented in different modules which can be arranged in parallel or in series. The heart of the sensing module is the sensing membrane or sensing layer. A considerable variety of such membranes for neutral as well as charged analytes is available. The membrane chemistry refers to thermodynamically reversible or steady state reactions which are the basis of continuous monitoring. Primarily, sensors based on electrochemical and optical transducing principles are addressed.

Examples involving ethanol and glucose measurements in-line of a fermentation process, monitoring of free and total calcium ions in milk, monitoring of the active molality of magnesium ions in blood plasma, as well as chloride in human urine where shown to be feasible. In addition, the chemical prerequisites for many other analytes to be monitored continuously are given [1]. Specifically attractive are novel heavy metal selective layers, optical monitoring of nitrite and ammonia, and monitoring of dissolved amines and oxygen based on chromo- and luminescent reactands. An overview will be presented.

[1] U.E. Spichiger (ed.), *Chemical Sensors and Biosensors for Medical and Biological Applications*, Weinheim: Wiley-VCH, 1998.

7.2

Quartz Crystal Microbalance for the determination of affinity constants of biomolecular interactions

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The determination of biomolecular interactions, mostly described by the association and dissociation rate constants of equilibrium reactions, is a valuable tool in screening and evaluation of new antibodies as well as of new pharmaceuticals. We developed a new device based on the quartz crystal microbalance technique. In case of a mass accumulation at the surface of the quartz crystal due to an immunological reaction, the resonance frequency decreases. The mass dependency of the frequency shift is described by the Sauerbrey formula:

$$\Delta f_r = \frac{2 f_r^2}{\rho \cdot \nu} \cdot \frac{\Delta m}{A}$$ The Sauerbrey formula [1]

Dissociation and association can be observed on-line. Association and dissociation rate constants, k_a and k_d respectively, can be obtained by nonlinear curve fitting of the time dependent signals due to adsorption and desorption processes. The frequency shift due to association and dissociation can be described by the following mathematical models:

Association

$$\Delta F = -\frac{k_a \cdot C \cdot \Delta F_{max}}{k_a \cdot C + k_d} \cdot \left(1 - e^{-(k_a C + k_d)(t - t_0)}\right)$$

Dissociation

$$\Delta F = -\Delta F_0 \cdot e^{-k_d (t - t_0)}$$

ΔF is the change of the sensor signal, C is analyte concentration, t is the time and ΔF_{max} is the signal change of a completely covered surface.

Measurements were conducted with a VP73 virus protein and an anti-VP73 monoclonal antibody as a model system. The fitting result for k_a was $1.1 \cdot 10^4$ $(Ms)^{-1}$ and for k_d it was $3.1 \cdot 10^{-4}$ s^{-1}. The equilibrium dissociation constant was $2.8 \cdot 10^{-7}$ M which was in good agreement with ELISA measurements.

[1] G. Sauerbrey, Z. Phys. **155** (1959) 206

7.3

IMPRINTING WITH SENSOR DEVELOPMENT - ON THE WAY TO SYNTHETIC ANTIBODIES -

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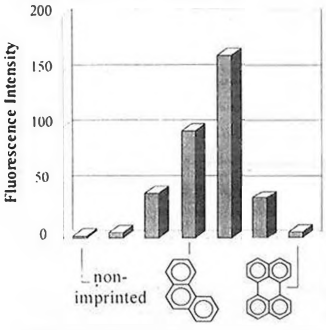
Taylored molecular cavities have been proven to be very successful materials for solvent vapour detection via chemical sensors. A substantial improvement of layer synthesis is offered by the strategy of molecular imprinting [1] since synthetic efforts are reduced. Highly cross linked polymers are generated in presence of the analyte acting as a template. This print molecule is evaporated or washed out of the layer leaving behind adapted cavities and diffusion pathways for re-inclusion.



This idea can be used for the detection of polycyclic aromatic hydrocarbons (PAHs) in drinking water [2] with sensor layers suitable for fluorometric as well as mass-sensitive measurements. The layers yield a remarkable selectivity to each PAH of interest as a function of the template molecule as shown in the adjoining figure. Furthermore, the non imprinted polymer layer gives only a negligible response due to surface adsorption in contrast to the bulk effects of imprinted layers. The PAHs can be detected in drinking water down to some ng/l.

A major advantage of molecularly imprinted layers is their possibility to be used for analyte characterization of complex mixtures of even unknown chemical composition. For example it is a very challenging task to monitor the degradation process of automotive engine oil. The oil of interest was used as template material. These imprinted layers were applied to QMBs and show mass-sensitive sensor responses correlated to the time the engine oil was on duty, nearly indifferent to various types or oil compositions.

[1] F.L. Dickert, S. Thierer, Adv. Mater. **8**, 987 (1996).
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7.4

ELECTROCHEMICAL GAS SENSORS BASED ON POROUS ELECTRODES DEPOSITED ON SOLID POLYMER ELECTROLYTES

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Amperometric gas sensors for monitoring toxic and industrially important gases down to ppb concentrations at room temperature are presented. The design of the sensors is based on a porous electrode chemically or vacuum deposited onto one side of a solid polymer electrolyte, which acts as the sensing electrode for the trace gas to be determined. The sensing electrode is placed in direct contact with the gas containing atmosphere, whereas the solid polymer electrolyte faces an internal compartment containing an electrolyte solution in which counter and reference electrodes are placed.

Although this design is not new [1], it has not been exploited to its full potential. In this paper we show that this sensor may be adapted to the analysis of trace gases in air and in controlled environments. The design of the amperometric cell is well suited to miniaturisation and readily adaptable to in situ analysis, offering a cheap and simple alternative to conventional expensive and cumbersome analytical equipment (gas chromatography, IR). Moreover, the detection limits (low ppb) and response times are much improved compared to commercially available electrochemical gas sensors on the market today.

The properties and advantages of this cell design are discussed, and the influences of parameters such as electrode preparation and pre-treatment, flow rate of the gas, humidity and choice of materials on the sensing behaviour will be highlighted.

Careful selection of the component materials and experimental conditions enables the selective determination of a specific gaseous analyte. The sensitivity and selectivity of the sensors may be increased further by applying a suitable potential program to the sensing electrode. The use of potential pulsing, for example, opens the possibility of preadsorbing specific gases on the electrode surface prior to electrochemical detection.

[1] G. Bontempelli, N. Comisso, R. Toniolo, G. Schiavon, *Electroanalysis*, 9 (1997) 433-443.

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7.5

PROPERTIES OF ION SELECTIVE MEMBRANES CONTAINING DIFFERENT QUATERNARY AMMONIUM SALTS

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In the past it was commonly accepted that the selectivity of the ion selective membranes based on quaternary ammonium salts (QASs) is determined by the Hofmeister series and does not depend upon the chemical structure of the QAS. However, recent literature [1-2] indicates that the structure of QASs may influence the membrane characteristics. The aim of our work was to correlate the potentiometric properties with the structure of the QASs and to give a connection between the bulk resistance and the selectivity of ion selective membranes. It was found that the dielectric properties of the plasticizer is the determitive parameter for the membrane properties, e.g. changing from o-nitrophenyl octyl ether (NPOE) to the less polar bis(2-ethylhexyl) sebacate (DOS) the response slope for chloride and bromide increased whereas the bulk resistance of NPOE membranes was 15 times lower than observed with DOS membranes. Though the QAS structure had an influence as well, e.g. an increasing chain length of the alkyl radicals lead to diminished influence of lipophilic interfering anions. In contrast to this the basic anions influence in that case was growing. Moreover, it was shown that membranes with more lipohilic QASs had better response slopes what is due to their constant bulk resistances during the exposure to the analyte solution.

References:

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[2] E. M. Rakhmanko, V. V. Egorov and N. D. Borisenko, *International Congress on Analytical Chemistry, Moscow, Russia*, 1997.

7.6

FLUORO- AND CHROMOREACTANDS. A NEW CONCEPT TO OPTICAL SENSING

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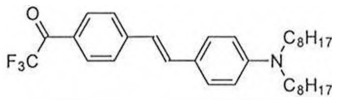
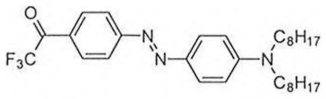
The new concept using fluoro- and chromoreactands as selective sensing elements operates on the basis of a specific reversible chemical reaction associated with a reversible change of the reactand's spectrum. The change in fluorescence and absorbance is based on the nucleophilic addition of the analyte to the trifluoroacetyl group of the reactand, thus causing a change in the electron configuration.



Fluororeactand ETH[T] 4004



Chromoreactand ETH[T] 4001

Based on these trifluoroacetyl reactands, optical sensors for alcohols, humidity and amines can be prepared. The reactands are incorporated into a thin sensor layer and exposed to sample solutions. The selectivity of the layers to the different species is governed by the addition of a catalyst, by varying the polymer matrix, and by the pH of the sample solution.

The ethanol sensor membranes exhibit a linear response to aqueous ethanol in the range of 1 - 50 vol% with a detection limit of 0.5 vol% ethanol. The humidity sensor membranes show a non-linear response to relative humidity with maximum signal changes in the 1% - 40% relative humidity range. The amine-sensitive membranes exhibit high sensitivity to lipophilic primary amines, e.g. aqueous 1-butylamine in the range of 1 - 100 mM with a detection limit of 0.3 mM 1-butylamine.

7.7

IMMOBILIZATION OF FLUORESCEIN DERIVATIVES FOR THE PREPARATION OF FIBRE-OPTIC pH SENSORS

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Fibre-optic pH sensors are commonly prepared by the immobilization of a pH sensitive indicator onto the distal end of an optical fibre. The immobilization of the indicator is usually achieved by physical entrapment in a sol-gel matrix. However, as there is no covalent link between the indicator and the sol-gel leeching of the indicator can occur. To overcome this problem an alternative photo- and an electro-chemical method for the immobilization of pH sensitive derivatives of fluorescein are presented.

The photochemical method requires the preparation of fluorescein acrylamide. The fluorescein derivative is then polymerized with hydroxyethylmethacrylate (HEMA) using photo-initiated polymerization [1]. The resulting polymer consists of fluorescein acrylamide covalently bound to the polymer and the polymer is covalently bonded to the optical fibre surface.

The electrochemical method requires the preparation of a fluorescein derivatised monomer unit based on either thiophene (Figure 1) [2], pyrrole or indole. The new monomer unit can be electrochemically immobilized on Pt coated optical fibres.

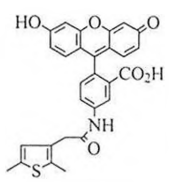

Figure 1

The pH response of the new fluorescein-derivatised polymers are similar to that of fluorescein in solution.

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9.1

Development, Validation and Maintenance of Chromatographic Methods

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Chromatographic method development and validation for methods used in quality control under GMP/GLP or ISO 9000 has to fulfil minimum standards. Systematic approaches for optimisation are widely used and have advantages concerning efficiency, quality, cost, method transfer and later adaptations to user requirements.
From the method development and the validation the System Suitability Test (SST) can be established. A good validation and SST is the scientific base for later adjustments without the need of revalidation.
The maintenance of methods used in routine laboratories in a regulated environment is restricted to small adjustments of the methods. Modifications are often limited by the high cost of a Revalidation of Methods and the cost of world wide update of registration documentation. It is not evident what are tolerable adjustments of methods and what are modifications with the need a of new validation and prior approval of registration authorities.

Criteria for Chromatographic operating parameters will be proposed for existing and official methods (e.g. in Pharmacopoeias) when given a HPLC and GC method can be adjusted and when a modification needs full new validation and registration.

9.2

HEAVY METALS IN WATERS BY ICP-AES – A QUALITY ASSURANCE SCHEME

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The accreditation bodies have an important role in promoting the credibility of analytical work. The application of the ISO 45001 certifies the quality of the laboratory organisation and enables customers and accreditation bodies to control the analysis documentation. Nevertheless the accreditation bodies are also obliged to certify the technical aspects of the analytical laboratory. However the accreditation of a laboratory seems to be not enough to protect it from large mismatch of results in interlaboratory assays. There are no complete answers to solve some analytical systematic errors.

This work proposes a quality assurance scheme for the validation and quality control of the determination of heavy metals in waters by ICP-AES.

The validation scheme was developed for the detection of some common sources of systematic errors, namely:

Lack of fit of the mathematical model used to describe the calibration curve;
Digestion step recoveries;
Contamination;
Different sensitivity of the method for standards and sample.

The estimation of results uncertainties was implemented for comparison with reference values. Results from the analysis of reference materials and spiked samples are presented.

The digestion step proved to have an efficiency of 100% and an associated insignificant uncertainty when compared with others steps.

The quality control was also implemented on uncertainty estimation substituting the inflexible expected/obtained percentage deviation criterion.

9.3

Depth-Resolved Analysis of Coated (Painted) Materials by Radio Frequency Glow Discharge Atomic Emission Spectroscopy (rf-GD-AES)

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Layered materials of many sorts are becoming increasingly important in a wide range of technological areas. For example, in the automotive industry painted sheet metal makes up the outer body of cars, while a seemingly homogeneous windshield can be composed of layers of glass and polymeric material. Direct solids elemental analysis of these types of systems is particularly challenging because one must produce accurate compositional information in a depth-resolved fashion. One must know the distribution of different elements across structures extending in thickness from 0.1 - 100 micrometers. This range of depths preclude the use of conventional optical and ion probes on the basis of their limited 'information depth' and the time consuming removal of the various layers. Glow discharge devices have long been used as effective spectrochemical devices for generating depth profiles of 'thick' layers of the dimensions described above. The use of direct current (dc) powering, though, limits applications to metallic layers such as galvanized treatments. Use of radio frequency (rf) powering allows the direct sampling of nonconductive coatings such as paints, polymers, oxides, and the like [1,2]. We will describe here the use of rf glow discharge atomic emission spectroscopy (rf-GD-AES) as a tool for the depth-resolved analysis of a wide variety of coating/substrate combinations. Target applications will include painted automotive components, mirrors, and electronic materials such as superlattice structures.

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9.4

MONITORING THE QUALITY OF CHEMICAL MEASUREMENTS AGAINST SI-TRACEABLE VALUES USING IMEP

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In today's world, chemical measurements, especially those of amount of substance, often play an important role. More and more, the customers who request such measurements expect them to be comparable across geographical, discipline and 'time' borders. This is not obvious and such comparability of data requires the concept of SI-traceability.
The International Measurement Evaluation Programme (IMEP) was started at IRMM in 1988 to create awareness and demonstrate the absence of such comparability. It is now operated under the auspices of e.g. IUPAC and CITAC. It offers SI traceable values to the participants for element amount content to an international analytical community. The main features, results and observations of this programme are described. In the mean time, eighth rounds have been completed, and another three are on their way. In the various rounds, participants were asked to measure trace element concentrations in important matrices like human serum, water and polymer using their own analytical methods.
At the heart of this programme lies the concept that metrological values for chemical measurements, although tedious to establish, are useful as far as only those can serve as 'anchors' offered to a broader measurement community. Such values are established using those procedures which are currently best understood, i.e. primary methods of measurement (as defined by the BIPM/CCQM). Often they are based on the technique of isotope dilution - mass spectrometry.
Whereas IMEP was initially conceived as an awareness programme, it has now matured into a demonstrator project, showing the feasibility and usefulness of a structured, hierarchical measurement system in chemistry (similar to other measurement sciences). Such a system is neither based on formal status nor on decreed competence, but on provable traceability and uncertainty.

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9.5

THE PRINTING INDUSTRY: A NEW APPLICATION FIELD FOR INDUCTIVELY COUPLED PLASMA SPECTROMETRY

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Inductively Coupled Plasma Spectrometry (ICPS) was successfully used for quantitative measurement of the amount of ink transferred to paper in offset printing and for detecting of small changes in ink composition during its transfer.

Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES) provided a rapid and accurate method, applicable over a wide range of concentrations on all printing substrates. The method should be equally adaptable to other printing processes. The detectable atoms can be a structure part of the pigment or the resin molecule or can be in the form of an ink additive, provided it is uniformly dispersed.

In the experiment described, Horizon Sequential Inductively Coupled Plasma Spectrometer was used. Offset ink containing copper phthalocyanine pigment was printed on coated papers. The technique was compared with X-ray fluorescence and it was found that ICP-AES gives more accurate results and more sensitivity for detecting lower levels of pigmentation in the printed film.

The technique is not only the concern of the printing researchers but also of ink makers and substrates manufacturers.

9.6

SEQUENTIAL INJECTION ANALYSIS WITH ACCURACY ASSESSMENT

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The concept of accuracy assessment in flow analysis was recently proposed [1] and applied to chloride determination in river waters. The sample was processed by two quasi independent methods, leading to intrinsically more accurate results. However, the system was somewhat complex, and this drawback is circumvented here where SIA analyzer is used.

The feasibility of the proposal was demonstrated in the spectrophotometric determination of aluminium in soil extracts by two different methods based on Aluminon and Chromazurol S reagents. A critical comparison between FIA and SIA systems to accomplish this is carried out and potentialities/limitations are discussed.

The proposed SIA system is robust and yields reproducible measurements (r.s.d. usually < 5% for 2.0 - 10.0 mg L-1 Al), consuming about 85 µg and 13 µg of Aluminon and Chromazurol S per determination. Intrinsically accurate results are obtained as average of data related to different methods. For atypical samples, interference effects which may eventually arise are promptly observable.

[1] C.C. Oliveira, R.P. Sartini, E.A.G. Zagatto, J.L.F.C. Lima, Anal. Chim. Acta, 350 (1997) 31.

9.7

Explorative Data Analysis of Fermentation Data for Multivariate Statistical Process Control

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Yields of biotechnological antibiotics-production usually show strong variations, that can be due to different operation of the production. In the fermentation of antibiotics the multitude of measured process variables and the time series characteristic produce complex data matrices that require special transformations for the application of multivariate statistical methods. Historical data was analyzed by principal component analysis (PCA) and partial least squares-(PLS-) regression [1]. Various scaling- and refolding-techniques were explored to identify those with most interpretative power. The appropriate number of principal components was calculated by cross validation. The developed tools of interpretation permit the identification of influential process variables, fault detection and the selection of special batches that can be used as reference batches in multivariate statistical process control (MSPC). Additionally, the application of PLS results in a prediction model which is able to predict product yields from new observed trajectories of process variables with a quantified statistical prediction error. Data analysis by multiblock methods resp. multilinear methods such as tri-PLS and PARAFAC-algorithm show results well comparable with standard techniques and can be used for higher dimensional data problems. A proceeding for fault detection and for identification of reference batches is suggested on the basis of our studies.

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10.1

METHYLXANTHINES IN ENERGY DRINKS AND OTHER BEVERAGES

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The increased provision of choice in foodstuffs for the consumer in the 90's has included the introduction of a range of "energy" drinks to the market in the UK. The labelling of such products in some cases indicates caffeine to be present at a concentration greater than normally found in traditional soft drinks. As the energy drinks have only recently become widely available, this elevated caffeine content has not been verified in surveillance data reported previously.

To gain an improved understanding of the potential for the dietary intake of methylxanthines from beverages, a survey of theobromine, theophylline and caffeine in teas, coffees, colas and energy drinks has been carried out. The methylxanthines were determined using reversed-phase high-performance liquid chromatography with spectrophotometric detection at 273 nm. Limits of detection were 0.1 mg/litre for theobromine and theophylline and 0.2 mg/litre for caffeine. Average recoveries were 97%, 94% and 96% for these analytes respectively.

Concentrations of caffeine up to 350 mg/litre were found in the energy drinks studied. Lesser amounts of theophylline and theobromine, the latter up to 6 mg/litre, were present in some cases. Comparisons are presented for these determinands in a variety of tea, coffee and cola preparations.

10.2

BIOGENIC AMINES DETERMINATION FOR FOOD QUALITY EVALUATION USING A DIAMINE OXIDASE ENZYME ELECTRODE

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Biogenic amines are aliphatic, alicyclic and heterocyclic organic bases of low molecular weight. They are synthetized in animal and plant cells and also produced by microbial decarboxylation of aminoacids. The importance of the estimation of the levels of biogenic amines in food is related to their impact on health and food quality. The variation of the biogenic amines content during processing and storage has been proposed as index of chemical quality of food.

The determination of biogenic amines is usually carried out with chromatographic methods coupled with fluorimetric or pulsed amperometric detection. We developed a diamine oxidase based amperometric electrode for the rapid determination of biogenic amines in food. The enzyme was purified from plant tissue (cicer) and covalently immobilised onto a polymeric support. The general reaction catalysed is the following:

$$R\text{-}CH_2\text{-}NH_2 + O_2 \rightarrow R\text{-}CHO + H_2O_2 + NH_3$$

Hydrogen peroxide was detected and related to amines concentrations in the samples. Analytical parameters as pH, buffer, response time, immobilisation procedure, electrochemical transducer have been optimised for more than 10 amines. The detection limit varied from 5×10^{-7} mol/L for putrescine and cadaverine to 2×10^{-6} mol/L for tryptamine. The measurement was partially automated using the biosensor in a FIA configuration. Measurement of amines content in salted anchovy samples, in apricots and cherries and in different type of cheese demonstrated the suitability of the procedure for food storage and processing control.

10.3

ANALYSIS OF SEVERAL REAL MATRICES USING NEW MONO-, OR BI-ENZYMATIC, OR INHIBITION PEES

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Many enzymes were shown to be catalytically active in a wide variety of different organic solvents, their catalytic efficiency in organic media being comparable to that one in water; as a consequence several different enzymatic electrodes were developed which are able of operating in organic phase currently named OPEEs (organic phase enzyme electrode). From an analytical point of view there are several potential advantages in carrying out enzymatic reactions in organic media instead of in aqueous solutions: efficient catalysis may be achieved with substrates poorly soluble in water; undesirable side reactions in organic media as well as substrate and product inhibition may be reduced; thermal stability of the enzymes is enhanced; immobilisation is often unnecessary as enzymes are insoluble in organic solvents; whenever immobilisation is desired, adsorption onto non-porous surfaces is satisfactory as enzymes are unable to desorb from these surfaces in non-aqueous media; microbial contamination is eliminated on recovery and reuse of the enzyme is easier.

At the present, various organic-phase enzymatic electrodes have been developed by several authors to analyse some water-insoluble substrates.

In this presentation we describe principal recent researches of our group in this field, including an OPEE with good potential applications that has captured the attention of several working groups, namely the tyrosinase enzyme sensor firstly used to analyse chlorocresol in ointments then to perform polyphenol determination in olive oil and other fats using n-hexane as organic solvent due to the excellent solubility of olive oil in this solvent. As applications this biosensor was used to make a reapid check on the authenticity of an olive oil and to evaluate its degree of stability to oxidative processes. Indeed a good correlation has been found between polyphenol content and stability to oxidation of the product. This is evidence of the important antioxidant role played by polyphenols in "virgin" olive oil and of the interest to perform rapid inexpensive analysis using new OPEE. Recently the authors of the present communication also developed an OPEE to determine hydrogen peroxide in several polar (chloroform) and low polar (toluene) organic solvents, using immobilised catalase enzyme. Applications were performed in the field of cosmetic control and in course to be realised in the case of foodstuff; in addition an OPEE based on the superoxide dismutase enzyme for superoxide free radical analysis in dimethylsulfoxide is now under study.

Recently we also examined the possibility of building a bienzymatic sensor for lecithin determination, able to operate in organic solvents, in which lecithin is more readily soluble, as well as to analyse food matrices. At the present we are studying also the possibility of fabricating a new OPEE *i.e.* a bienzymatic inhibition biosensor, for the analysis of organophosphorus and carbamate pesticides, able to operate also when dipped directly in non-aqueous medium.

Lastly we studied the new tyrosinase and catalase biosensors to carry out detailed investigations on the possible correlation between the nature of the organic solvent and the sensitivity of the response of the enzymatic sensor (and therefore enzymatic activity), between the current variation rate and the more classical indicators as the dielectric constant value (DEC) ald log*P* value of the solvent used, taking into account well known role played by the aqueous microenvironment constantly surrounding the enzyme, so it is a key factor in optimising the enzymatic reaction and thus also the biosensor response. Therefore we carried out an experimental study to determine the water content in a typical enzyme both in the lyophilised form and dried after its treatment with an organic solvent.

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10.4

DEVELOPMENT OF AN ENZYME-LINKED IMMUNOSORBENT ASSAY FOR BENALAXYL

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A rapid quantitative determination of pesticide residues in vegetable and fruit crops, or an estimation of distribution and persistence of pesticides in different parts of plants is possible using a sensitive, specific, simple and rapid analytical method as immunoassay.
We have developed a competitive enzyme-linked immunosorbent assay (ELISA) for the determination of benalaxyl (methyl N-phenylacetyl-N-2,6-xylyl alaninate), a fungicide widely used in grape and vegetables (peppers, tomatoes) cultivation.
The molecular structure of the pesticide was considered to obtain a highly specific antiserum: a derivative of benalaxyl (hemiglutarimido-N-phenylacetyl-N-2,6-xylyl alalinate, Bn-HG) was synthesised and linked to bovine serum albumin (BSA). The so obtained immunogen was used to immunise three mice and one chicken, which responded by producing specific antibodies to benalaxyl with negligible cross-reactivity to various structurally related pesticides. The binding capacity was studied by mouse and chicken antiserum titres obtained on Bn-HG-ovoalbumin conjugates (corresponding to different hapten protein reaction ratios) and on Benalaxyl-acid (Bn-COOH)-ovoalbumin conjugate immobilised on microtiter plates. Different concentrations of immobilised conjugates were considered to obtain highest sensitivity.
The optimised calibration curve in buffer has a working range of about 0.5 - 50 ng/ml, with a detection limit of 0.35 ng/ml (with mouse antibodies) and of 0.20 ng/ml (with chicken antibody). The assay has been applied for determination of benalaxyl in acqueous samples: tap and river-water samples spiked with benalaxyl show quantitative and reproducible recoveries ranging from about 80 to 120% in a working range of about 0.5 - 50 ng/ml. Further studies to determine benalaxyl in wine are in progress.

10.5

Determination of toxins in liquids using Quartz Crystal Microbalance

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The determination of toxins in drinking water or juices is of great importance in the fields of quality control and investigations of endemic intoxication. Using a quartz crystal microbalance immunosensor [1] the microbial toxin Staphylococcus enterotoxin B (SEB) and the mycotoxin Ochratoxin A (OTA) were determined in water and juices, respectively.
The SEB-test was a direct immunoassay with a monolayer of immobilized antibody. In contrast to that a competitive immunoassay with immobilized antigen (an OTA/protein conjugate) was used for the determination of OTA. In case of a mass accumulation at the surface of the quartz crystal due to an immunological reaction, the resonance frequency decreases. The quartz crystal was integrated in a flow injection analysis (FIA) system. The samples were injected in a continuous buffer flow of 50 µl per minute. After the binding process was finished the receptor layer was regenerated using a solution with low pH-value. In this way, several measurements could be performed consecutively using the same quartz crystal.
The lower detection limit was 50 ng/ml for the SEB and 2 ng/ml for the OTA. The difference is caused by the different molecular mass of the substances bound to the receptor layer on the quartz surface. Full activity of the receptor layer was maintained after 5 regeneration steps on the anti-SEB quartz. With the immobilized OTA/protein conjugate at least 25 regeneration steps were possible. The regeneration of the quartz surface enabled the measurement of calibration material and samples on the same quartz crystal.

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10.6

IMMUNOSENSORS FOR ENVIRONMENTAL ANALYSIS

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The Laboratory of Sensor Development at University College Cork is currently developing biosensors for environmental monitoring using amperometric, piezocrystal quartz microbalance and optical transducers.

One of the main areas of interest is that of toxins. Amperometric and optical immunosensors lave been developed for the detection of low levels of seafood toxins, such as okadenic and domoic acid as well as saxitoxin and brevetoxin. These sensors exploit the high specificity of the immunogenic reaction and it is anticipated that the occurrence of DSP and NSP can be eliminated by carefully monitoring toxin levels of the sea and seafood. An optical sensor for aflatoxin is being investigated and gives a very low detection limit. The native fluorescence of aflatoxin is measured, following specific capture by its antibody on an optrode tip.

A quartz crystal microbalance is being used to control milk spoilage by detection of *Pseudeomonas aeroginosa*. *Ps. aeroginosa* cells are coated on the crystal surface followed by antibodies to *Ps. aeroginosa*. A sample of milk is added and the *Ps. aeroginosa* cells present in the milk displace the antibodies on the crystal surface causing a change in mass and subsequent change in frequency.

An amperometric immunosensor is also being developed for Listeria monocytogenes. In this case a sandwich assay incorporating alkaline phosphatase-labelled anti-listeria monocytogenes is used. Projects in the early stages include development of an optical fiber sensor for Biological Oxygen Demand (BOD), as well as gas phase biosensors for NO_x and CO_2 detection.

10.7

RAPID DETERMINATION OF PROTEIN AND CASEIN IN RAW MILK BY THE FOURTH DERIVATIVE UV-SPECTROSCOPY

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Casein to whey protein ratio in the milk is of importance for the technological performance and the need exists for rapid and direct determination of this ratio. Derivative UV-spectroscopy, based on the UV light absorption by tryptophan and tyrosine, each with characteristic maxima and minima in the range of 270 to 300 nm, proved to be an adequate method for protein quantification.

Preliminary aim was to develop a simple and rapid method for determination of milk protein in general, and casein content in particular, in raw milk by using the fourth derivative UV-spectroscopy, without involving preparation procedures such as casein precipitation. Fresh whole milk samples were diluted with 6 M Guanidine buffer before performing spectroscopic scanning. The total protein and casein content of 45 milk samples determined by this method were not different from the values obtained by the reference method of the International Dairy Federation, a method based on Kjeldahl determination. By using the fourth derivative UV spectroscopy, determination of total protein and casein content in milk can be achieved directly in a single run. Treatments of milk such as heating, homogenization, preservation or proteolysis of protein had no influence on the accuracy of protein determination in milk by this method.

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11.1

TIME DOMAIN NMR SPECTROSCOPY A NEW TOOL FOR THE QUANTITATIVE STUDY OF HETEROGENEOUS SAMPLES

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Low resolution NMR spectroscopy is used as a routine technique for different types of controls of very heterogeneous products as found in the food-industry. However, it can exploit the spin-lattice (T_1) or spin-spin (T_2) parameters to characterise different states of components in complex heterogeneous products. Indeed, water can be in a « bound » or « free » state or even have « solid-like » behaviour.
The fitting of FID relaxation curves by Gaussian functions, allowed to obtain « quantitative » information on both solid and liquid phases, and in particular on entities having an intermediate state between a solid and a liquid [1]. Confirmation of the « goodness » of fit has been obtained on starch-water samples [2]. Moreover, the use of a continuous method (CONTIN program) allows the determination of quantitative distributions of apparent relaxation times (T_2*). Using this treatment, the occurrence of a small amount of an intermediate phase has been shown to be evident in milk fat [1], and the behaviour of sorbitol in starch-sorbitol films has been determined, showing both « solid-like » and « liquid-like » states.
T_1 relaxation time can also be a good parameter to characterise mobility inside a solid sample, in an amorphous or in a crystalline state (sucrose), and even to characterise the polymorphism of fats for example. Very different T_1 distributions have been obtained for α, β' and β forms of tristearin and even between β'_1 and β'_2 forms.

1- D. Le Botlan and L. Ouguerram, Anal. Chim. Acta, 1997, 349, 339.
2- Y. Rugraff, P. Desbois and D. Le Botlan, Carbohydr. Res., 1996, 295, 185-194.

11.2

JOINED APPLICATION OF KNOWLEDGE- AND SIGNAL PROCESSING FOR INFRARED SPECTRUM INTERPRETATION

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The derivation of chemical substructures from infrared spectra may be performed by three general procedures: 1) library search methods; 2) numerical procedures as pattern recognition or neural networks; and 3) application of symbolic logic that rely on known spectrum-structure-correlations (SSC). All three approaches have weaknesses. One reason is that they approximate only isolated capabilities of the human expert. The library search fails when no reference spectrum is contained in the spectral library. Procedures of mathematical logic are applied to a spectral feature list. As consequence the information on peak shapes is lost. It can be only poorly approximated by the band width but is an important source of information for the spectroscopist. In contrast, numerical procedures may use the full information content of the spectrum, but they make no use of the SSCs already derived by the spectroscopists.
Here an approach is outlined that combines properties of those three general procedures 1) a library search is performed to select the best matches; 2) the data vectors are spectral intervals chosen according to the SSCs derived by human experts; and 3) the intervals are not reduced to peak lists but contain the full spectral information.
The interrelations between the selected intervals are considered by application of fuzzy logic and the cross correlation function is applied as numerical procedure for calculating the similarity in the spectral ranges.
The application of partial cross correlation functions to spectral intervals selected by SSC's possess the advantage to correct wavenumber shifts due to modified chemical environments individually for the chosen intervals.
The normalised maxima of the partial cross correlation functions are interpreted as fuzzy truth values and are combined by fuzzy logical operators. By application of that procedure larger common substructures were derived from the reference spectra than by a maximum common substructure search based on the complete spectra.

11.3

TIME-RESOLVED EXCITATION EMISSION SPECTRA (TEES) WITH FIBEROPTICAL SENSORS: A NEW TOOL FOR MULTIDIMENSIONAL FLUORESCENCE SPECTROSCOPY

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Fluorescence spectroscopy is a sensitive method for detection of anthropogenic pollutants, e.g. PAH, in our environment. However, for applications with fiberoptical sensor systems static emission spectra do not provide sufficient information due to their broad and featureless character. In addition, in the case of complex mixtures (oil residues) the Kasha rule is no longer in effect so that the fluorescence emission spectra show a pronounced dependence from the excitation wavelength. Hence, additional orthogonal dimensions like decay time and excitation wavelength are needed. The presentation will address the experimental set-up for the fiberoptical observation of time-resolved excitation-emission spectra (TEES). The mobile system is based on a Raman-shifter pumped by a quadrupled Nd:YAG-laser at λ = 266 nm and allows the simultaneous generation of several coherent excitation lines between 240-400 nm. Different excitation wavelengths can be coupled in to 8 excitation fibers which illuminate the sample simultaneously. The fluorescence is guided through 8 emission fibers to an imaging spectrograph with an intensified CCD-camera. The fluorescence emissions from the fibers are spatially separated on the CCD-chip and a gating of the image intensifier allows the simultaneous recording of time-resolved emission spectra. Typical detection limits in the ng l^{-1} range for native fluorophores were achieved with a time resolution < 1 ns. The chemometrical methods for the generated 4dimensional data sets, i.e. PARAFAC and three-way principal component analysis, will be also addressed. Finally, we will demonstrate the versatility of TEES for investigations of oil contaminated soil samples. These results will also be compared with regard to other diagnostic methods for oil contamination like IR- and UV-spectroscopy.

11.4

ESTABLISHMENT OF MOLECULAR FORMULA OF ORGANIC COMPOUNDS FROM IR AND NMR SPECTRA: A NEW APPROACH BASED ON THE EXPERT SYSTEM APPLICATION

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The main task of qualitative organic analysis is known to be the determination of the chemical composition and the structure of an unknown compound. There exist expert systems intended for the molecular structure elucidation (X-PERT [1], for instance), while the molecular formula (MF) being considered as an independently determined item of initial data. In this report, we have shown that the expert system itself can be used as a new tool for the molecular composition determination.
The approach takes into account the fact that the information about the chemical composition and structural formula of a substance is "smeared out " over spectra of different origin, while there exists a relationship between the chemical composition, structure and spectra. The problem solving is transferred into the space of structural isomers, the families of which can be generated, in principle, from given molecular formulae fitting into the molecular masses. This also makes it possible to derive equations which allows one to evaluate quantitatively the amount of structural information carried by the molecular mass and molecular formula. Fairly frequently isomer structures are shown to have IR and NMR spectra, in some sense, rather characteristic for their molecular formulae. This dependence was used for spectral filtering the molecular formulae generated from a given molecular mass. The X-PERT application combined with program for ^{13}C NMR prediction allows one to carry out all main operations necessary for choosing the most probable MF and the molecular structure. Examples illustrating the features of the approach suggested are given.

1. M.E.Elyashberg, E.R.Martirosian, Yu.Z.Karasev, H.Thiele, H.Somberg. **Anal. Chim. Acta.**, , **337** (1997) 265; **348** (1997) 443

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11.5

ADVANCES IN SIMULTANEOUS MULTI-ELEMENT GFAAS WITH FLOW INJECTION-FURNACE COUPLING

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The ability to collect volatile hydrides within a graphite atomizer allows ng/L detection limits to be achieved. This approach has found widespread use, but generally for single element applications due to the element-specific chemical treatment required prior to hydride generation. Another important advantage of this technique, which so far has found less attention in the literature, is the separation of the hydride generation and signal atomization processes. This allows the differences in sensitivity obtained for, *e.g.*, the oxidation states As^{3+} and As^{5+} in conventional HG-AAS to be considerably reduced.

This presentation will discuss the chemical and methodological parameters studied to allow application of hydride generation and collection of the hydrides in the graphite tube for simultaneous multi-element determinations for As, Sb, Bi and Se using a FIAS-400 flow-injection system coupled to a SIMAA 6000 simultaneous multi-element GFAA spectrometer. The design of the experimental system and software control will be outlined. This multi-element approach requires a careful consideration of the hydride generation chemistry especially with respect to the reduction process and the requirements of the collection or 'trapping' within the graphite tube. These issues will be discussed and possible solutions proposed. The ability of this system to determine As, Sb and Bi at ng/L levels in environmental samples will demonstrated.

11.6

Mid-Infrared Spectroscopy Using Optical Fibres in the Marine Environment

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Due to the increasing pollution of the oceans accurate analysis systems for monitoring the marine environment gain substantial importance. The present analytical techniques for the determination of chemical seawater pollutants are mainly based upon collecting and analysing discrete samples. This fact imposes considerable limitations on the ability to survey and evaluate the extend of hazardous waste in the marine systems.

Recently, our research team has presented a new fibre optic physico-chemical sensor for chlorinated hydrocarbons (CHC) in sewage. The coupling of polycrystalline silver halide fibres to a portable Fourier transform infrared (FTIR) spectrometer enabled us to design a mid-infrared sensor system utilising the principle of fibre evanescent wave spectroscopy (FEWS). The fibres act both as signal transfer lines and as the actual sensing element, which is coated with a thin polymer layer. The coating acts simultaneously as an extractor phase, enriching the analytes in vicinity to the sensor element, and as a protective layer avoiding direct contact between the silver halide fibre and the corrosive seawater.

It could be demonstrated that an unprotected silver halide fibre exposed to artificial seawater decomposes within a few days, while the polymer coated fibres showed constant signal transmission after six weeks of constant exposure. Using ethylene/propylene copolymer coated fibres, it was possible to detect tetrachloroethylene (TCE) in artificial seawater down to 300 ppb.

As part of the EU-project "Spectroscopy using optical fibres in the marine environment" (SOFIE), a miniaturised and ruggedised FTIR-spectrometer module is developed. Combining this instrument with a newly designed and optimised sensor head will enable the realisation of a sensor prototype suitable for qualitative and quantitative CHC detection at the lower ppb-level in real-world seawater.

11.8

OPTIMISATION AND CALIBRATION IN SPECTROCHEMICAL ANALYSIS (TRELIBS) OF MOLTEN METALS

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As 80% of the total analysis time in traditional spectrometric analysis of molten metals is sample taking, sending and preparation, investigations has been carried out aiming at the direct analysis of the molten metals, metal-alloys in the melting furnace. According to earlier experimental results [1], time-resolved laser induced breakdown spectroscopy (TRELIBS)can be successfully applied.As the analysis of the molten phase requires a separate optimisation and calibration[1], this was done in the following steps: 1. For analysing commercial grade metals, the repeatability has been chosen as main target parameter for determination of optimum delay-and gate-time (τ_d , τ_g); beacuse of their much shorter life-time, ionic lines were used for this ; 2. applying the optimum τ_d and τ_g (e.g. 100 ns, 1000 ns), the effect of argon atmosphere, salt-additives, their optimum flow-speed and quantity has been determined; 3. considering the possible time-changes of the line profiles[1], using a special developed software [2] various line-intensity measurement modes has been compared :peak-and area-measurements, using subjective and various mathematical-statistical designation of the line area; 4. as final step the calibration has been performed by the aid of CRM materials molten in laboratory crucibles. For Al- alloys the mean error of calibration for Mn,Si and Mg was,6.6%, 8.9%, 0.9% in range 0.2-2.0 % ; for Zn alloys that for Mg and Pb : 7.4, 7.7 % , in range 33-995 ppm, or 10-199 ppm. All curves were fitted using relative intensities and linear regressions.

[1] L. Paksy, B.. Német, A. Lengyel, L. Kozma, J. Czekkel: Spectrochim. Acta Part B, 51(1996) 279-290.
[2] L. Paksy, O. Bánhidi, A. Lengyel: Microchem. Journal, 55 (1997), 72-80.

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12.1

TIME-OF-FLIGHT SECONDARY ION MASS SPECTROMETRY OF INDUSTRIAL MATERIALS

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Surface phenomena are important in numerous technological areas, such as adhesion, biocompatibility, catalysis, polymers or composite research. Most of the critical parameters affecting stability and specific response of industrial products to the environment are controlled by the chemical composition of the uppermost monolayers of the material. Since many of the technological important systems are of organic nature, the demand for detailed molecular information has become vital for specific modification of surfaces with respect to their adhesion, friction, wettability or biocompatibility properties. The chemical characterization of surfaces usually demands answers to the nature, location and concentration of the molecular species present ('what is it, where is it, and how much').
Time-of-flight secondary ion mass spectrometry (TOF-SIMS) is developing into one of the most significant and versatile analytical techniques for characterizing the surface chemistry of inorganic, organic and biological materials [1]. Secondary ions are generated as consequence of the impact of a pulsed primary ion beam (Cs^+, Ga^+) onto the surface. The high transmission and excellent mass resolution ($M/\Delta M$ = 7500 at mass m/e = 28) of time-of-flight analyzers are responsible for the possibility to detect very low concentrations of chemical identities under static conditions (primary ion flux density $\leq 10^{13}$ ions/cm^2), i.e. with minimal removal of material from the surface. Imaging the lateral distribution of chemical species with a useful resolution of ca. 1 µm can be achieved by rastering the primary ion beam over a selected area of the substrate.
The application of the TOF-SIMS technique to a series of industrially relevant problems will be discussed. In order to reveal the true potential of the method, information about possibilities and restrictions in praxis will be addressed where necessary.

[1] B.A. Keller; Helv. Phys. Acta 69 (1996) Separanda 1, 1-2

12.2

MOLECULAR ANALYSIS ON THE NANOMETER SCALE

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Despite recent progress, molecular analysis is, in contrast to elemental analysis, still limited in spatial resolution. Current methods with high chemical contrasts (e.g. IR, Raman, MS, etc.) are so far limited by diffraction (i.e. $\approx \lambda/2$).

This limitation can be overcome by means of scanning probe microscopes, like the Scanning Tunnelling Microscope (STM) or the Atomic Force Microscope (AFM). Among them only the Scanning Near-field Optical Microscope (SNOM) allows to gain real molecular information.

As recently shown, with a SNOM setup in combination with an optical spectrometer, Raman and morphological images with a lateral resolution of below 100 nm can be obtained simultaneously [1]. When using pulsed laser radiation, laser-induced ablation of sub-wavelength sized areas can be used for molecular nano-sampling [2]. An interface allowing to collect and transport the desorbed material to a mass spectrometer is being developed, allowing analyses complementary to vibrational spectroscopy.

With the fabrication of smaller scanning probes the lateral resolution of topographical **and** real chemical analysis can be as small as a few tens of nanometers - an increase of an order of a magnitude compared to current techniques.

[1] V. Deckert et al., Data presented at the 24th Annual Conference of the Federation of Analytical Chemistry and Spectroscopy Societies Oct. 1997; (FACSS '97)

[2] B. Dutoit et al., J. Phys. Chem. B, 1997, **101**, 6955-6959

12.3

ON-LINE COUPLING OF CAPILLARY ELECTROPHORESIS WITH HR - ICP - MS: A POWERFUL HYPHENATED TECHNIQUE FOR METAL SPECIATION

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The toxicological properties of heavy metals are strongly dependent on their chemical binding forms. Consequently, it is necessary to quantify not only the total amount of metal but also the amounts of the single species which appear in environmental or biological samples.
Capillary Electrophoresis is a modern separation technique with a high resolving power for charged analytes like metal species, but the detection limits using a conventional UV-VIS detector are at the mg/L level. This is far too high for trace analysis in environmental samples for instance.
Inductively Coupled Plasma - Mass Spectrometry is a very sensitive method with a multielement capability for the determination of trace concentrations of elements but in principle the technique is unsuitable for metal speciation.
Our aim is to develop an analytical technique for multielement / multicompound analysis in environmental and biological samples.
In this contribution we present our recent results on hyphenation of capillary electrophoresis with a high sensitivity ICP - sector-field - MS. An interface has been developed which enables the separated species from the capillary to be introduced into the plasma. The on-line coupling has been validated with respect to stability, calibration, reproducibility of separation as well as stability of the electrical current.
Using this hyphenated technique it is possible to determine metal species at the µg/L level so that it can be utilized for trace analysis of environmental samples. The technique has been applied to metal species having different oxidation states as well as organometallic compounds e.g. of arsenic and lead.

12.4

NEW CHEMILUMINESCENT REACTIONS FOR TRACE ORGANIC ANALYSIS

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Chemiluminescence (CL) is becoming increasingly popular for trace analytical detection, especially in flow injection (FI) systems. This lecture will describe the continuing search for novel CL reactions for use in FI systems, and concentrate on three successful developments, each providing detection limits in the pmol region. These are the determination of traces of:

(a) 1,2,2'-thiodiglycol and related compounds;

(b) carbonyl compounds, by conversion to hydrazones;

(c) phenols and amines, after reaction with p-acetobenzene-sulfonyl chloride.

Each reaction involves a selective oxidation. Evidence for the mechanisms of the CL processes will be discussed, and applications of some of the reactions to real samples will be described.

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12.5

FROM HEAT FLUX TO IC CALORIMETRY

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In the last 50 years, calorimetry presented different, successive phases of development. Like in many fields, this development is, itself, strongly dependent on the development of electronical components. It is, of course, obvious that the performance of the instrument directly depends on the quality of the electronics used for temperature control and the calorimeter output amplification. But, there is another consequence of the development of new electronical components : The design of the heart of the calorimeter itself. Following the evolution of the components used in the construction of the transducers three periods may be considered :

- the thermocouple period (TC)
- the semi-conductor period (SC)
- the integrated circuit period (IC)

Each type of these components (thermocouple, semi-conductor and integrated circuit) made it possible the design of instruments with, sometimes, very different properties such as :

- absolute and specific limit of detection
- available volume for the sample
- time constant

The first period has been strongly influenced by the work of A. TIAN and E. CALVET in the early fifties. Hundreds of calorimeters were built according to the so-called « Tian-Calvet » type. The main characteristics of these instruments are high sensitivity and a lot of researches were initiated with what appeared as a new tool.

When semi-conductors came available on the market as components, a new series of instruments became possible : higher sensitivity coupled with shorter time constant made it possible the investigation of smaller effects on smaller samples or at the contrary on very large volumes.

More recently, integrated circuits playing themselves the role of a calorimeter were produced : in the same integrated circuit, the heat flow transducer with temperature sensor and even calibration by Joule effect may be found. The main characteristic of this new family of calorimeters is its very short time constant and the small size of the instrument which opens new perspectives of applications.

This type of calorimeter works with a small amount of sample from -20°C to 100°C. Its low power consumption makes it possible an easy moving and testing on site. **The portable calorimeter is born !**

12.6

LUMINESCENCE OF LANTHANIDES IN THE NEAR IR REGION: THE BROAD PERSPECTIVES FOR ANALYTICAL PRACTICE

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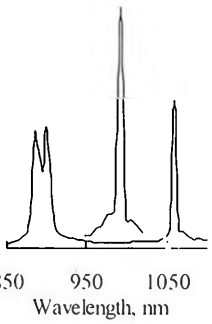
The luminescent properties of Ln(III), such as Eu(III) and Tb(III), are widely used in analytical practice. However, IR luminescence of Ln(III) is insufficiently applied, meanwhile it is known that this region is of special perspective for the analysis of biological objects.

More than twenty Nd(III) and Yb(III) complexes with calix[4]arenes of phenolic and resorcinol types have been investigated. Maxima of the luminescent bands are at 880, 903 and 1060 nm for Nd(III) and 980 nm for Yb(III)(Fig.). Luminescence is observed at room temperature in organic (DMF, DMSO, acetonitrile, ethanol) and water-organic solutions[1]. The quantum yields of luminescence are in $(0.6\text{-}1.1)\times10^{-3}$ interval.



In order to increase luminescence efficiently the methods dealing with the optimization of ligands' structure have been discussed. Perspectives of the development of spectrometric equipment and sensitive detectors for the near IR region have been given a special consideration.

[1] S.Shevchuk, N.Rusakova, A.Turianskaya, Yu. Korovin, N. Nazarenko, A.Gren and Yu.Shapiro, Anal. Commun., 1997, 201.

12.7

SEMICONDUCTOR SENSORS FOR THE DETECTION OF FLUOROCARBONS, FLUORINE AND HYDROGEN FLUORIDE

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Field-effect semiconductor chemical sensors have been developed using silicon and the large band gap material silicon carbide for measurements at room temperature and temperatures up to 400°C respectively. The sensitive two layer system LaF_3/Pt was prepared in a way leading to the formation of a three phase boundary with the gas under investigation. A typical multi-layer system characterised by high frequency capacitance-voltage measurements was SiC/epi-SiC/SiO_2/LaF_3/Pt.

The sensitivity was investigated for fluorocarbons (CF_3CH_2F, CF_3CCl_3, CF_3CH_2Cl, $CHClF_2$ and CCl_3F), fluorine and hydrogen fluoride at different concentrations in synthetic air. Fluorine and hydrogen fluoride have been detected in the whole temperature range from room temperature to 400°C using the SiC based device. The Si based sensor was operated up to 180°C only because of the band structure of the semiconductor. For both sensor types a stable sensitivity and a fast response was found at room temperature. However, no significant improvement was achieved at elevated temperatures.

For fluorocarbons no sensitivity was detected at room temperature. In the temperature range 200-330°C a very complex behaviour was observed. This can be used to distinguish between the different gases but higher temperatures are preferable for a stable sensor behaviour. At a temperature of 380°C a fast response and a selective detection of molecules containing fluorine is achieved. This selectivity compared to molecules without fluorine is caused by the F^--exchange properties of the LaF_3.

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WS1.1

HIGH THROUGHPUT ANALYTICS FOR HIGH THROUGHPUT SYNTHESIS: MEETING THE CHALLENGES OF COMBINATORIAL CHEMISTRY

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Combinatorial chemistry technology has captured the imagination of pharmaceutical, biotechnology and agrochemical industries as a means to an end for accelerating compound/drug discovery. Unfortunately, this technology has created a conundrum for analytical chemistry community. Whereas syntheses are performed inherently in parallel, analyses have been performed sequentially (*i.e.*, in series). The increased productivity of the chemists as a result of advances in combinatorial chemistry has necessitated the development of high throughput techniques for both analysis and purification. The challenge to the analytical community has been to develop novel strategies to address this analysis/purification bottleneck. At CombiChem, we have taken a multi-tiered approach to augmenting our analytical and purification throughput.

The first has involved developing a "miniaturized" version of PrepLCMS [1], a system we developed for automated, unattended purification of combinatorial libraries, for lead generation activities to permit direct analysis from shallow-well and direct collection into deep-well microtiter plates. Compounds synthesized in microtiter plates at the low-mg and sub-mg level have enabled us to utilize shorter columns with shorter analysis times for both analysis and purification.

The second approach has involved developing a fully automated parallel PrepLCMS system [2] to increase are sample throughput. In this new system, effluent from two (and up to four) HPLC columns is directed into a PE SCIEX IonSpray ion source, modified by us with a dual IonSpray "sprayer". Inputted masses of the expected products from the two HPLC columns are used to trigger fraction collection into dedicated fraction collectors for the two columns. The system is under full software control and permits two analytical or preparative columns to operated in parallel.

The third approach has been the development of a multiple probe autosampling system for rapid FIA-MS [3]. The system permits 8 samples to be drawn up and loaded simultaneously. Upon loading of all eight samples, the injector valves are sequentially rotated from "load" to "inject", initiating mass spectral data acquisition. In our current system, samples pass into the mass spectrometer ion source every 3 seconds, thus leading to a total analysis time of 28 seconds for all eight compounds. Mass spectral data acquisition is initiated by contact closure upon switching of the first injector from "load" to "inject". Combinatorial libraries synthesized in microtiter plates and PrepLCMS fractions collected directly into deep well microtiter plates have been analyzed with this multiple probe autosampler. Using this system, we have been able to process an entire microtiter plate in 7 minutes, providing a significant speed advantage over current FIA-MS methods.

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[2] Zeng, L. and Kassel, D.B.: "Developments of a Fully Automated Parallel HPLC/Mass Spectrometry System for the Analytical Characterization and Preparative Purification of Combinatorial Libraries", (1998) Anal. Chem. (in press).
[3] Wang, T., Zeng, L., Strader, T., Burton, L. and Kassel, D.B.: "A New Ultra-High Throughput Method for Characterizing Combinatorial Libraries Incorporating A Multiple Probe Autosampler Coupled With FIA-MS Analysis", (1998) Rapid Commun. Mass Spectrom. (in press).

WS1.2

SINGLE BEAD ANALYSIS FOR COMBINATORIAL STUDIES

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Combinatorial compound libraries are collections of molecules generated simultaneously by combining structural elements from a set of building blocks. This approach allows for the synthesis of a large number of molecules in a relatively short amount of time. Chemical synthesis is carried out on solid supports such as polystyrene beads. A library is a large collection of such beads and can contain from just a few compounds to a few millions of them. Structural elucidation of both the end products and the intermediates is necessary for library quality control and reaction optimization, respectively. Analysis of the libraries as mixtures often represents a difficult challenge because of the sheer number of compounds, isomers, adducts, and side-products present in them. However, each single bead in the library undergoes a unique series of reactions and carries a unique set of components (desired product, side-products, adducts) making it an attractive target for analysis. Therefore, a μHPLC/MS method was developed for automated single bead analysis which allows to obtain an insight into the reactions occurring on the beads, to assess the quality of the libraries, and to identify active compounds on beads.

The technique is routinely used on 30-80 μm beads with loadings between 1-200 pmol/bead. The chromatographic step allows to resolve isomers and side-products and to distinguish between isobaric compounds (same mass, different retention times) which are frequently found in large combinatorial libraries. This adds the advantage of a second dimension to the approach. A third dimension is achieved when the ions are fragmented in the mass spectrometer, giving structural information that helps in compound identification.

Selected examples that illustrate the usefulness of this technique in the development of combinatorial compound libraries will be presented.

WS1.3

MONITORING SOLID PHASE SYNTHESIS BY IR -SPECTROSCOPIC TECHNIQUES

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Solid phase synthesis is often used in combinatorial chemistry, especially in split and mix approaches but also in parallel synthesis. Analytical tools are needed during the development of the solid phase reactions as well as during the production phase. Ideally these analytical tools enable direct identification of the solid phase bound synthesis products, because cleavage of the products from the solid phase and subsequent analysis is time and material consuming. It has been demonstrated that MAS-NMR techniques fulfil in part these requirements. This presentation deals with the use of IR spectroscopic techniques for a structure proof of solid phase bound synthetic products. It is demonstrated that an ATR-IR-microscope enables such an analysis on single beads. Using signals from an internal standard for calibration semi - quantitative results concerning reaction turnover are possible.

WS1.4

FLOWCELL - NMR TECHNIQUES FOR STRUCTURE ELUCIDATION OF MIXTURES

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Monitoring chemical mixtures with NMR faces two challenges. Fast 1D-NMR is being challenged by overlaying signals even at high fields, 2D-NMR experiments regularly run into acquisition time problems.

One approach to overcome these problems is to directly link a chromatographic technique to NMR detection, as accomplished in HPLC/NMR.

Monitoring similar chemical mixtures in order to find characteristic differences can be done with fast onflow-^{1}H-NMR acquision, combined with a semi-automatic interpretation.

Chances and limitations of this methodology will be discussed.

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WS9.1

QUANTITATIVE COMPETITIVE PCR FOR THE DETECTION OF GENETICALLY MODIFIED ORGANISMS IN FOOD

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Whereas none of the approximately 30 genetically modified organisms (GMO) approved world wide so far needs to be labelled as "GMO" in the USA, regulations in the EC and in Switzerland require labelling. Firstly, GMOs have to be approved for marketing by the national or supranational authorities such as the Swiss Federal Office of Public Health or the European Commission. Food containing approved GMOs needs to be labeled according to the EU Novel Food Regulation and to the Swiss Food Regulation, respectively. The current methods for the analysis of GMO containing food used by European food control laboratories specifically detect transgenic DNA sequences by means of the polymerase chain reaction (PCR). Besides product specific methods screening methods are available that allow the detection of almost any GMO approved for food use. Clearly, present PCR detection methods only allow the qualitative detection of GMO in food without quantitation of the GMO content. However, the availability of quantitative detection methods for GMO analysis is an important prerequisite for the introduction of threshold limits for GMOs in food. PCR is well known to be quantitative if internal DNA standards are co-amplified together with the target DNA. This quantitative competitive (QC) PCR was first described in the early nineties and is widely used nowadays. We have developed and evaluated quantitative competitive (QC) PCR systems for the quantitative detection of Roundup Ready' soybean (RRS) and Maximizer maize (MM) in food samples. Three DNA fragments differing from the GMO specific sequences by DNA insertions were constructed and used as internal standards in QC-PCR. These standards were calibrated by co-amplifying with mixtures containing defined amounts of RRS DNA and MM DNA, respectively. The calibrated QC-PCR systems were applied to several commercial food samples containing RRS and to three certified RRS flour mixtures (Fluka standards). Recently, quantitative methods for the detection of RRS were successfully tested in a collaborative study involving twelve European control laboratories. Thus, QC-PCR methods will allow to survey "de minimis thresholds" of GMOs in food.

WS9.2

THE VALIDATION OF PCR FOOD ANALYTICAL METHODS ON AN INTERNATIONAL LEVEL

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Mutual recognition in the sector of food control has been established in the EU with for example the Additional Measures Food Control Directive which will be fully implemented in 1998. Food control laboratories are required to be accredited to EN 45000 and to participate in proficiency testing. In addition, there are requirements concerning the use of validated methods which can be more difficult to meet because the validation of analytical methods by a minimum of eight laboratories is a time-consuming and an expensive process to undertake. However, validated methods are necessary in order to establish performance criteria of the methods. It is necessary that the validation is carried out on an international level in order to obtain a harmonisation of methods which shall proof compliance with labelling or with the requirements set in the European Directives.

The Council Regulation (EC) No 1139/98 concerning the labelling of certain foodstuffs produced from genetically modified organism indicates that at this stage the presence in foods and food ingredients of protein or DNA resulting from genetic modification constitutes the criterion best complying with the requirements set in the Regulation. Qualitative PCR methods can be used as an initial screen of food products in order to detect genetically modified organisms (GMO).

The Joint Research Centre in Ispra, Italy has completed the validation of a screening method based on PCR suitable for the detection of genetically modified organisms in food. The samples (0 %, 0.1 %, 0.5 % and 2 % GMO soy beans and maize) were prepared in the Joint Research Centre in Geel, Belgium. Samples were derived from raw material.The participants were requested to follow a protocol that was based on performance criteria. The results of this validation study demonstrate that this screening method is suitable for the detection of GMO in raw material derived from soy beans and maize.

WS9.3

ENFORCEMENT OF LABELLING RULES FOR FOOD PREPARED WITH TRANSGENIC SOY AND MAIZE IN THE NETHERLANDS.

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Genetically modified soy and maize were introduced in The Netherlands in 1996, well before EC258/97 came into force. Mandatory labelling of foods prepared with GMO soy was at that time not considered necessary as it was thought that enforcement of these labelling was not possible. As a consequence of raised public concern, fuelled by several NGO's this opinion was changed in March 1997, when the Ministry of Health declared article 4 of EC labelling directive 79/112/EEG applicable if expressed transgenic protein could be detected in a food item. The basic reason for chosing protein based, rather than DNA based techniques might have been the wish to dispense soybean oil and lecithin from labelling requirements.

The Ministry of Public Health then had a test developed by TNO-Nutrition to detect the EPSPS protein. This test requires preliminary separation of proteins by SDS-electrophoresis followed by blotting and staining of the blot with a monoclonal antibody developed against a transgenic peptide motif. The technique is however quite insensitive (detection level of RR soy >0,5%). Validation of this assay with respect to different processing conditions and different foods are under way.

The laboratories of the Food Inspection Services diverted to techniques based on DNA. Two different PCR techniques to detect transgenic soy were made operational: one based on amplification of a sequence containing the CTP-EPSPS junction and another one based on the CMV35S-CTP junction. Both methods were carried out in the "nested" fashion. The detection limits of these methods were 0,1%, resp 0,01%.

A survey carried out in 1997 showed that of a number of 120 soy containing food samples analyzed, 16 (14%) contained RR soy (detection level 0.01%). None of these samples was labelled as "contains soy produced by modern biotechnology". On the other hand: no RR soy could be detected in any of the 13 food items explicitly labelled as containing genetically modified soy. Though this may be a consequence of lack of sensitivity of our test, or failure of isolating sufficient DNA, a more probable explanation may be that producers wished to avoid any troubles with respect to labeling and were putting the mandatory clause on the label without actually knowing whether the soy used was transgenic or not.

During the spring of 1998 a second survey was carried out, on the presence of transgenic maize in finished foods. A number of 27 samples was analysed by amplifying the CAM35S/bar gene junction (detection limit 0.0025%) and in some cases also with primers amplifying a sequence on the CryIA(b) gene or the bar-gene. Of the 27 samples investigated, two were found to contain small amounts of transgenic maize, at a level of about 0,0025%.

Given the frequent yes/no debates which followed our investigations it is stressed that more quantitative methods and statistically sound sampling schemes are needed to make enforcement of labelling feasible.

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RK3

NEW METHODS FOR ORGANIC AEROSOL ANALYSIS

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Aerosol constituents - inorganic as well as organic - have been determined in the past predominantly in the laboratory from filter or impactor samples collected in the field. Only recently new techniques have emerged that allow on-site determination of aerosol constituents with a time resolution of hours or minutes. The most versatile method in use for real time aerosol analysis at present is the combination of a wet denuder with a steam condensation and aerosol growth based aerosol collector (*Simon* and *Dasgupta* 1995a). The instrument has been used for the detemination of inorganic aerosol constituents (*Simon* and *Dasgupta* 1995a, b; *Blatter et al.* 1994). Based on the *Simon* and *Dasgupta* design we have developed a "gas - and aerosol monitor" (GAMS) for the determination of ambient levels of fluoride, chloride, nitrite, nitrate, sulfate, ammoniuum, potassium, calcium, magnesium as well as for the organic ions formate, acetate and oxalate (*Tscherwenka et. al.* 1998). The detection system in our configuration is isocratic IC for cations and gradient IC for anions. The detection limits achieved are in the range of 20 - 100 ng m^{-3} depending on the ion. The GAMS has been applied for investigations of the gas/aerosol fractionation of the organic acids at a cold remote site in the Alps (Sonnblick, 3106 m).

Other polar organic compounds are present in ambient aerosols at much lower levels than the organic acids mentioned above. Thus no automated techniques are in use at present. While for monofunctional compounds (acids, aldehydes, ketones, ester, ether) laboratory techniques for the determination are established (using GC-MS or HPLC) there are only few reports about the determination of polyfunctional organic compounds in atmospheric aerosols. Polyfunctional compounds are, however, expected in aerosols as a consequence of atmospheric oxidation processes. Here we report about a combination of solid phase extraction and derivatization methods followed by GS-MS determination for mono- and polyfunctional organic compounds in aerosols. Target compoundes with our method at present aredicarboxylic acids, keto- and hydroxy-carboxylic acids (*Limbeck* 1998).

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RK4

MYCOTOXIN ZEARALENONE: NEW ANALYTICAL METHODS FOR THE DETERMINATION OF AN ENDOCRINE DISRUPTER

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in memoriam Prof. *Robert Kellner*

The contamination of food and animal feed by fungi is a worldwide problem. Numerous surveys and monitoring studies on the presence of mycotoxins produced by fungi indicate that the *Fusarium* mycotoxin zearalenone (ZON) belongs to the 5 most prevalent mycotoxins with respect to agricultural production in Europe. ZON shows marked oestrogenic (endocrine) and anabolic properties and can cause severe reproductive and infertility problems in farm amimals, particularly in pigs. Therefore, livestock producers but also food and feed processors are showing increasing interest in the analysis of ZON in cereals.

We will discuss new trends in the analysis of ZON in cereals. The performance of immuno-affinity columns for the clean-up of ZON and subsequent determination by HPLC-DAD will be discussed. The suitability of LC-APCI-MS for the determination on ZON will also be reported. Due to the selectivity of MS detection, it was possible to quantitatively determine ZON in raw extracts without prior clean-up. Finally, an only recently developed ELISA method based on the utilization of chicken yolk antibodies will be presented, which is capable of screening ZON in the relevant µg/kg-range.

In this context we will also present selected results of an interlaboratory comparison test on the determination of ZON organized by us.

This study clearly demonstrates that excellent results can be achieved with the modern analytical techniques presented.

RK5

Enhanced sensitivity in flow injection based vibrational spectroscopy using disposable microbeads

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The hyphenation of molecular specific detectors such as FT-IR or FT-Raman spectrometers with flow injection analysis has increased the problem solving capabilities of these instruments as a significant increase in flexibility as well as precision could be achieved. However, one still existing drawback especially when measuring in aqueous solution is the limited sensitivity of vibrational spectroscopy in general.

In this paper we present a new approach using microbeads such as ion-exchanger (anionic as well as cationic) which are placed in the flow through cell. Doing so charged compounds can be enriched as well as retained at the place of measurement. As a consequence detection limits can be lowered as an increased amount of analyte is present for measurement (increased signal). Furthermore the measurement time can be prolonged hence allowing efficient signal averaging which reduces the noise level significantly.

The new approach will be shown on the example of the determination of alkaline phosphatase (ALP) activity and the determination of organic acids. ALP releases p-nitrophenol upon enzyme action on p-nitrophenylphosphate which, in an alkaline medium, can be efficiently retained on an anion-exchanger. The determination of organic acids in wine using microbeads owns the additional advantage that the strong absorbing and hence interfering matrix (alcohols and sugars) can efficiently be removed. The retained organic acids are quantified using by multivariate analysis (PLS) of the obtained spectra.

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RK6

DETERMINATION OF ORGANIC ACIDS BY FLOW INJECTION FT-IR SPECTROSCOPY USING pH GRADIENTS

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Organic acids like acetic-, citric-, lactic-, malic- or tartaric acid among others are analytes of interest due to their wide-spread occurrence as e.g. constituents in food and beverage samples and their key role in atmospheric chemistry such as ozone degradation. The standard methods for their determination in both cases are ion-exchange chromatography or HPLC, which have already been well developed for routine applications. In our contribution we show a new rapid approach using flow injection (FI) FT-IR spectroscopy avoiding the time-consuming separation step. The proposed technique is based on the chemometric evaluation of a series of FT-IR spectra from the sample recorded at different pH-values. A 3D-FT-IR-data array (FT-IR absorption vs. wavenumber vs. pH) is recorded, being the multidimensional equivalent to a titration curve recorded e.g. by potentiometry. The experimental set-up contains two flow lines of constant flow rate which are mixed at a confluence point. The first flow line contains the sample whereas a pH-gradient is formed in the second line prior to merging with the sample flow. The 3D-FT-IR data array is obtained by recording FT-IR spectra after the confluence point. As the pH in the resulting flow is varying with time spectral changes of the sample occur due to protonation or deprotonation of the analytes (organic acids). The matrix absorption, resulting from sugars and alcohols present in the sample, remains unchanged and can therefore easily removed by calculation of difference spectra. The data array recorded combines the information contained in the molecular characteristic mid-IR spectra with the likewise substance specific titration curves. The application of chemometric methods for peak deconvolution and multivariate data analysis allowed the identification and quantification of single organic acids in synthetic mixtures as well as in real samples. The new technique was applied to wine analysis showing significantly improved results in terms of accuracy with respect to direct multivariate FT-IR spectroscopic analysis and speed compared to separation techniques such as HPLC.

RK8

STATUS QUO IN INFRARED EVANSCENT WAVE SENSING

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During the last decade Chemical Sensors have gained considerable acceptance as versatile and flexible analytical systems for the evaluation of compound- or ion-specific or -selective signals produced by specific or selective chemical reactions taking place at the interface between the chemically modified sensor surface and the substrate. The introduction of new fiber optic materials and enhanced optica sensing schemes has greatly contributed that sensors are considered now as the "third supporting pillar of Analytical Chemistry" besides separation techniques and spectroscopy.

The aim of this presentation is to review the state-of-the-art of IR fiber optic evanescent wave sensor systems using chemically modified mid-IR transparent waveguides as sensing elements for the on-line analysis of various organic compounds such as chlorinated hydrocarbons in aqueous solutions and in the gas-phase.

The development of fiber optic chemical sensors (FOCS) during the last years benefits from the tremendous progress in the field of optical fibers, an offspring of the telecommunication industry. With the investigation of new matrerials besides the well known quartz fibers for the UV/VIS/NIR-range during the last ten years the optical window for fiber optic sensors has been enlarged from 0.2 to 20 μm. This large spectral range now allows to analyze compounds through their characteristic mid-IR absorptions. New applications for environmental, food and clinical sensing as well as process analysis are the driving force for modern research in IR optical fiber sensors using mainly sapphire (Al_2O_3), chalcogenide (As-Se-Te) and silver halide (AGBr/AgCl) fibers.

Within these applications FTIR spectrometers as well as Tunable Diode Lasers (TFL) in special cases were used for spectroscopic measurements using the principle of evanescent wave spectrscopy (EWS). Combining this well established principle with the fiber optic materials mentioned above results in a number of new FOCS with great potential for industrial applications as well as environmental and process analysis.

Particular attention will be given to new approaches for understanding and optimizing analyte/sensor interaction as well as current work aiming on design of miniaturized and field operable devices for effluent monitoring and marine pollution profiling (EU projects "EWALD" and "SOFIE").

RK7

SPECIATION ANALYSIS OF ORGANOTIN COMPOUNDS BY LC-APCI-MS*

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The growing awareness over the environmental fate of organotin (OT) compounds is reflectedin the great efforts to develop and improve analytical techniques for their speciation [1][2]. Organotin compounds have widely varying chemical and toxicological properties which strongly depend on the number and nature of organic groups bound to the tin atom. Presently, most of the methods applied to speciation analysis in environmental samples are based on separation by gas chromatography and detection/identification by a molecule specific (e.g. MS) or element specific detection technique (e.g. atomic emission, absorption, or fluorescence). This however requires the transformation of the ionic organotin species into their volatile derivatives by alkylation (using *Grignard* reagents or sodium tetraethylborate) or hydrisation. This derivatisation step is of concern, since especially in complex environmental matrices it can be strongly interfered and also due to the fact that redistribution of the organotin species during derivatisation has been reported [3]. Consequently, techniques based on liquid chromatography (LC) have thus been proposed for this task in order to avoid analytical artifacts related to the derivatisation step [4]. They suffer however from the drawback, that in contrast to gas chromatographic speciation techniques, a powerful, that is, both sensitive and specific detector was hardly available for liquid chromatography. This shortcoming has recently been overcome by the commercial introduction of LC-MS techniques based on atmospheric pressure ionisation (API) [5]. API denotes a family of LC-MSinterfacing techniques whose common feature is that ionisation takes place at atmospheric pressure. In addition to making the operation of the interface more robust and easier to operate, the principal advantage is, that with these interfaces sensitivity is significantly increased as compared to other LC-MS interfaces operating at reduced pressure (e.g. the particle beam and thermospray interfaces).

This makes the development of a speciation technique of OT compounds, based on LC-API-MS, feasible. While in the few LC-MS speciation work published up to now the electrospray interface has been considered the preferred interface, we report here on the developent of a LC-MS technique for the speciation organotin based on atmospheric pressure chemical ionisation (APCI). This technique produces useful diagnostic ions of both the parent compounds and adducts with the solvent molecules or other available ligands which exhibit the characteristic isotopic pattern of tin. The optimisation of the parameters for the detection of OT compounds will be discussed and their spectra interpreted. The figures of merit of the method will be presented and its applicability for the analysis of environmental samples will be proven by the analysis of a reference material (BCR CRM 462) with certified contents of butyltin compounds.

* Dedicated to the late Prof. *Robert Kellner*

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EURA1

Lecture Abstracts

1. EURACHEM / CITAC Guide 2: "QA in R&D and Non-routine Analysis"

Mr D. G. Holcombe, LGC, UK & EURACHEM CITAC WG Secretariat

The use of ISO Guide 25 and related standards as a basis for accreditation is now established internationally as the preferred way of assuring the quality of data in routine chemical analysis. However it was recognised that a large numbers of laboratories across the world were concerned with maintaining quality but for various reasons had not sought accreditation of their quality management systems. CITAC recognised that there were various elements of good QA practice that laboratories ought to implement whether or not they were accredited or compliant with other quality standards. These principles had much in common with ISO Guide 25 but it was clear that further interpretation was appropriate to make the practice more accessible to chemists. The consequence was the development and publication of CITAC Guide 1: "International Guide to Quality in Analytical Chemistry", in 1995. This spelt out good practice for mainly routine work.

Following this publication, the logical progression was to produce a companion guide covering good practice for non-routine work and research and development (R&D). Development of this second guide was carried out by CITAC and EURACHEM through a joint working group. A wider group, consulted less formally, ensured the guide was written from a solid base of experience. It is expected that this guide will be published by the time the workshop takes place.

This presentation presents a brief history of the development of the R&D Guide and discusses the structure and particular aspects of its content, outlining some of the key issues for discussion later on in the workshop.

EURA2

2. QM Systems for Non-Routine and R&D Analytical Work - Accreditation of Non-Routine Laboratories

Dr W. Steck, BASF AG, EURACHEM, CITAC, & EURACHEM / CITAC WG

These days many testing laboratories are familiar with formal QM-Systems like EN 45001 (ISO Guide 25), ISO 900X (EN 29000 ff) or GLP.

Laboratories engaged in R&D face several QM-systems which are suitable for carrying out Non-Routine and R&D analytical work. To make the appropriate choice it is however necessary that the laboratories know the application fields, scopes, benefits and drawbacks of the various systems. Hence this presentation tries to give both survey and insight into the concerned QM-systems like EN 45001, ISO 9001 and GLP as well as the future ISO 17025. The pros and cons for more or less harmonisation of the various standards will also be discussed.

While from the beginning ISO 9001 and GLP allowed more or less efficient to deal with Non-Routine analysis and R&D the accreditation scheme according to EN 45001 has not become flexible enough until the last few years. By using the *type-of-test* approach to define the scope several accreditation bodies developed a very promising way, which has since then been increasingly practised successfully, e.g. in Switzerland or Germany.

As for laboratories seeking third party recognition of their technical competence accreditation looks more appropriate than the other systems this lecture also adddresses some aspects of the accreditation of non-routine analysis. Based on his own experience the author will give some practical hints on how to prepare a multi-disciplinary non routine laboratory according to the *type-of-test* approach.

Participants interested in these issues can become more involved by joining the discussion group in the afternoon today.

EURA3

3. QA Aspects for the Academic World

Prof B. Neidhart, Institute of Physical and Chemical Analysis, GKSS Forschungszentrum Geesthacht GmbH & EURACHEM.

Introduction

Quality control is defined according to Brockhaus as: "all the measures which are deemed necessary to guarantee the appropriate state or condition (in terms of quality, excellence, or soundness) of a product for the purpose for which it is designed, ... the means for achieving this are the planning of controls and tests, analysis, quality control checks, test of the functionality, tests involving environmental simulations and qualification and acceptance tests."

In the case of chemical measurements however, i.e. the identification and quantification of analytes be they elements or compounds, one is not dealing with a product but rather with a provision of a service whose quality can only be assessed with difficulty, since the "true" content of the analyte in the sample to be investigated is generally not known and is not accessible by any other means. In this area therefore, there is a need for the development and application of special practices with which the quality of the "analytical service provided" can be guaranteed and documented.

In this situation it is clear what goal has to be achieved via a quality control system for achemical measurements (Analytical QA), viz. **the comparability of results, independent of the parameters time and place, equipment and personnel**. Here it should be noted that an analysis begins with the taking of the sample and the quality of the analytical result can never be better than that of the first step in the analytical method.

Motivation and Reasoning

Scientific-political

The concepts of Analytical Quality Assurance (AQA) and Analytical Quality Management (AQM), which were developed in the wake of harmonisation of the European Market and in connection with the globalization of the world's major trading zones, have now been formally established via the appropriate directives and norms (ISO Guide 25, EN 45001 and others). Although these developments have become accepted as market-regulating elements by the chemical industry and independent laboratories for routine chemical analysis and are now practised extensively in the form of accreditation - **a confidence generating measure with the goal of a mutual recognition of test results** - their implementation in the universities and research organizations has been very hesitant, with varying intensity and with varying degrees of competence . A sector which prides itself on its constant high quality and its recognized competence has difficulty in accepting that henceforth it will have to demonstrate proof of quality and moreover invest in expensive measures to maintainit. In the short to medium term this will be to the disadvantage of those institutions which do not develop such activities.

In the future, universities and research organisations that participate in national, European and international co-operative projects will have to secure and document the quality of their chemical measurements via validation of methods, employment of reference materials, participation in round-robin tests and auditing. **The need for action arises, in particular, as a result of the policy of the external funding bodies who are increasingly making awards of research grants (EU, BMBF) dependent on proven AQM.**

Criteria for analytical quality which should lead to comparability of analytical results have been established, parallel to AQA. Use of these criteria allows comparability to be achieved via the traceability of results to national and international standards through an unbroken chain of comparisons . Within the framework of an AQA system it is essential to be able to identify unequivocally the corresponding sample to which such a high quality result pertains; this criterion is defined as trackability. Validation remains the central task in the development of an analytical method whose analytical capability in a concrete application can be estimated with the aid of the measurement uncertainty. Finally proficiency testing serves to demonstrate the comparability in terms of the scatter of the results, e.g. in round robin tests.

Consequences

In the R&D Sector it is not necessarily a matter of accreditation, but rather a matter involving confidence generating measures of an alternative form, for which an organizational framework first has to be created. Regardless of the nature of these QA measures, the uppermost goal is the comparability of results since only then can future co-operative projects and international co-operation be meaningful. The CITAC/EURACHEM Guide on "Quality Assurance for Research and Development and Non-routine Analysis" is a good basis for the development of criteriaand procedures for the implementation of QA Principles in universities and research organisations.

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EURA5

5. Analytical Task Quality Elements

Dr P. R. Radvila, SACh. & EURACHEM / CITAC WG

Contrary to routine analysis , the the sample matrix and concentration range of the analyte are known, the analytical method has been validated and is tried - the method is fit-for-purpose - analysis in non-routine situations and in R&D may be a tortuous problem solving process. Although many basic quality elements are the same as in routine analysis, unknown factors such as unpredictable behaviour of the sample , unknown composition of the matrix and interdependance with the analyte, even uncertainty about the choice of the instrumental method, require not only a new focus on existing quality elements , but - due to the unpredictability of the analytical procedure and extent of effort - also additional organisational quality elements.

The uncertainties in non-routine analysis and R&D require careful consideration of the problem and required or available analytical techniques, planning and organisation of work, supervision of the analytical progress and adequate presentation and quality od results. Project management allows structuring of all aspects - both technical and organisational - of non-routine and R&D Work and defines responsibilities and competences of the personnel.

Analytical task quality elements are:

Phase 1: Preparation and planning before starting work
- definition of task and project design
- project design and research plan
- resource management of task

Phase 2: Work in progress
- progress review / monitoring analysis
- data verification
- changing direction

Phase 3: Work completed
- achievement review
- reporting, technology transfer and publication
- archiving

Essential elements of project management are co-operation and communication

After adapting or developing a method, its usefulness relies mainly on
⇒ documentation of procedures andequipment
⇒ validation
⇒ reference materials (external or internal)

It is essential that results can be reliably reproduced and results are correct - either in your own laboratory or externally. A high standard of education and experience as well as organisation talents are important prerequisites.

Despite the very nature of non-routine analysis and R&D, quality elements are extremely useful and can be implemented in systems, if a flexible framework is used, leaving room for anticipation and creative problem solving.

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ACA L1

SPECIATION OF ORGANIC AND CONDENSED PHOSPHATES IN WATERS AND SEDIMENTS USING FLOW ANALYSIS AND CHROMATOGRAPHIC TECHNIQUES

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Phosphorus is commonly the limiting nutrient for primary production in natural waters, and is often implicated as one of a number of causal factors in the occurrence of nuisance cyanobacterial blooms. Inorganic phosphorus, in the form of orthophosphate is most commonly measured as an estimator of the amount of phosphorus which is most readily bioavailable. However other non-orthophosphate components of the biogeochemical phosphorus cycle such as organic and condensed phosphates may also comprise important longer term sources of bioavailable P. The importance of these forms of phosphorus in aquatic ecosystems has been largely ignored because of difficulties associated with the specificity and sensitivity of their measurement.

This paper describes the development and application of hyphenated flow injection and chromatographic techniques which are both sensitive and specific, for the determination of condensed and inositol phosphates in waters, wastewaters and sediment extracts. In the case of the condensed phosphate species, these techniques have been used to elucidate the major hydrolytic mechanism involved in wastewaters. A similar range of techniques has been applied to determine the abundance of various inositol phosphate congeners found in sediments.

ACA L2

DETERMINATION OF METAL-ORGANIC INTERACTIONS IN NATURAL WATERS A DUAL RADIOTRACER/VOLTAMMETRIC APPROACH

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This paper describes a dual approach to study trace metal speciation using a radiotracer technique and cathodic voltammetry. The work involved the development of a radio-analytical technique to study sorption kinetics of trace metals in natural waters, and the application of the developed technique to a number of natural waters to study metal-organic interactions.

Radiotracers are extremely useful for the study of trace metal speciation and trace metal sorption kinetics in natural waters. For this study we employed the unstable isotope Cu-64 for the study of Cu partitioning in natural waters. The application of this isotope for trace metal speciation and kinetics work is uncommon, because of its short half-life (12.6 h). Studies using this unstabel isotope can therefore only be performed at an establishment with a nuclear reactor, ensuring a minimal delay between irrdiation of stable Cu to obtain Cu-64 and radiotracer experiments.

The development of a chromatographic technique for metal-organic investigation in natural waters resulted in a solid-phase separation scheme, using imino-diacetate (Chelex-100) and C-18 (Sep-Pak) columns. This method enabled us to separate weakly complexed dissolved Cu-64 from more strongly complexed Cu-64 (Chelex) and hydrophobic Cu-64-organic complexes from more hydrophilic Cu-64-organic complexes.

Three different natural water samples were obtained (Scheldt estuary, Rotterdaam Noord Canal and Delft Canal). Cu-64 was added to 1 litre of sample, the sample was stirred and 8 samples were collected at various time intervals, to enable us to model the reaction kinetics. On-line filtration (0.4 µm membrane filter) was performed followed by on-line solid-phase chromatography. The filtrate was collected and counted using a gamma-counter. The particulate material retained by the membrane filters was also counted. The results showed that within ca. 200 min, added Cu-64 had formed complexes with natural metal complexing organic matter. The experiments were performed at 2 different levels of Cu-64 additions (*e.g.* 7.4 and 52 nM for the Scheldt).

In addition to the Cu-64 experiments, natural Cu complexing ligand concentrations were determined in the water samples using voltammetric ligand competition techniques. The obtained results allowed us to determine the reaction kinetics in natural waters involving dissolved Cu, particulate material and dissolved organic matter.

ACA L3

LASER-INDUCED PLASMA SPECTROSCOPY (LIPS): A VERSATILE TOOL FOR MONITORING HEAVY METALS IN AEROSOL STREAMS

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Particulate heavy metals can cause severe toxic and carcinogenic effects when inhaled in higher concentrations. Therefore, it is desirable to establish a versatile instrumentation for a rapid monitoring of particulate emission (e.g. in waste incineration) to assess hazard levels, to evaluate control systems, or to provide feedback for process control. Due to the small mass involved, the determination of the elemental chemical composition is currently achieved by filter sampling, digestion and a subsequent analysis with conventional methods. These techniques are time consuming and do not qualify for construction of robust, mobile sensor systems. The aim of this work was to develop a transportable, low cost system for a direct analysis of aerosol filter samples based on Laser-induced Plasma Spectroscopy (LIPS), which provides quasi-on-line information on the elemental composition. The system consists of a 19"-rack with a laser unit and a spectrometer/detector unit connected to a miniaturized sensor-head via fibre optics. A plasma is created by focusing the beam of a Nd:YAG-laser on the surface of a quartz-fibre filter. The filter is placed on a filter holder which can be rotated by a stepping motor for getting spectra from different locations of the filter. Only minor dependence of the LIPS-signal on the matrix was observed and the dynamic range was found to be more than three orders of magnitude. Total reflection x-ray fluorescence (TXRF) was established as an independent reference analysis for calibration of the method. Detection limits for heavy metals range from about 50 ng cm^{-2} to about 500 ng cm^{-2} and measurements done on filters taken in incineration plants fit well into calibration graphs established with filters loaded with laboratory-generated aerosols. Besides these analytical merits of the technique we will also address the outcome from measurement campaigns at a waste incineration and other industrial plants, where an automatic isokinetic filter sampling interface for particulate emission was employed.

ACA L4

SPECIATION ANALYSIS OF METHYLATED ANTIMONY COMPOUNDS.

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Work by our group has shown that the group 15 element antimony can undergo biomethylation to trimethylantimony. This phenomena has been shown to occur with both a single culture (*Scopulariopsis brevicaulis*) and mixed cultures of micro-organisms from environmental samples. Antimony and its compounds are considered priority pollutants by the US EPA, a comprehensive study is required to determine the environmental fate of these compounds.

Trimethylantimony undergoes rapid oxidation with atmospheric oxygen to form non-volatile species, hence a number organoantimony species will be present in the environment. Speciation methods that can determine various organoantimony compounds, at low environmental levels, need to be established. We have interfaced gas and liquid chromatographic separations with antimony specific detection to analyse these species. Hydride generation coupled with purge and trap GC-quartz furnace atomic absorption spectroscopic detection has been used to analyse gaseous samples from antimony rich microbial systems. Trimethylantimony is the only volatile antimony compound detected in either system. HPLC-hydride generation-atomic fluorescence spectroscopy has been applied to the liquid culture fluids from which biomethylation has been observed.

This work can be used in combination with the known chemistry of trimethyantimony to model environmental pathways and to predict the fate of organometallic antimony compounds in the environment.

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ACA L5

Evaluation of Immobilised Macrocycles for On-line Column Preconcentration and Separation for Electrothermal Atomic Absorption Spectrometry

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Although electrothermal atomic absorption spectrometry (ETAAS) is a robust technique for the determination of many elements in a variety of samples, direct analysis of environmental and biological samples can lead to serious problems when analyte concentrations are low or when the matrix concentration becomes too high.

Flow injection (FI) techniques offer the possibility to relatively easily separate analytes from solution matrices. Furthermore FI preconcentration techniques can offer ways to increase sensitivities to levels required for trace element determinations. Various materials can be used for on-line preconcentration and separation. New, highly selective solid sorbents consisting of immobilised macrocycles make it possible to separate analytes from complex matrices with minimum of sample preparation. The use of such immobilised macrocycles packed in columns and used for on-line preconcentration and separation of sea water and urine samples for analysis with ETAAS will be discussed. Typically RSD values less than 5 % can be obtained even in the ng/L range.

ACA L6

THE EFFECT OF SUNLIGHT UPON FLOATING OIL - DIBENZOTHIOPHENE PHOTODEGRADATION

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Polycyclic aromatic sulfur heterocycles (PASH) such as dibenzothiophene (DBT) and its alkylated isomers are important oil constituents. Large amounts of these compounds are brought into the environment each year following oil spills and combustion processes. Nevertheless little is known about their environmental transformation pathways and the potential environmental hazards related to these compounds.

In this presentation we will focus on the photodegradation of DBT and alkylated DBTs as studied in simulation experiments. Methanol/water-solutions exposed to artificial sunlight have been used in a first step and quantitative data will be given for these experiments.
Furthermore we will report on the degradation of these compounds exposed to natural as well as artificial sunlight in crude oil films on water and seawater, experimental conditions which represent the environmental oil spill situation.

Liquid and Gas Chromatography coupled with UV-diode array, atomic emission and mass spectrometric detectors (partly after derivatization) have been used as analytical techniques. Products and the corresponding pathways will be presented.

The resulting water phases have also been used for toxicity screening tests which show higher toxic potentials for the water soluble fractions of the DBT-spiked oils exposed to sunlight.

ACA L7

THE EFFECTS OF SURFACTANTS ON THE ANALYSIS OF ORGANIC POLLUTANTS IN NATURAL WATERS

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This paper investigates the interference effects of non-ionic surfactants on the determination of polyaromatic hydrocarbons. A method was developed for the determination of biphenyl, fluorene, anthracene, phenanthracene, chrysene, pyrene, naphthalene, and acetanaphthalene with on line pre-concentration using a 1 cm ODS pre-column. Separation was carried out by HPLC on a 15 cm ODS alaytical column using gradient elution with a mobile phase of water and acetonitrile and UV detection at 254 nm. Limits of detection in the range of 1 μgL^{-1} were obtained with recoveries of between 90 and 102%. The % RSDs for the recoveries were 0.1-10% depending on the samples. Linear alcohol hydrocarbon chain (C13 and C15) non-ionic surfactants with a mixture of 3, 7, 11, and 20 polyoxyethylene head groups (Synerponic A3, A7, A11, and A20) were introduced into the PAH standards in levels found in natural waters and the recoveries measured. All the surfactants were found to have an effect on the extraction and recovery, but the degree of effect depended on the hydrophobic chain length and the analyte. Synerponic A3 and A7 had particularly adverse effects for all the PAHs except chrysene. The effects of changes in the sample pH (pH 6-8) and ionic strength on the recovery were also studied. The presence of large amounts of sodium chloride in samples reduced the recoveries. The analysis of natural river waters with known concentrations of PAHs was then demonstrated to be affected by spiking the samples with the surfactant. Several methods were investigated to overcome this problem and optimisation of the organic modifier in the mobile phase was found to be most useful.

ACA L8

SELECTION OF A REPRESENTATIVE TRAIN SET FOR THE CLASSIFICATION OF DEMOLITION WASTE

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Nowadays, separation of demolition waste is done manually. Automation of this process is beneficial for reasons of increased throughput, better working conditions and reduced costs. In the E.C. supported *AUTOSORT* project, the goal is the separation of demolition waste into three fractions:

- (Un)treated wood, paper, and cardboard,
- Plastics, and a
- Rest fraction, mainly stone, glass, and ceramics.

From demolition waste objects, mini-spectra consisting of 6 spectral regions in the near-infrared range are recorded. Linear Discriminant Analysis (LDA) is used to do a classification. To obtain an LDA model, a representative train set has to be selected from a complete "real world" data set.

For a "practical" implementation, questions are: how many objects, which ratios of selected objects between the three fractions, how to generate a constant test set, and how to select the objects? Furthermore, the selected objects can be used to monitor the performance in time (quality control).

To obtain a train set, objects are randomly selected from a constant data set. Statistical tests are executed to check the reproducibility. This method is compared to the Kennard-Stone object selection method. Kennard-Stone is preferred, because the objects are equally selected in LDA-space.

The presentation will discuss the applied statistical tests, Kennard-Stone, and the results.

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ACA L9

CURRENT PERSPECTIVES IN ENVIRONMENTAL ANALYTICAL CHEMISTRY

Title: Theoretical investigation of Flow-Injection Responses

Author: *Jens E.T. Andersen*

The technique of Flow-injection Analysis (FIA), now aged almost 25 years, offers unique analytical methods that are fast, reliable and consuming an absolute minimum of chemicals. These advantages together with its inherent feasibility for automatisation warrant the future applications of FIA as an attractive tool of environmental analytical chemistry. The need for an even lower consumption of chemicals has motivated a study of the FIA peak itself, that is, a theoretical model is developed, which provides detailed knowledge of the flow of liquids in pipes. On the basis of this knowledge, it is suggested that the consumption of chemicals may be reduced, in particular during the calibration steps of the experiments. It is shown that the FIA peak may be described in terms of three basic parameters related to friction and diffusion. Moreover, the theory predicts that the flow is laminar of a type not published previously, which, despite the small Reynolds numbers, contradicts the classical model of Poiseuille flow, as evidenced by experiments. A few examples and the consequences for the technique FIA are discussed.

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EUROANALYSIS 10

September 6–11, 1998, Basel, Switzerland

ABSTRACTS OF POSTERS

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Session K	Nutritional Analytical Chemistry	K1–K20
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H1

APPLICATION OF IMPROVED CHEMOMETRIC TOOLS FOR SIGNAL PROCESSING OF NON-SELECTIVE SENSOR ARRAYS

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Chemical sensor systems and detector arrays are widely applied for determination of organic vapors, gases and odours in the atmosphere. A piezoelectric quartz crystal can be used as a chemical sensor that is able to measure the chemical concentration reversibly.

In the current contribution, a chemical sensor array consists of four detectors is presented. AT-cut quartz crystals with 9 MHz fundamental frequencies were used. The crystals were arranged in an array and coated by gas chromatographic stationary phases like OV1 (Poly-dimethyl siloxane, SUPELCO), OV275 (Poly-cyanoakryl organosilane, SUPELCO), ASI50 (Poly-methyl-phenil siloxane, Applied Science Laboratories Inc.), and polyphenil-ether (Carlo Erba), respectively. The appropriate stationary phases were found by experimental and theoretical way based upon a principal component analysis. The thin film of the coating was formed by solvent evaporation. The coated surface was 0.2 cm^2 and the frequency of the quartz crystals decreased usually about 8 kHz. Nitrogen was used as carrier gas and 20 L/h mass flow was maintained by a GFM17 3½ digit flow controller. The nitrogen contained 30 ppm water vapour and it was dried by a CRS 202268 packed GC column to remove the traces of water. The analyte was injected by a syringe. A NAFION drying unit was set into the carrier line for declining the interference of the trace amount of moisture. Data handling card was built and a computer program was developed to measure the frequency changes. The computer program compared the measured frequency to that of the clock of the computer.

The requirements for a reliable piezoelectric chemical sensor are the sensitivity, selectivity and reversibility towards the analyte to be determined. However, to find an entirely selective material for only one analyte is almost unrealisable. On the other hand, application of the chemical sensor in the environmental analysis is hampered by the fact that several compounds are in the matrix and generally only one has to be detected. Mathematical algorithms have to be developed for the data processing, and chemometric methods are necessary to explain the behaviour of non-selective chemical sensors. Principal component analysis (PCA), pattern recognition (PARC) artificial neural network (ANN) and Fuzzy Clustering methods were applied to perform the data evaluation. The artificial neural network based upon the biological neurone model approach and the fuzzy clustering was proved to be the best for classification of the volatile organic compounds.

H2

SIMULTANEOUS SPECTROPHOTOMETRIC DETERMINATION OF TARTRAZINE, SUNSET YELLOW AND PONCEAU R BY PARTIAL LEAST SQUARES AND PRINCIPAL COMPONENT REGRESSION MULTIVARIATE CALIBRATION METHODS.

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Tartrazine (E-102), Sunset Yellow (E-110) and Ponceau R (E-124) are three synthetic azo dyes available as yellow, orange and red powder respectively, that can be present in common food. The contents of these dyes must be controlled because can induce allergic and asmathic illness in sensitive people.

Three multivariate calibration methods, partial least squares (PLS-1 and PLS-2) and principal component regression (PCR) were proposed and successfully applied to the resolution of ternary mixtures by ultraviolet-visible absorption spectrophotometry, working at pH 4.8, supplied by HAc/NaAc buffer solution.

At first, calibration matrix must be designed: a training set of 21 samples was taken varying T concentration between 1.6 and 20.0 mg/L, S concentration between 1.6 and 24 mg/L and P concentration between 1.6 and 36.0 mg/L. The spectral region placed between 420 and 540 nm was selected for the analysis.

The selection of number of factors was achieved obtaining values of 3, 3 and 4 as optima for Tartrazine, Sunset Yellow and Ponceau R determination by PLS-1 model.

Also the PLS-2 and PCR models were optimized by using the same set of standards samples and a number of 3 factors was found to be the optimum for the three components in both cases.

The external validation of the PLS-1, PLS-2, and PCR chemometric method was made over one set of 16 synthetic mixtures obtaining recoveries between 94.5 and 105.3 % and over several commercial products (two gelatins and a creamy dessert) containing the three dyes; the obtained results are in agreement with the found ones by an HPLC method proposed by us.

Repeatability and reproducibility studies (with the Students's and F's tests) were achieved over two series of nine standards for each dye, showing not significative differences at 95 % confidence level.

H3

PRINCIPAL COMPONENT REGRESSION IN KINETIC DISCRIMINATION OF SECONDARY AMINES

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Based on reaction rate differences, the discrimination between two very similar organic compounds is feasible in a very simple manner. To prove it, mixtures of dimethylamine and diizopropylamine have been investigated. They reacted with carbon disulphide in a slightly alkaline and homogenous medium that was obtained by using borate buffer and 3% Triton X-100. The formed dialkyldithiocarbamates rapidly complexed the Cu^{2+} - ion, also present in solutions, and the absorbance increase was monitored at 436 nm for 7 minutes, 121 values of absorbances being available in each recording.

To perform a principal component regression (PCR) in this case, a calibration set of 25 solutions was employed and two principal components were selected in the regression model.

The results obtained by PCR on 16 mixtures of the two secondary amines are compared with those computed by more methods of multivariate linear regression. They are favourable to the PCR concerning both the bias and the precision that characterize the two analyte concentration estimations.

H4

Maximum Entropy Chromatogram Reconstruction

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Maximum entropy has been successfully applied to problems of optical images and NMR spectroscopy. In this paper we present the results of maximum entropy deconvolution applied to simulated and real chromatographic data. A brief theoretical discussion is given. The technique is tested both qualitatively and quantitatively using simulated data. Peak resolution can be dramatically improved but quantitative accuracy is limited. The technique is applied to a re-analysis of Pioneer Venus chromatographic data and to storage column data.

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H5

CHEMOMETRIC EVALUATION OF ENVIRONMENTAL ANALYTICAL DATA

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The development of evaluation method for a multitask monitoring has been set as an aim. The basic principle of the building up was the use of the appropriate chemometric methods (e.g. for evaluation of trend, etc.,). This approach includes the following possibilities:

a/ analysis of the imission data including the quality assurance of the measurement method; comparison to the given tolerance values;
b/ remark of trends for various time intervals (hours, days, week , etc.);
c/ calculation of correlation among the various components of the polluted air, water, etc., to recognise relationships for modelling of the pollution mechanism; showing of the potency of the natural and anthropogenic influences.

A description is given including the experiences obtained using these methods in case of a city referring to the polluting components (CO, NO_2, O_3, dust, SO_2) of the air in a city, as well of the river (Na, K, Ca, Mg, Sr, Zn, Ni, Ba, As, Pb, Fe, Cu, Si, P) and the evaluation performed by software DATAPRO 3.0 [1]. The results obtained enable to build up a model to show elements which have unanimous anthropogenic influences (and origin), i.e. it can be considered to be an artificial system. The calculation is based on the correlations, as well as on comparison of the trends.
The choice of the appropriate chemometric method strongly depends on the given case, e.g. on the distribution [2].

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H6

CHEMICAL PARAMETERS OF pH REFERENCE BUFFER SOLUTION $Ca(OH)_2$ (SATURATED)

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Abstract

A new computer program has been developed for the calculation of pH, pOH, hydroxide ion concentration, m_{OH}, species distribution coefficients, α_i, ionic activity coefficients, γ_i, ionic strength, I, buffer capacity, β, solubility product, K_{s0} and the two dissociation constants, K_{b1} and K_{b2} corresponding respectively to first and second dissociation steps of $Ca(OH)_2$ in aqueous solution.
Previously developed methodology, for the calculation of pH, α_i, γ_i, I and β parameters of pH buffer solutions, starting from the corresponding acidity constants, has been tested for standard solutions, for wide range of pH value [1]. In the case of $Ca(OH)_2$ aqueous solutions, for which the pertinent stoichiometric relationships are different from those applicable to mixtures of acids and their salts, the methodology has been revised and adapted.
The results show that, contrary to what is currently assumed, the first dissociation is far from being complete. Values are given for the concentrations and activities of species $Ca(OH)_2(aq)$, $Ca(OH)^+(aq)$ and Ca^{2+} in saturated solution of calcium hydroxide at 298K.

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H7

MULTIVARIATE DATA ANALYSIS OF SEWAGE

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Seventy nine samples comprising 65 domestic sewage samples, 2 industrial waste water samples, 7 samples from waste water treatment plant influents and 5 domestic water supply samples were analyzed to obtain information about the nature and origins of pollutants in sewage in Melbourne, Australia. Altogether 88 chemical parameters including basic wastewater characteristics (like BOD, COD, TOC, TDS, TSS, NH^{4+}), and concentrations of 28 elements, some phthalate esters, chlorinated hydrocarbons, PAHs, amines and ethers, were determined.

The data were studied with principal component analysis (PCA) and discriminant partial least squares (DPLS) analysis. Data analysis showed that the mix of pollutants in the samples was different between typical weekdays and weekends and also depended on the weather at the time of sampling. PCA plots were used to visualize the results and proved to be very informative in classification of the samples.

The composition of samples taken on Sundays reflected typical human functions and weekend activities; they were characterized by high levels of Sr, Ca, NH^{4+}, total phosphorus and nitrogen, TDS, TSS and sulfate. Also there was a trend wih time, with observations made early on Sunday morning differing from those made later in the day and in the evening. On weekdays the sludges were characterized by high levels of pollutants from industry, such as Co, AG, Al, B, Ni, Cd and TOC. The samples collected in hot and sultry weather were dominated by variables such as BOD, COD, TSS, TOC, while samples collected in cool and rainy weather contained lower levels of these pollutants.

H8

ERRORS THEORY IN ANALYSIS

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The results of theoretical calculation of the standard deviation in some analytical methods allow to develop the errors theory in analytical chemistry. The improvement of the theory in atomic analytical spectrometry opens the way for the receipt of the equation which connects the standard deviation with the parameters of analytical apparatus and the concentration of determined element. This theory can be applied for any analytical method The process of analytical measurement is described theoretically by the dependence of the standard deviation from the characteristics of the used instrument. This approach allows to receive the theoretical description of known linear approximation for standard deviation in analytical chemistry and theory of measurements.
The possibilities of theoretical description of the standard deviation can be used for the control of the instrumental parameters. The linear approximation of the standard deviation from the element concentration is valid for instrumental value of the standard deviation in linear range of calibration curve. This equation is presented enough completely by the instrumental detection limit and instability factor of analytical apparatus. These relations are calculated theoretically and can be determined also experimentally. The concordance between the experiment and theory shows the good work of analytical instrument.
In the conditions of the real analysis, the noninstrumental factors play the great role. This theory allows the study the noninstrumental errors in analysis. The comparison of the waited instrumental errors with the obtained random errors in analysis opens the way for the characterization and study of noninstrumental errors of examined analytical methods. The theory gives the possibilities of the general theoretical description of the influence of the different noninstrumental factors on the common error in analysis. The effect of noninstrumental factors in analysis is examined theoretically and experimentally.
The theory permits to describe theoretically the instrumental standard deviation and detection limit, to study the instrumental and noninstrumental errors in analysis and examine theoretically the characteristics of any analytical methods. The theory shows the relations between the ground parameters of apparatus and analytical method. Thus this theory can be useful for the development of the general theory in analytical chemistry.
The problems of general theory in analysis are based on the theoretical dependence of the standard deviation from the concentration and the parameters of the analytical instrument. This dependence is described by the equation with five terms. The instrumental sensitivity and the blank value in this equation includes the theory of the used method and instrument. The first three terms are to linear range of the measurements. These terms describe theoretically the linear approximation in measurement theory. The last two terms concern the nonlinearity in analysis and the nonlinear errors in measurement. The further development of the theory in analysis is connected with the improvement of the methods of theoretical description of the noninstrumental and nonlinear errors. The use of the theory for the different analytical methods is important. The theory allows to improve the practical methods of the standard deviation and detection limits determination and the parameters of analytical methods characterization and standardization. This theory can be useful for theory and practice in analytical chemistry.

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H9

THE FUZZY LOGICAL ALGORITHMS AND THE CHOICE OF THE REAGENTS IN SPECTROPHOTOMETRY

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Computirized advising and expert systems takes great importance to take a dicision in the current analytical chemistry. It is well known that chemical analytical system, for which there are no precise mathematical models, are theobjects of investigation in analytical chemistry. Fuzzy logical models can be considered to hold the greatest promise. This article suggests the fuzzy algorithm of choice of the reagents in spectrophotometry.

Numerical or lingvistic information about parameters of the reaction for each reagent can be represented by propositional variables ai. The importance of each parameter may be described by fuzzy set of chemister's preferences (set { pi }). The formula of degree of truthfulness for the fuzzy logical statement on the application of reagent to determine a specific element in a specific subject is as follows:

D = min(max(a1, 1-p1), max(a2,1-p2),..., max(an,1-pn)).

It is evident that the best reagent has the greatest amount D.

The choice algorithm was composed on the basis of the obtained formulae and then was computerized. The reagents for spectrophotometric determination of some heavy metals in natural objects were chosen.

H10

A NEW APPROACH FOR DATA ANALYSIS OF ELECTROCHEMICAL AC IMPEDANCE SPECTRA

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Impedance Spectroscopy is a well established technique in electrochemistry for investigating electrode properties, e.g. bulk resistances of ion selective membrane electrodes [1]. Data analysis is nescessary for evaluating the spectra. Nowadays, this task is done by the complex nonlinear least square fitting method (CNLS) [2]. Here we want to introduce a new approach for analyzing impedance data presented in the complex plane plot. It is possible to describe a circle with three data points on the circumference (fig. 1). Knowing the trigonometric function the radius, representing the bulk resistance, can easiliy be calculated. By considering the standard deviation σ_r of all N data points the error of the fitted circle is exactly determined. The best fit can be obtained by calculating the circle with all possible data triples. Comparing the standard deviations of the radii for all circles the one with the least value for σ_r is found to be describing the measured data best. The efficiency of our method has been shown by analyzing impedance spectra of different networks and comparing the results with those obtained by CNLS fitting procedure. However, for performing the CNLS method on a computer a special data evaluation software is nescessary. In contradistinction to this, our method described in this paper can be applied by the use of commonly available spreadsheet calculation software like Microsoft Excel™.

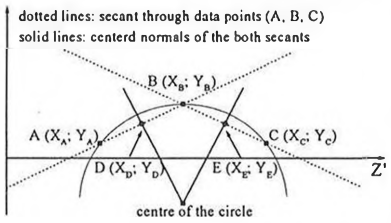

Figure 1: Calculating the real part of the impedance Z

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H11

SELF-MODELING TECHNIQUE FOR DATA TREATMENT IN MIXTURE ANALYSIS

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Evolving factor analysis algorithm with iterative target transformation procedure for complex analytical data sets treatment is suggested.

Some problems for complex (including GC, MS, GC/MS, UV-VIS, IR and chemical elements composition) analytical data sets treatment are discussed. It was shown, that the adequate choice of limites and standardized requirements assured the fit iterative target transformation procedure.

A solution constructed in the form of (*n-1*)-dimensional rectilinear simplex with unity altitude is an essential feature of the proposed algorithm, where *n* - is a number of components. The apexes of simplex conform to pure components, ribs - to binar mixtures, faces - to three-component mixtures and so on. Simplex apexes projections on axes of initial natural co-ordinate system conform to pure-component spectra.

Compared are two ways of method testing - with simulated data and well-studed mixtures data sets. The simulated data were compared with real GC/MS data to resolve peaks, to recover pure-component spectra from the overlapped spectra mixtures and to quantify component contents.

The proposed technique was used to resolve and recover pure-component spectra from the overlapped spectra mixtures, for curve resolution, signal-to-noise reduction, assessment of peak purity in chromatography with multi-channel detectors, small chromatographic peaks detection, trace component in complex mixture detection, identification and quantitation, and for source apportionment in environmental problem concerning polyciclyc aromatic hydrocarbons.

H12

EVALUATION OF SIMILARITY OF MACRO-ELEMENT COMPOSITIONS OF SAMPLE AND CALIBRATING RSM IN MULTIELEMENT AEA

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Modern spectral instruments controlled by computer, ensure the high level of automation when receiving and recording of arc atomic-emission spectra of rock, ore, sediment, soil samples of different composition.

The described algorithmical software of the computer processing of spectra is intended for creating methodology of visual analysis. Calibrations for three types of analytical matrices have been used for the visual interpretation of the rock and soil spectra usually. The difference of their compositions may be characterised by the value of the effective ionisation potential of matrix, their variations depending on Ca, K, Na, Al concentration. These parameters are used as the criterion of classification and the choice of reference standard materials (RSM) for calibration when determining 25 elements in rocks, sediments and soils.

The spectra have been obtained by the method of complete evaporation of 20 mg sample from carbon electrodes in the direct current arc. Spectrograph DFS-8 (0.6 nm/mm) is used. Spectra are recorded by device with CCA-arrays.

Expert conclusions in the program are based upon the computing of the Si lines areas and comparison on the obtained relationships in the spectrum of investigated sample with received for three analytical bases. If the calibrations of determined elements for three types of matrices in database are presented, the choice corresponding to the matrices and the kit of calibrations is fulfilled automatically. If for some reason the calibrations for one of analytical matrices are absent, the message about noncorrespondence of the macro-element composition of some investigated sample and reference standard materials used for calibration appears on the screen and in the sheet of results.

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M1

PRECONCENTRATION AND SPECIATION OF TRACE ANIONS USING A DIAMINOCALIX[4]ARENE.

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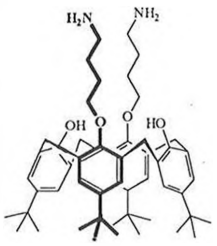
As anions are demonstrated to play an important role in biochemical processes, it is of fundamental importance to determine their concentration, even at trace levels. The ability of a diaminocalix[4]arene (figure) to extract several anions (SeO_4^{2-}, SO_4^{2-}, CrO_4^{2-}, SeO_3^{2-}, NO_3^-) from a chloride medium was studied by means of liquid-liquid extraction and the performances of this ligand for preconcentration and speciation analysis of inorganic anions were tested.



The influence of parameters such as pH, ligand concentration, nature of the diluent and ionic strength was investigated in order to determine the optimal conditions of extraction. Results show that this calixarene exhibits a selectivity towards dianions which allows their preconcentration. Moreover, in presence of an excess of ligand, we demonstrate that selenate is quantitatively extracted while selenite stays in the aqueous phase. The potential application of this calixarene in the speciation of inorganic species of selenium is then considered.

M2

MASS-TRANSFER COEFFICIENTS AT THE URANIUM ADSORPTION FROM SOLUTION ON ION EXCHANGE RESINS

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The process of uranium adsorption on ion exchange resins is a mass-transfer process of solid-liquid nature associated with chemical reaction. Mathematical models used in these studies considers a spherical ion exchange resin grain where on its surface and its pores is taking place the chemical reaction. The steps of process are involved ion mass-transfer from liquid phase to the solid surface of grain, diffusion through its pores and chemical reaction. In the field of ion exchange are used several models which are described one of the steps of the process, but also there are models who take into consideration all the three steps as „shell progressive reaction mechanism" model.

This paper presents experimental data of the uranium adsorption from alkaline solutions on a strong basic ion exchange resin, second type in chlorine form.

Using the „shell progressive reaction mechanism" model was identified - depending on way of contact - main stage of ion exchange process.

The resin and the solution are contacted in two way: fixed bed and perfect mixing. For each and every kind of contact was studied the variation of the partial mass-transfer coefficient as a function of the granulometry of resin.

Also, criterial relations were established between mass-transfer process variables, impulse transfer and equipment geometry used for the experiments.

The optimal granulometric resin size was also established for uranium adsorption from alkaline solutions.

„Shell progressive reaction mechanism" model is a good approximation for uranium adsorption from alkaline solutions process giving the information for design of the requested equipment.

M3

EXTRACTION OF THIOCYANATE COMPLEXES OF SILVER WITH POLYMETHYNE DYES FROM WATER-ORGANIC MEDIA

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The extraction of silver ion associates (IA) with thiocyanate ions and basic polymethyne dyes derivatives 1,3,3.trimethyl-3H-indolium from water-organics media has been studied.

An introduction of the water-soluble donor-active organic solution (DAS) substantially increases the extraction of IA und supresses simultaneously that of the ordinary dye salts. On the example of extraction of silver IA with polymethyne dye Astraflocsine FF it has been shown that the DAS concentration required for the maximum extraction of IA regularly decreases in series 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, one can achive the selective extraction of silver.

The IAs of silver are extracted with polymethyne dyes in the pH range 1-6. The composition and the principal chemical-analytical characteristics of coloured silver associates have been determined. The possible mechanism of their production and extraction from water-organic media has been suggested. The molar absorptivity for different polymethyne dyes is as high as (0,68-1,11)x10^5. New high-sensitive and selective method of the extractive-photometric determination of silver in alloys, semiconducting materials has been developed. The possibility of the extractive photometric determination of silver in the form of IA in the presence of surfactants has been demonstrated.

M4

STUDY OF COMPLEX FORMATION OF THALLIUM(III) WITH XYLENOL ORANGE IN MICELLAR SOLUTION

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The present work describes a simple, rapid, selective and sensitive spectrophotometric method for determination of thallium(III), based on the colour reaction between the metal ion and xylenol orange(XO) in micellar solution. The effects of different kinds of surfactant on the spectral characteristics of thallium(III)-XO complex are examined. Sensitive spectrophotometric procedure for thallium(III) determination based on the formation of Tl(III)-XO-cetylpyridinium chloride(CPC) ternary solubilized complex has been established. The important analytical parameters and their effects on the reported system are investigated: pH effect, buffer selection, amount of acetate buffer, amount of the XO, amount of surfactant, order of addition of reagents, complex stability, oxidization effect of Tl(I) to Tl(III) and adherence to Beer's Law. The formation of the ternary complex is accompagnied by a increase bathochromic shift in the maximal absorption of the complex, hence, there is a difference ($\lambda_{Tl(III)-XO} - \lambda_{XO} = 149$ nm; $\lambda_{Tl(III)-XO-CPC} - \lambda_{XO-CPC} = 164.5$ nm; $\lambda_{Tl(III)-XO-CPC} - \lambda_{Tl(III)-XO} = 13$ nm). Ternary complex colours are instantaneously established at room temperature, and the absorbance value remains unchanged for least 168 hr. In the absence and presence of cetylpiridinium chloride, 1 : 1 binary and 1 : 2 : 4 ternary complexes having molar absorptivities of 3x 10^3 and 7.2x 10^4 l.mol^{-1}.cm^{-1} at 585.5 and 598.5 nm, and apparent stability constants of 1.57x10^6 and 2.27x10^{10}, respectively. The optimum pH range for the reaction is 3.5 -5.5 and Beer's law is obeyed over the concentration range 0.817-17.167 µg/ml of thallium(III). The interference of various ions has been studied by taking a constant concentration of metal ion and determining its concentration in the presence of large number of foreign ions.The xylenol orange is not selectivity for thallium(III) but the addition of appropriate masking agents allows the thallium determination in the presence of accepted amounts of some cations.

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M5

SORPTION RECOVERY OF HEAVY METAL IONS BY CHELATING POLY(ACRYLAMIDOXIME) FIBERS

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Utilization of chelating sorbents as substrates to bind heavy metal ions provides an effective mean of solving waste water problems.
Chelating fibers are new types of sorbents which have several advantages over resins: high specific areas, much higher sorption rate and sorption capacity for ions.
The fibrous chelating sorbents containing amidoxime groups, -$C(NH_2)$=NOH were synthesized by published procedures [1,2] from commercial polyacrylonitrile fibers (Melana-ROMANIA).
The functional group was confirmed by IR spectra and TG. Owing to the amphoteric nature of amidoximes, the cation exchange and anion exchange capacity were measured.
The chelating fibrous sorbents were used for the concentration of Cu(II), Cd(II), Pb(II), Hg(II) from aqueous solution. Optimum conditions for maximum recovery of metal ions with poly(acrylamidoxime) chelating fibers were developed with respect to pH, temperature, equilibration time, weight of sorbent and amount of metal ion.
The experimental results point out the possibility of chelating amidoxime fibers utilisation for the removal of heavy metal traces from natural or waste waters in the presence of high concentrations of univalent cations.
The metal ions released from the chelating fibers with mineral acid solutions have been determined by AAS and by spectrophotometric methods.

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M6

COBALT DETERMINATION AT PPB LEVELS BY X-RAY FLUORESCENCE AFTER ITS PRECONCENTRATION ON POLYURETHANE FOAM

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A sensitive method based on the preconcentration on powdered polyurethane foam (PUF) has been developed to determinate cobalt at ppb levels by X-ray fluorescence. Cobalt was adsorbed as thiocyanate complex at pH 2.0 on 120 mg powdered PUF. The system was mechanically shaken for 50 min. The PUF was then filtered under vacuum through a filter paper ∅ = 2.0 cm and was washed with 0.2 M potassium thiocyanate solution. The thin circular PUF was dried by squeezing under vacuum, covered with a Myler® film, and taken to the X-ray fluorescence measurements. Parameters as sample volume, extraction time, interference by cations and anions, were studied. The system cobalt-thiocyanate-PUF-XRF presents a linear relationship up to 250 μg/L, and the coefficient of variation for five measurements at 50 μg/L of cobalt is 5 %. The detection limit is 5.5 μg/L. The higher interference was iron(III) ions but could be eliminate by using asorbic acid. This method was certified using steel reference materials. The optimum conditions were developed to determine cobalt in references materials, waste water, and sea water.

M7

Microencapsulation of EDTA with PVC for the use of Preconcentration of Trace Metals in Aquatic samples

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Toxic effects of some metal ions found in natural water are very high although their concentration may be low. That's why correct analysis of these ions is very important for environmental chemistry. But analysis of trace elements is one of the most difficult and complicated analytical task. In order to obtain reliable data, the best way is to separete and these elements from the matrix constituents and to determine them in the isolated state. After enrichment, the elements can be determined by sensitive methods.

Probably the most well know preconcentration is the solvent exttraction by use organic reagents. But most of the organic solvents have cancerogen effect.

This study is based on the application of capsulated EDTA by PVC as sorbents in order to concentrate of trace metals. Trace amounts of Cu(II) and Zn(II) have been enriched from aqueous solution on this sorbent. After the metal ions sorbed on the sorbent is eluted , it is analysed by flame atomic absorption spectrometry. Metal ions are eluated with 2M hydrochloric acid.

The batch technique was used for determining the exchange capacity, the effect of pH, sorbent volume, and the effect of shaking time. The sorption of metal ions is obtimum at 8-9 pH. Equilibrium is established within a short period.

The colum technique was used for preconcentration. Optimum conditions such as eluent and sample flow rates, the effect of sample matrix on the recovery, and concentration of metal ions were determined. Cu(II) and Zn(II) ions very efficiently preconcentrated from 0.1 mg ml^{-1} solutions with this column technique and 100% recovery was achieved in every instance.

M8

THE USE OF PALMITOYL HYDROXYQUINOLINE-FUNCTIONALIZED AMBERLITE XAD-2 COPOLYMER RESIN FOR THE PRECONCENTRATION AND SPECIATION ANALYSIS OF GALLIUM (III)

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Gallium is a valuable element in electronics industry for manufacturing semiconductors and lasers. The processing of bauxite ores for the recovery of Ga as well as high level purification of the raw Ga product as required by electronic applications necessitate effective speciation analysis of this element. For differentiating chemically important Ga (III) species, the Amberlite XAD-2 polystyrene-divinylbenzene copolymer was chloro-methylated using $AlCl_3$ as catalyst, and later, 5-palmitoyl-8-hydroxy-quinoline was covalently bound to this chloromethylated product via Friedel-Crafts reaction resulting in the synthesis of a Ga-specific resin (Amberlite XAD-2-P.Ox).

This resin has been shown to preconcentrate Ga selectively from basic aluminate solution [1]. The investigation of the effect of acidity on Ga recovery revealed that Ga was quantitatively retained on the resin between pH:3-7. The sorbed Ga could be eluted with 1 M HCl. A 100 mL-volume of 2 ppm Ga showed 100 % uptake by 10 g of resin using a flowrate of 1 mL. min^{-1}. Here, all simple inorganic salts of Ga (e.g., Ga (III) nitrate, chloride, perchlorate etc.) as well as the free Ga^{3+}(hexaaqua-complex) species exhibit quantitative retention.

On the other hand, oxalate-, tartrate-, citrate-, and EDTA complexes of gallium (III) were not retained by the resin under identical conditions. Thus, the synthesized chelating cation-exchanger showed selective affinity to simple inorganic Ga (III) salts, in a way acting as an ion-selective electrode for Ga^{3+}, while excluding coordinatively saturated Ga-complexes.

[1] H. Filik and R. Apak, Sep. Sci. Technol. 33 (1998) in press.

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M9

POSSIBILITIES OF REMOVAL OF Fe^{3+} AND Cr^{3+} IONS BY POLY-(AMIDEHYDROXYURETHANE)

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Several polymeric materials have proved efficient in treating waste waters due to their ability of complexation with heavy metal ions.[1]

Poly-(amidehydroxyurethane) (PAHU) a polymer soluble in water can make a complex with Fe^{3+} and Cr^{3+} ions forming insoluble products specifically coloured and well defined. PAHU has a structural unity that corresponds to:

The optimal conditions for the precipitate to form have been established: pH, time, temperature, stirring. Based on quantitative results we have found that the complex formation occurs at the combination ratio M/PAHU:1/1 for Fe^{3+} and 1/3 for Cr^{3+}.

The complexes have been characterized by IR spectrometry and thermogravimetrically.

The experimental results point to the possibility of using PAHU to remove heavy metal ions Fe^{3+} and Cr^{3+} from industrial effluents.

[1] *** Environmental Remediation, G.F. Vandergrift, D.T. Reed, I.R. Tasker Ed. (A.C.S. Symposium Series 509), American Chemical Society, Washington DC 1992, p161

M10

DETERMINATION OF NICKEL IN ALKALINE SALTS BY ICP-AES AFTER SORPTION ON AMBERLITE XAD-2 LOADED WITH PAN

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The determination of metal traces in alkaline salts by ICP-AES is difficult because the aspiration of solutions with high salt concentrations in plasma can cause problems such as blockage of the nebulizer, considerable background emission, chemical interferences with consequent drop in sensivity and precision. Thus, trace determination in saline solutions always need a prior separation.
The present paper describes the use of Amberlite XAD-2 resin loaded with PAN reagent for separation, preconcentration and determination of nickel ($ng.g^{-1}$) in alkaline salts using Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) technique.
The method proposed is based on the solid-phase extraction of nickel(II) in cation the form of 1-(2-pyridylazo)-2-naphtol complex. Parameters such as: effect of pH on the nickel sorption, effect of flow rate and aqueous volume on the sorption, sorption capacity of the resin, nickel desorption from the resin and analytical characteristics of the procedure were studied.
The results demonstrate that the nickel(II) cation in the range of 0.02 to 55.0 µg, and pH 6.0 to 11.5, contained in a solution volume of 25 to 200mL, can be extracted by using 1g of Amberlite XAD-2 resin loaded with PAN reagent. The precision of the method, evaluated as the relative standard deviation obtained after analyzing a series of seven replicates, was 3.9% at 10.0µg of nickel contained in a solution volume of 50mL.
The proposed procedure was used for nickel determination in alkaline salts of analytical grade and food salts. The standard addition techniques was used and the recoveries obtained revealed that the proposed procedure shows good accuracy and precision.

[CNPq, FINEP, CAPES]

M11

APPLICATIONS OF SOLID PHASE EXTRACTION FOR PRECONCENTRATION OF MICROAMOUNTS OF PLATINUM PRIOR TO GFAAS DETERMINATION

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Metals of the platinum group have found important application in technology and industry. Platinum and rhodium are emitted to the environment with the exhaust gases from the motor cars catalysts. Compounds of these metals display a broad spectrum of toxic effects on the organism.

The determination of platinum in biological and environmental materials was possible by the development of very sensitive analytical methods as e.g., adsorptive voltammetry or inductively coupled plasma – mass spectrometry (ICP-MS).

In this work we developed the procedure of preconcentration and determination of trace amounts of platinum. The graphite furnace atomic absorption spectrometry (GFAAS) was used for the determination of analyte, while for its preconcentration we applied the solid phase extraction technique (SPE). The preconcentration factor of 50 (for 20 ml of sample solution) was obtained using columns packed with 250 mg of alumina and 2 mol/l ammonia solution as eluant. Calibration was done using platinum ammonia solutions, and under these conditions the characteristic mass was 46 pg, and detection limit for the sample was 0.17 ng/ml. The precision and recovery were satisfactory at this level and equal 9.4% and 99%, respectively.

M12

APPLICATION OF THE ION CHROMATOGRAPHY FOR THE SPECIATION OF THE SAMPLE COMPONENTS IN ATOM ABSORPTION SPECTROSCOPY

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Speciation of metals ions with different oxidation stages is of a great practical interest (e. g. Cr(III) is toxic but Cr(IV) is not. Atomic absorption spectroscopy (AAS), a widely used technique for metal determination has disadvantage of being nonspecific. On the other hand, ion chromatography (IC) provides opportunity to separate ions with different oxidation stages.

In this work the possibility to use IC for sample preparation for AAS was investigated. Experimental set up consisted of flame AAS spectrometer (SP 9, Pye Unicam), high pressure pump (Incrom, Tallinn), ion exchange column and conductivity detector (Knauer). A simple T - piece was connected to the outlet of the conductivity cell and inserted immediately before the nebulizer for the compensating the nebulizer uptake rate and chromatographic flow rate with air.

The results of using different ion exchange columns for metal ions speciation will be presented.

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M13

ANALYSIS OF MINERAL OIL HYDROCARBONS IN DRINKING WATER USING AUTOMATIC SOLID PHASE MICRO EXTRACTION (SPME)

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The measurement of mineral oil hydrocarbons (MOHC) is in most laboratories nowadays carried out by liquid-liquid extraction with 1,1,2-trichloro-trifluoroethane (TTE) followed by IR spectroscopic analysis of the organic extract. (DIN 38 409-H18)
TTE, known as Freon 113, is an ozone depleting compound and its use and disposal is a potential environmental hazard. Furthermore, by this method only a semiquantitation of MOHC is possible below 50 µg/L. According to German Drinking Water Regulation the limit value for MOHC is set to 10 µg/L, therefore, a precise analysis at and below the limit value is hardly possible using conventional methods.
Taking above mentioned reasons into consideration, there is an urgent need for development of a new analytical technique for the precise quantitation of MOHC's in the required concentration. This work describes an alternative new method based on automatic Solid Phase Micro Extraction (SPME), a new solvent free extraction technique, recently developed by Pawliszyn.
Mineral oil hydrocarbons are very hydrophobic and their extraction on a non-polar 100 µm PDMS (polydimethylsilyl) fiber is very efficient. In order to extract also the long-chain alkanes, SPME has to be used for determination of MOHC's by extracting directly from drinking water sample into SPME fiber. The SPME fiber can automatically (or manually) be transferred into a GC injector for thermal desorption onto a capillary column. The detection can be carried out in either a flame ionisation detector or in a mass spectrometer (MS). By this method a concentration down to 1 µg/L can be detected and assures an accurate quantitation of MOHC's at the set limit of 10 µg/L drinking water. A fingerprint chromatogram allows in addition the characterisation of different mineral oil classes, e.g. gasoline, diesel and others. The use of an MS allows differentiation between aromatic and aliphatic hydrocarbons.

M14

THE INFLUENCE OF PARTICLE SIZES ON THE METHOD FOR RAPID BULK CHARACTERIZATION OF OIL SHALE KEROGEN

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The alkaline permanganate method, based on the consumption of permanganate under standard experimental conditions, was shown earlier [1] to be useful for rapid characterization of oil shales in exploration studies.

Within the further development of this method for prospection studies, in this paper the influence of particle sizes on the consumption of permanganate was studied for two series of kerogen concentrates of the Aleksinac (Yugoslavia) oil shale. Each of them consisted of four fractions which were obtained by three DIN 4188 sieves (corresponding diameters were 1.60, 1.25 and 0.63 mm, respectively). For each fraction the consumption of alkaline permanganate was determined for different reaction time (5, 15, 30, 60 and 120 minutes).

As expected, the increase of permanganate consumption was observed with the decrease of average particle size. The greatest differences were found for reaction time 15 minutes. Results indicated considerable influence of particle sizes on permanganate consumption as the observed differences could not be attributed entirely to the different content of pyrite, kerogen or its structural characteristics.

The study of IR spectra of samples before and after treatment of concentrates with alkaline permanganate confirmed increased structural changes for smaller particles (the decrease of aromatic components and increase of carbonyl structures due to the oxidation).

[1] Krsmanovic, V.D., Pfendt, P.A., and Vitorovic, D., "Rapid bulk characterization of oil shale kerogen concentrates by alkaline permanganate degradation", Euroanalysis VII , Vienna, Austria, 1990.

M15

HEAVY METALS FRACTIONATION IN SOILS WITH DIFFERENT PEDOGENESIS

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The distribution and accumulation of heavy metals in soils depends upon numerous factors including soils properties (pH, soil organic matter, clay minerals, Eh-conditions), soil pedogenic processes, soil-plant relationships as well as amounts, forms and origins of the heavy metals. The sequential extraction procedures were applied to explain the heavy metal origin. Experimental fields are located in the most environmentally stressed areas in the Eastern (near Rudňany) and Central (near Banská Štiavnica) Slovakia. The studied soils were dystric cambisols and fluvisols affected by gleyic processes.

The used extraction scheme distinguishes the following fractions: soil solution and exchangeable , specifically adsorbed, organically bound, occluded by soil hydroxides, residual fraction. The concentration of metals obtained after sequential extraction procedures were determined by atomic spectrometry methods (ICP-AES, ETAAS, HG-AAS). Effects of individual extraction reagents on the reliability of the results were studied and the optimal experimental conditions of determination were selected. Furthermore the single extractions with EDTA and acetic acid were applied. The obtained results were compared by the analysis of CRM 483 (BCR, Brussels, extractable trace elements in sewage sludge amended soil).

The work is an attempt to examine factors affecting the overal distribution of heavy metals in soil environment. The results show as the distribution and accumulation of heavy metals are influenced by the origin and geochemical nature of heavy metals as well as by the soil pedogenic precesses. The importance of the accumulation of soil organic matter or iron hydroxides under different geochemical conditions are discussed more detaily.

M16

PRECONCENTRATION OF TRACES OF NON-IONIC SURFACTANTS AND POLY(ETHYLENE GLYCOLS) BY SOLID PHASE EXTRACTION

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Concentration levels of non-ionic surfactants (NS) and their major metabolites - poly(ethylene glycols) (PEG) in tap water are unknown because of lack of adequate analytical methods. The aim of this work is the preconcentration of NS and PEG by solid phase extraction to achieve a concentration level accessible to tensammetric methods. C18 and XAD-4 cartridges are used. The samples of tap water are passed through the cartridge or the cartridge is suspended for several days in a bottle containing the sample. The adsorbed substances are washed with chloroform, the solvent evaporated and the residue divided into NS and PEG fractions by successive extraction with ethyl acetate and chloroform. The newly developed adsorptive stripping indirect tensammetric technique (AdS-ITT) is used for the final determination of NS and PEG. This technique rather than the indirect tensammetric technique is intended for the determination of lower concentrations. Recovery of 5 µg of Triton X-100 was checked and found to be satisfactory. C18 and XAD-4 cartridges yield similar results.

Several tap water samples are analysed according to the developed schemes. An average concentration of 8 µg l^{-1} for NS and 6 µg l^{-1} for PEG was found for tap water in Poznan. These results were successfully confirmed by the AdS-ITT measurements with gas-stripping separation of NS from large volume tap water samples.

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M17

SEPARATION OF NON-IONIC SURFACTANTS INTO FRACTIONS BY SUCCESSIVE LIQUID-LIQUID EXTRACTION

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Non-ionic surfactants (NS) constitute the major group of anthropogenic pollutants of the aquatic environment and the largest supplier of chemical species. Approximately one thousand individual substances belonging to NS may be distinguished as well as a similarly large number of NS metabolites. Poly(ethylene glycols) (PEG) belong to the major and more recognised NS metabolites. The determination of separate substances in the mixture of NS and their metabolites is an unrealistic task due to the large number of individuals. Separation of a mixture of NS and their metabolites into several fractions is a much more realistic approach. The determination of the concentration of particular fractions provides considerably broader information concerning NS and their fate in the environment than the methods currently used which only determine NS having 5-30 oxyethylene subunits (EO). Ethoxylates having less than 5 or more than 30 EO, as well as NS nonethoxylate structure are left unmeasured. The aim of this work is to develop schemes for separation of NS from the water matrix and their subsequent division into fractions.

The developed scheme consists of four extraction steps: a fraction of n-hexane containing short-chained ethoxylates, non-ethoxylate NS and free fatty alcohol; a fraction of ethyl acetate containing ethoxylates having 10 - 30 EO and a dichloromethane fraction consisting of ethoxylates having over 30 EO and long-chained PEG's. Distinguishing ethoxylates having over 30 EO and long-chained PEG's is possible using the two-monitor indirect tensammetric technique. The developed scheme is successfully used for the separation into fractions of NS from raw and treated sewage of three sewage treatments plants and ten river water samples. A final determination is performed by one of the tensammetric techniques.

M18

XEROGELS MODIFIED BY METAL SALTS AS INDICATOR POWDERS FOR THE DETERMINATION OF ORGANIC AND INORGANIC SUBSTANCES

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The possibilities to use porous silica powders doped with metal ions for the preconcentration and the determination of various substances have been investigated. For the immobilization of metal salts sol-gel technique has been applied. It is based on the introduction of substance to be immobilized into a mixture of tetraethoxysilane, water and ethanol. After hydrolysis the gel produced should be dried. Dry gel (xerogel) obtained contains the substance being attached. A method to preparate xerogels doped with Co(II), Co(III), Cu(II), Fe(III) and Hg(II) has been developed. Ammonium hexafluorosilicate has been used as a catalyst for hydrolysis of tetraethoxysilane. For a wet gel to dry a microwave irradiation has been suggested.

The data of IR-spectroscopy investigation of xerogels involved show that hydrolysis has proceeded quantitatively. Metal ions seem to be retained in xerogels by interaction with silanol groups.

The interaction between xerogel doped with metal ions and different substances has been studied by means of solid phase spectrophotometry. Metals included in xerogels have the ability to produce complexes with various ligands. Immobilization does not change the complex-forming properties of metals.

Xerogels modified by metal salts have been used for the determination of amines and some inorganic substances in waste waters and biological samples.

M19

SORPTION OF Cu(II), Cd(II) AND Zn(II) ON 4(BENZYLCELLULOSE)-5-AZO-8-HYDROXYQUINOLINE

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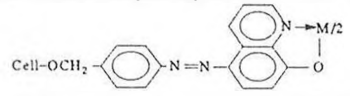
The 8-hydroxyquinoline groups present onto a polymeric matrix confer to the material a high selectivity-comparatively with various elements. Chelating sorbents containing such groups have been synthesized for utilization in the concentration and separation different elements [1,2].

The present paper discusses the mechanism of sorption of Cu(II), Cd(II) and Zn(II) on the chelating sorbent [3] obtained from PAB-cellulose through diazotation and coupling with 8-hydroxyquinoline in a weakly alkaline medium. In order to establish the sorption mechanism of the three elements on considered sorbent the following aspects have been studied: dependence of the distribution coefficients on pH, at 25°C, sorption isotherms at 25°C, calculation of the apparent free enthalpy, IR and electronic reflexion spectra of the sorbent both before and after sorption. The results of the study performed by batch method, along with the data provided by spectral analysis have evidenced that physical sorption of the three elements is accompanied by chemical sorption, adsorption being predominant for Cd(II) and chemosorption for Cu(II) and Zn(II), being much more pronounced for the first element. The chemical sorption involves formation of chelates without the participation of the azo group:



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M20

SOME CLASSING GENERALIZATIONS ON IONIC EQUILIBRIA IN ANALYTICAL CHEMISTRY

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Classing generalizations have been made on ionic equilibria within the analytical chemistry course for Universities. *Intramolecular factors effecting protolytes strength.* Dissociation enthalpy and entropy of proton bond with adjacent atom. Charge of molecular system. Electronegativity and radius of atom (ion) combining with proton. Inductive and mesomeric effects, hyperconjugation. Intramolecular hydrogen bond. Field effect. Molecular electrostatic potential. Steric factor. Solvation (that could be considered as neither pure intramolecular nor merely outside factor, since it is determined by the properties both of solute and solvent). *Types of complex compounds.* Ordinary (typical) complex compounds (CC). Chelates and intracomplex compounds. Polynuclear complexes. Iso- and heteropolycompounds. Binary salts. Ionic associates. Peroxide compounds. Polyhalogenides. Polyhalcogenides. Polyphosphides, polyarsenides. Intermetallides of Na_4Pb_9 type. Thiosalts. Supercomplex compounds. CC with metal - metal bonds (cluster compounds). π-Complexes. Coordination hydrides. CC compounds formed by the organometallic compounds coupling. "Guest - host complexes. Podands, coronands, cryptands, spherands, thorands. Cyclophanes. Calixarenes, calixspherands, double-cavity calixarenes. Cyclodextrines. Cavitands. Fullerenes. Inclusion compounds (IC). Clatrates. Zeolytes. "IC in solution". Clatrochelates. Catenanes, rotaxanes, knots. Charge-transfer complexes. Hydrogen-bound complexes. Weak complexes between non-polar molecules. *Mechanisms of precipitate aging.* Recrystallization of primary species. Thermal aging. Transformation of metastable crystalline modification into more stable form. Chemical aging: dehydration and hydration, polymerization (polycondensation). Reasons for chemical aging by Wasserman. Mechanisms of aging of individual hydroxides by Chalyi.

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M21

CONCENTRATION OF HYDRONIUM IONS IN THE SOLUTIONS OF BIPROTIC ACIDS COMPLETELY DISSOCIATED ON THE FIRST STEP

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For choosing the conditions of chemical processes and analytical determinations conducting in terms of substrate existence forms, rapid estimation of the $[H^+]$ concentration in the solutions of polyprotic protolytes is important. The aim of the present work is the analysis of the expression for $[H^+]$ in the solutions of biprotic acids H_2X (H_2SO_4, H_2SeO_4 *et al.*) completely dissociated on the first step, the dissociation being not complicated by polymerization and other competing reactions, with the substantiation of asymptotics of $[H^+]$ function under the conditions when the concentration constant (K_2) of H_2X acid dissociation on the second step and total molar concentration of the acid (C) are strongly diversed. K_2 value can be found from the thermodynamic constant taking into account the activity coefficients or using correlation equations linking K_2 and C. In suggestion that H_2X protolyte dissociates completely on the first step, and regarding the equilibrium of dissociation of HX^- ion, one could obtain the expression for $[H^+]$: $[H^+] = 0.5\{-K_2 + C + [(K_2 + C)^2 + 4K_2C]^{1/2}\}$. (1) Let us consider two limiting cases. 1. $K_2 >> C$. The formula (1) may be represented as follows: $[H^+] = 0.5K_2[-1 + C/K_2 + (1 + 6C/K_2 + C^2/K_2^2)^{1/2}]$. Neglecting the value of C_2/K_2^2, one obtains: $[H^+] = 0.5K_2[-1 + C/K_2 + (1 + 6C/K_2)^{1/2}]$. (2) Expanding $(1 + 6C/K_2)^{1/2}$ in McLawren series and remaining two initial members of the series $(1 + 6C/K_2)^{1/2} = 1 + 3C/K_2$, (3) as a result of a substitution of (3) into (2), one obtains $[H^+] = 2C$. 2. $K_2 << C$. The expression (1) may be modified as follows: $[H^+] = 0.5C[1 - K_2/C + (1 + 6K_2/C + K_2^2/C^2)^{1/2}]$. Neglect of the value K_2^2/C^2 gives $[H^+] = 0.5C[1 - K_2/C + (1 + 6K_2/C)^{1/2}]$. (4) Expanding in the series $(1 + 6K_2/C)^{1/2} = 1 + 3K_2/C$ (5) and a substitution of (5) into (4) lead to $[H^+] = C$.

M22

PRECONCENTRATION OF PENTACHLOROFENOL IN OXINE INMOBILIZED ON GLASS AND DETERMINATION IN WOOD

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Pentachlorophenol is widely used as a wood preservative. It is a polar priority pollutant than can be toxic to living microorganisms. Due to its low levels of occurrence it is necessary to preconcentrate the sample before analysis. Adsorbentes such as carbon, macroreticular polymeric resins, polyuretane foams, styrene-divinylbenzene copolymer containing quaternary ammonium groups and reagents immobilized on glass have been used for preconcentration of pentachlorophenol.

A method has been developed for determination of pentachlorophenol in wood based on preconcentration using a microcolumn (2 cm x 2.5 mm) filled with quinolin-8-ol (oxine) inmmobilized on controlled pore glass. Recoveries were studied on powdered wood spiked with pentachlorophenol in concentration between 1 and 3 μg/g. Pentachlorophenol was extracted using 0.5 M NaOH. Samples were filtered, pH adjusted at 1 with hydrochloric acid and finally were passed through the microcolumn. Retention was carried out at a flow rate of 1 ml/min and pure acetonitrile is used in a one step elution at the same flow rate. Determination was performed by using liquid chromatography with detection at 242 nm. Twenty microliters of the eluate was injected into the chromatographic system; the mobile phase used was 30 mM amonium acetate (pH 5.1):acetonitrile:methanol (40:25:35). Recoveries for wood were between 78-95% for 1-3 μg/g of pentachlorophenol.

M23

SOLID-PHASE EXTRACTION OF TRACE AMOUNTS OF SELENOMETHIONINE

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The biological effect of selenium id dependent not only on its concentration level but also on chemical form, with different toxicity being exhibited for organic and inorganic compounds. Organoselenium species, including Se-substituted amino acids, are produced by biological reduction of inorganic species.

The objective of this work was to determine the chromatographic behaviour of selenomethionine with a range of solid sorbents for its preconcentration and separation from inorganic selenium species. Selenomethionine was chosen as the organic form of this element, because it is a good model for naturally incorporated selenium in the food chain.

The best results were obtained with copper-treated Chelex 100 resin. Selenomethionine adsorbed on the resin was eluted with 8 ml of 1.5 mol l^{-1} of ammonia solution and determined by electrothermal atomic absorption spectrometry. The limit of detection when using 100 ml sample for preconcentration was 32 ng l^{-1} (as Se). The column chromatography with Cu-Chelex and anionic functionalized cellulose sorbent Cellex T was applied to separate organic and inorganic selenium species from the same sample.

M24

SPME AS AN ALTERNATIVE SAMPLING METHOD FOR REDUCED ORGANIC SULFUR COMPOUNDS IN AIR?

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Sulfur containing volatile organic compounds (SVOCs) are known for their extremely low olfactory threshold limits. Sulfides, thiols, disulfides and also H_2S, CS_2 and COS are held responsible for odour nuisance near pulp and paper industry, garbage dumps and sewage treatment plants and often are the reason for complaints. The analysis of reduced SVOCs is complicated by their great chemical affinity towards metal surfaces, their instability under the presence of oxidants and the low levels, which can already cause significant odour nuisance.

The reactivity of the organosulfur compounds has to be taken into account when developing analytical methods for their identification and quantitative analysis. All materials which come into contact with the sample have to be chosen carefully to avoid the formation of artifacts.

Presently sampling of reduced organosulfur compounds is done by adsorption onto solid sorbents, chemisorption onto metallic surfaces or cryogenic sampling. The sample is then transferred onto the GC-column by thermodesorption. We have demonstrated that artifacts are likely to occur when the thermodesorption unit exhibits a lack of inertness. Therefore a system was constructed, in which the sample is exposed only to a minimum surface area of silanised glass. The adsorption tubes are prepared to offer a maximum of inertness. Ozone scrubbers during sampling are obligatory and for the low molecular weight compounds drying techniques have to be used. These precautions make the described sampling and thermodesorption procedures time consuming and can still not always prevent the formation of artifacts.

SPME has the potential of being a simple and quick alternative sampling method. Advantages are the ease of use, the small surface areas the sample comes into contact with during adsorption and thermodesorption and the remarkably low detection limits for the Carboxen/PDMS fiber in combination with GC-AED (in the low ppt range for SVOCs). Nevertheless artifacts do occur and limit the usefulness of the method. The results of storage stability tests and the applicability to real samples are presented. Quantitation strategies are evaluated and the advantages and drawbacks of SPME-GC-AED for the analysis of organosulfur compounds are discussed.

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M25

SEPARATION AND RECOVERY OF URANIUM FROM DILUTED SOLUTIONS USING SOLVENT IMPREGNATED RESINS

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Solvent impregnated resins offer an attractive alternative to liquid-liquid extraction processes. In recent years, a great effort has been made to develop solvent impregnated resins by physical adsorption of extractants onto polymeric matrices as a possible alternative to solvent extraction for separation and recovery of metals.

In this work, the synergistic extractant di-(2-ethylhexyl)phosphoric acid-tributylphosphat has been physically immobilized in a polymeric matrix of SERDOLIT PAD I and their metal extraction behaviour with uranium has been studied. Uranium extraction properties of these impregnated resins have been checked in sulphuric solutions, both by batch and column experiments.

The experiments have been carried out at different concentrations of the two solvents in the extractant mixture, using initial aqueous solutions of different pH and variable uranium content.

The distribution coefficients were determined as a function of both pH and ionic medium and the data were analyzed graphically, using the slope analysis method.

Uranium containing solutions were prepared for the spectrophotometric determination by reducing uranium hexavalent ions to tetravalent ions which form with Arsenazo III reagent a series of complexes with characteristic colour suitable for such spectrofotometric measurements. The method allowed very low uranium contents of 1 ppm to be determined.

M26

THE EFFECT OF DRYING CONDITIONS ON THE IN-DEPTH DISTRIBUTION OF COMPOUNDS ON TLC AND HPTLC PLATES INVESTIGATED BY PHOTOACOUSTIC SPECTROSCOPY

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Photoacoustic spectroscopy (PAS) was applied to investigate the influence of drying process on the in-depth distribution of compounds inside the sorbent on TLC plates. The effects of drying conditions were investigated by drying TLC plates in a dryer, in a stream of warm air, in vacuum or in ambient air. All the measurements were obtained from two different compounds from Camag test dye mixture III. The results obtained by PAS studies from different TLC plates were compared to those obtained by reflectance mode slit-scanning densitometry. Significant differences in PA signals obtained from the same compound were observed under different drying conditions in the uppermost 31 μm thick layer. The largest differences were observed between the plates dried in the ambient air and those dried in a dryer or in the stream of warm air or in vacuum. Since the substances demonstrate the tendency to accumulate in the surface layers, results similar to those of PAS were also obtained by slit-scanning densitometry.

M27

DETERMINATION OF SOME IMPURITIES IN ALUMINUM NITRIDE BY ELECTROTHERMAL ATOMIC ABSORPTION SPECTROMETRY WITH SLURRY SAMPLING

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Slurry sampling combined with electrothermal atomic absorption spectrometry (ETAAS) is very convenient technique for the analysis of some inorganic samples, especially, difficult to dissolve refractory materials. Aluminum nitride is frequently used in semiconductor electronics, so purity of this material is very important from the viewpoint of its quality characteristics. The determination of Cu, Fe, Mn and Zn in a commercial sample of powdered aluminum nitride by ultrasonic slurry sampling Zeeman ETAAS was investigated in this study.

Palladium, platinum and magnesium salts were tested as chemical matrix modifiers. The effect of sample matrix was also studied. The limits of detection were 24, 60, 22 and 15 ng/g for Cu, Fe, Mn and Zn, respectively. The results of metal determinations by slurry sampling ETAAS are fully comparable with the results obtained by independent analytical methods.

The analytical technique presented in this paper is relatively rapid, eliminates the need for sample digestion and reduces greatly blank contamination.

M28

EVALUATION OF RELIABILITY OF DIFFUSIVE SAMPLING IN THE ENVIRONMENTAL MONITORING

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Diffusive sampling has been available as a replacement for active sampling for more than 20 years in occupational hygiene to determine the concentrations of toxic organic compounds in workplace air. Potentially diffusive sampling has many advantages including increased sampling reliability, convenience and lower unit sample cost.

On the other hand, its application in environmental monitoring is quite recent, though the advantages are obvious. In the literature the reliability of this technique, however, is subject to a great deal of controversy.

The growing interest in diffusive samplers has necessitated validation tests in the environment. In our study the reliability of diffusive sampling was studied and a very simple, inexpensive and novel method was developed for the determination of uptake rates of BTEX compounds on three different adsorbents (Tenax GR, Tenax TA, Carbopack).

From the results of our experiments we concluded that among the three adsorbents studied Carbopack proved to be the most efficient for the BTEX compounds, as uptake rates were the highest on this adsorbent. In contrast to the results found in the literature the uptake rates were quite different on Tenax GR and Tenax TA in the environment.

Upon choosing the sampling site and time it should be considered that a critical exposure dose must be exceeded - which is about 10 ppm•min for BTEX compounds - to obtain reliable results and to ensure that the simplified model of diffusive sampling holds.

It can be concluded that the main source of controversies in the literature is the fact that in environmental monitoring diffusive sampling can only be used reliably above a critical exposure dose.

Key words: diffusive sampling, uptake rate, reliability, BTEX compounds

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M29

KINETICS OF COFFEE INFUSION:

Use of ICP-AES in Kinetic Study of Mineral Ion Extraction from Medium Roasted Kenyan Arabica Coffee

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Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) was used to measure the rate of infusion of K^+, Mg^{2+}, Mn^{2+} and P as ($H_2PO_4^-$) into Milli-Q-Water from medium roasted Kenyan Arabica coffee beans at 80°C. Using Spiro's steady-state model, the first order rate constants were determined. Diffusion coefficient of the four mineral ions were calculated from the rate constants. These values have been compared with known diffusion coefficient of the same ions in water for the determination of hindrance factors. The low magnitude of the diffusion coefficient demonstrate that the diffusion of ions within the bean particle is a hindered process. Magnesium ion was found to be the most hindered of the ion investigated

M30

MICRODIALYSIS AND ULTRAFILTRATION AS ON-LINE SAMPLING TECHNIQUES

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Introduction
Blockage of fluid channels, long reponse times and/or fouling of the detection element in an (on-line) μTAS device are interface problems between the sample and the device. Sampling with microdialysis (MD) is one way of creating a better interface [1][2]. In MD, fluid is perfused through a tube, consisting of a semi-permeable membrane. However, MD has some drawbacks. The dilution factor of the analyte in the MD fluid (the so-called *recovery*) requires not only sensitive analysis methods, but also difficult calculations for absolute concentrations. Furthermore, this recovery may change during a measurement as a result of partial blockage of the membrane by elements in the sampling fluid. Alternatively, sampling can be performed with ultrafiltration (UF) (*Fig1*) [3][4]. UF is based on withdrawing fluid with a very low flow rate (<200 nl/min) through a semi-permeable membrane tube.

Aim of Research
Study intravenous UF sampling with slow flow rates for future intergrating in μTAS devices.

Results and Discussion
With the UF system, we were able to sample at least 8 hours without blockage of the system. We measured glucose in 50 nl samples (*Fig. 2*). The blood samples and UF samples matched well. The observed relative differences are explained by the absence of proteins in the UF sample, whereas the smouthening of the signal arised out of the detection system, as demonstrated in tests with and without the UF probe (not shown).
Our future work is aimed at integrating this UF sampling system with other miniaturized silicon components such as a conductivity sensor.

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O1

STRUCTURE-REDOX PROPERTIES CORRELATIONS VOLTAMMETRY OF PYRIDINE AND SOME PYRIDINE RING CONTAINING COMPOUNDS

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In the present paper some correlations are studied between the voltammetric behaviour (the values of the anodic peak potentials) and the overall energy of the π electrons (E_π) estimated by the Huckel molecular orbital method (HMO). By determining the atomic polarizabilities of the atoms in the molecules under study, the atoms of the maximum probability of the electron releasing (redox center) were settled.
The voltammetric runs were made in nonaqueous medium (methanol, acetonitrile) on Pt and carbon electrodes, with 10^{-1} M $HClO_4$, 10^{-1} M HCl, 10^{-1} M KCl as support electrolyte. The cyclization was performed within the -0.5 ↔ +1.8 V / S.C.E. potential range at 50 mVs^{-1} scanning rate.
The following compounds were taken in our studies: pyridine (I), quinoline (II) , acrydine (III), 2, 2' - dipyridyl (IV), 3 - aminopyridine (V), 8 - hydroxiquinoline (VI), 1, 10 - fenantrolyne (VII) and 2, 9 - dimethyl - 1, 10 fenantrolyne (VIII).
With aromatic heterocyclic compounds the following findings are mentioned:
- The heteroaromatic compounds containing only one pyridine ring (I,II,III) are increasingly stable and oxidized at increasingly positive potentials, when the number of the benzene rings condensed linearly increases.
- In the heteroaromatic compounds containing two pyridine rings (IV,VII) the second nitrogen atom requires more positive oxidation potentials. The energy of π electrons increases about two times (IV) and about 2.5 times (VII), respectively, compared to pyridine.
- The electronodonating substituents (-NH_2, -OH) decrease the nitrogen oxidation potential due to their +E_S effects, while the substituents showing +I_S effects (-CH_3) do not influence significantly the electrochemical behaviour of the compounds.

O2

ADSORPTIVE STRIPPING SQUARE-WAVE VOLTAMMETRIC BEHAVIOUR OF INSULIN

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Some proteins showed over the static mercury electrode a very strong adsorptive accumulation by fast voltammetric techniques [1]. In this work, a voltammmetric behaviour of the protein Insulin is presented.

The cyclic voltammograms obtained for 2.5 mg L^{-1} of Insulin in an unstirred 0.01 M phosphate buffer solution (pH 7.4) using two different scan rates of 50 and 100 mV s^{-1} gives rise to a cathodic peak at -0.70 V (peak A) and an anodic peak at -0.60 V (peak B). The cathodic and anodic currents gradually increase on repetitive scans. The peak currents of the adsorbed compound at saturation levels are several times higher than those of the solution species alone (determining from the intensity of the first scan)

In regards to the larger response obtained in the adsorptive stripping of Insuline by Square-Wave Voltammetry, it was felt that this technique might be successfully applied to the quantification of Insulin in 0.01 M buffer solution gave an adsorptive stripping voltammetric peak at -0.57 V using an accumulation potential of 0.0 V. Consequently, the parameters governing this voltammetric mode have been studied.

The stripping peak intensity increased very rapidly with increasing pulse amplitude, accumulation time, frequency, drop size, accumulation potential and scan increment.
As a consequence of these experiments it was found as optimun parameters, a pulse amplitude of 50 mV, an accumulation time of 30 s, a frequency of 75 Hz, a larger drop size, an 0.0 V of accumulation potential and a 4 mV of scan increment. These parameters provided analytical signals sensitive enough at a very reasonable scan rate of 300 mV s^{-1}.

Using the conditions cited above two calibration graphs were obtained for Insulin in the concentration ranges between 0.10-1.75 mg L^{-1} and between 1.75-2.75 mg L^{-1}.

The proposed method will be applied to the analysis of different pharmaceutical product that contains the Insulin as principal component.

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O3

ADSORPTIVE STRIPPING SQUARE-WAVE VOLTAMMETRIC BEHAVIOUR OF GESTODENE

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Gestodene is a synthetic steroid with an extremely potent progestational steroid. It is a new progestin appears to cause fewer adverse effects, such as acne and hirsuitism, and lower rate of weight gain, blood pressure changes, less androgenic effect and less lipid and carbohydrate metabolism changes that the older progestins.

The formulation of this steroid in tablets of low dosage, i.e. 50-100 mg. per tablet, presented a challenging analytical problem. A sensitive, accurate, and rapid procedure are desirable for content uniformity testing of the dosage form. The behavior of Gestodene (GTD) was studied by square-wave techniques, leading to two methods for its determination in aqueous samples and pharmaceutical formulations. The application of the square-wave mode shows the determination of GTD between $2x10^{-7}$ and $3x10^{-6}$ M at -1.30 V. GTD gave an adsorptive stripping voltammetric peak at the hanging mercury drop electrode at -1.30 V using an accumulation potential of -0.80 V. The effect of experimental parameters that affected this determination are discussed. By the stripping technique, GTD proved to be more sensitive, yielding signals seven times larger than those obtained by applying a square-wave scan without the previous accumulation. The calibration graph to determine GTD was linear in the range $3x10^{-8}$ M and $1x10^{-6}$ M by stripping mode. The relative standard deviations obtained for concentration levels of GTD as low as 7.5 x 10^{-7} M with square-wave was 2.3% (n=12) and for 1.5 x 10^{-7} M with stripping square-wave was 2.3% (n=12) in the same day.

The proposed method was applied to the determination of Gestodene in four different Spanish commercial low-dose oral contraceptives with good recoveries respect to the labelled values.

O4

VOLTAMMETRIC DETERMINATION OF PENICILLIN V IN PHARMACEUTICAL DOSAGE FORMS

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Electrochemical methods related to penicillin V were based on the reactions of products formed by the acidic or alkaline hydrolysis of the substance.

In the present study the voltammetric behaviour of alkaline hydrolysis degradation products of penicillin V was studied using poly(N-vinyl imidazole) modified carbon paste electrode in Britton-Robinson buffer solution at pH 11,5.The limiting current was found to be linearly dependent on penicillin V concentration in the range of $8x10^{-6}$-$1x10^{-4}$ M with a slope of $1.89x10^{5}$ μA/M,intercept of 10.96 μA , correlation coefficient of 0.999.

The proposed method was applied to the penicillin V tablets and syrups.Furthermore the results obtained for these preparations were compared to those obtained using official HPLC method (USP XXII). Statistical evaluation of the results revealed that the difference between voltammetric and official methods was not important.

In conclusion the voltammetric method presented in this study can be used for accurate.simple and rapid determination of penicillin V in pharmaceutical dosage forms.

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O5

STRIPPING VOLTAMMETRIC DETERMINATION OF HEAVY AND NOBLE METALS USING ELECTRODES MODIFIED BY CROWN-CONTAINING N-(THIO)PHOSPHORYL(THIO)UREAS

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Sensors based on chemically modified electrodes (CME) are widely used in various analytical methods. For metal determination electrodes are usually modified by organic compounds possessing ligand properties. The combination of macrocyclic compounds with (thio)phosphoryl(thio)ureas leads to so called lariat ethers with new ligand properties.

The complexation of crown-containing N-(thio)phosphoryl(thio)ureas with heavy (Co, Ni, Cu, Pb) and noble (Au, Pd) metals has been studied. Based on the data obtained by UV spectroscopy and potentiometry, it was concluded that metal complexation with these lariat ethers resulted in chelate formation. It has been established that metal complexes with these lariat ethers are more stable than the complexes with their component fragments. This fact permits to increase considerably sensitivity of metals determination with the help of CME modified by these lariat ethers.

Stripping voltammetric determination at CME involves stage of adsorption concentration of metal ions on electrode surface and stage of quantitative determination of formed complex by one of voltammetric variant.
Determination of Ni (II) and Co (II) involves metal ions concentration from analyte followed by registration of anodic voltammogram. In the case of other metals determination voltammograms were registrated after metal ions concentration at CME following by electrolysis at negative potentials.

Using the investigated lariat ethers as modifiers permits to lower the limit of detection for metal ions down to n.10^{-9} mol/l.

O6

ON THE ABILITY OF RUTHENIUM TO STABILISE INDIUM(III) HEXACYANOFERRATE(II/III) FILM ELECTRODES

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Stability of inorganic films is highly desirable in order to expand their use in numerous technologically relevant fields [1,2]. Indium(III)–hexacyanoferrate(II/III) (InHCF) is a Prussian Blue analogue that is very attractive for its application in electrochromic [2], electrocatalysis [3,4], and photoelectrochemical energy conversion devices [5], and as stabilising coating for photoelectrodes [6]. When the InHCF film is repetitively redox cycled between 0.0 and +0.9 V, the electrochemical activity deteriorates considerably. We have discovered a novel procedure that yield extremely stable inorganic films resulting from incorporation of ruthenium species by potential cycling the film electrode in millimolar solutions of ruthenium(III) chloride [7,8].

In this communication, we shall discuss the modifications occurred to InHCF films upon conditioning in the Ru(III) solution, using an approach similar to that employed for the ruthenium purple (RP) film electrode [7]. Simultaneous cyclic voltammetry and piezoelectric microgravimetry with an electrochemical quartz crystal microbalance (EQCM) have been used to follow the modification through the incorporation of ruthenium species. The resulting ruthenium–modified InHCF film has been characterised by cyclic voltammetry and X–ray photoelectron spectroscopy (XPS), while the stabilisation process has been investigated by EQCM. The enhanced stability observed in the Ru-modified InHCF system over the simple InHCF film seems to be related with the formation of robust oxo-bridged dinuclear species, that is Fe-O-Ru. The resulting inorganic film exhibits a remarkable electrochemical stability; the redox process was sustained without changes for at least 10^4 cycles in the potential window from 0.0 V to +0.9 V vs. Ag|AgCl. Thin films prepared by this procedure were analysed by XPS, which also supports the conclusions drawn from microgravimetric results obtained with EQCM measurements. Interestingly, Ru-modified InHCF film exhibits a high catalytic activity for the oxidation of several inorganic and organic compounds of analytical interest, such as As(III), $S_2O_3^{2-}$, cysteine, etc. The robust chemical nature of this highly stabilised film makes it good candidate in several technologically attractive areas for applications both in electrochemistry and in solid state devices.

O7

POTENTIOMETER DETERMINATION OF CARBOCROMENE USING A I.S.E. OF SCN^-

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Carbocromene, b-3-(g-diethilaminoethil)-4-methil-7-carbethoxi-methoxi-cumarine, is one of the new products having an arterial activity. For quantitatively determine of the Carbocromene is mentioned a spectrometrical and a volumetrical method [1].

We noticed that $NH_4[Cr(SCN)_4(NH_3)_2]$ and the analogous combinations of the type $NH_4[Cr(SCN)_4(amine)_2]$ where amine = anyline, benzylamine etc. precipitates the Carbocromene chlorhidrate in the form of complex salts as follows: CarbocromeneH$[Cr(SCN)_4(amine)_2]$. These red-violet precipitates hardly soluble in water are soluble in acetone, D.M.F., D.M.S.O.

We have already explained in a previous paper the way to termogravimetrically, spectrometrically and oxidimetrically determine the Carbocromene in this form [2].

In the present paper we show the way of determining potentiometrically the Carbocromene using a I.S.E. of SCN^-. For this we treat the solution of Carbocromene chlorhidrate with a hydroalcoholic solution of $NH_4[Cr(SCN)_4(amine)_2]$ in light excess when it precipitates the CarbocromeneH$[Cr(SCN)_4(amine)_2]$. Then we filter it after 10 minutes, wash it with distilled water until the filter is colourless. The precipitate then is taken quantitatively in a Berzelius glass. Then we add over it NaOH 0,5 % in excess, we boilit for about 10 minutes when the ions SCN^- are being freed. After wards the SCN^- is titrated with $AgNO_3$ 0,1 N solution with F = 1,000. We compute the titrating volume from the potential leap at the equivalence point out of which we calculate the quantity of Carbocromene.

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O8

POTENTIOMETRIC BEHAVIOR AND SURFACE ANALYSIS OF AN IODIDE ION-SELECTIVE ELECTRODE PREPARED BY CHEMICAL TREATMENT OF A COPPER WIRE

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Our paper describes a simple preparation of a iodide ion selective electrode by means of chemical pretreatment of copper wire with mercuric(II) chloride solution, alkaline sulphide and iodide solution. The electrode is sensitive to copper ions as well. It is inexpensive and simple to prepare. The electrode is further characterised by linear responses within the concentration range of iodide between 10^{-2} and $5x10^{-5}$ mol/L at the slope of 63.0 mV/pJ and between 10^{-2} and $1x10^{-5}$ mol/L in the concentration range of copper at the slope of +30.2 mV/pCu, and also by response times between 10 seconds and 2 minutes. In order to test the influence of foreign ions the mixed solutions method [1] was used with a constant concentration of iodide ($1x10^{-4}$ mol/L). The concentrations of interfering ions Cl^-, Br^-, SCN^-, SO_4^{2-} and $S_2O_3^{2-}$ were changed in the range between 10^{-1} and 10^{-6} mol/L. Only $S_2O_3^{2-}$ and SCN^- interfered at higher concentrations.

The surface analysis was made by a scanning electron microscope with an energy-dispersion X-ray microanalyser and with an Auger electron spectrometer.

The results confirm the presence of cooper(I) iodide in the surface layer, and also suggest the presence of the mixture of cooper(I) and cooper(II) sulphide, which is not in contradiction with the electrochemical properties of prepared cooper wire.

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O9

CHARACTERISTICS OF THE CONTINUOUSLY RENEWABLE SILVER ELECTRODE USED IN ANODIC-STRIPPING VOLTAMMETRY

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The usefulness of the silver rotating-disc electrode (Ag-RDE) in the determination of lead by anodic-stripping voltammetry without removal of oxygen has been demonstrated [1,2]. A detection limit of $5 \cdot 10^{-11}$ M (60-second electrodeposition and 10^4 rpm) was achieved with the use of a method of differences [3]. In this method the analytical signal is the difference between the voltammogram of the sample and that obtained with no electrolysis, recorded sequentially. Measurements at the sub-ppb concentration level are performed in a fast sequence enabled by the "project" option of the GPES-AutoLab software (EcoChemie, Netherlands).

A two-electrode cell consisting of a Ag-RDE working electrode and a large-surface silver wire acting as a combined counter/quasi-reference electrode is used. Hundreds of runs can be carried out with excellent reproducibility and without any pretreatment of the electrode. This is due to the continuous renewal of the electrode surface: during the electrodeposition step the large-surface silver counter/quasi-reference electrode generates silver ions that codeposit with lead at the Ag-RDE.

In the concentration range of 10^{-10} - 10^{-7} M, lead is deposited at an underpotential. It forms a uniformly distributed submonolayer that occupies 0.001 % - 1 % of the real electrode surface. Linearity in calibration plots is achieved up to 1 % electrode coverage; in terms of the experimental parameters rate of rotation and time of deposition, the condition for linearity is: $C_{Pb^{2+}} \cdot N^{1/2} \cdot t_d \leq 2.2 \cdot 10^5$ (nM $rpm^{1/2}$ s).

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O10

ELECTROCHEMICAL CHARACTERISTICS OF SOME 3D CEPHALOSPORIN ANTIBIOTICS

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It could be concluded from the data existing in the literature that most cephalosporins are electroactive giving a faradaic response to the working electrode (mercury or solid) [1,2].

This paper presents a study of electrochemical behavior of some third generation 3D cephalosporin antibiotics on solid (platine, gold and glassy carbon) mili- and microelectrodes, in aqueous media. The study was performed in Britton - Robinson (BR) pH = 2 - 12, and Clark - Lubs (CL) pH = 1 - 4 buffers, using different voltammetric techniques: cyclic voltammetry (CV), linear sweep voltammetry (LSV), and differential pulse voltammetry (DPV). The voltammetric studies proved that all cephalosporins investigated (ceftriaxone, cefotaxime and a new synthesized 3D compound) present adsorption phenomena at solid electrodes. The optimum pH range was 3.0 ÷ 5.5, and all analites have at least two well-defined reduction peaks (ceftriaxone presents two peaks in the range -0.65 V ÷ -0,82 V on Pt milielectrode vs. Ag/AgCl). Under special condition an anodic peak could be observed on solid electrodes (glassy C) for all three compounds. A reliable technique for detection of 3D cephalosporins seems to be DPV. A detection limit of 5×10^{-9} mol L^{-1} was attained in our experiments. All voltammetric techniques have a relative standard deviation between 1.4 – 2 %.

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O11

IODINE/IODIDE COUPLE AS INDICATING REDOX SYSTEM FOR BIAMPEROMETRIC DETERMINATION OF ON-LINE PHOTODEGRADATED NITROCOMPOUNDS

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The integration under the FIA approach of photodegradation processes and electrochemical detection offers the possibility of developing selective and "clean" analytical methods using unexpensive manyfolds. The selectivity comes from the working potential (a few mV by biamperometric detection) and the photochemical mechanism which provides more easy species to be detected at the electrode surface. The "cleanness" of such a method results from the own nature of light as reagent.

The proposed continuous flow-assembly comprises a photoreactor of PTFE coil wrapped tightly around a 8 w low pressure mercury lamp, a potentiostat controled by software running under the Windows operating system, and a home made flow-through cell constructed from two methacrylate blocks in which two platinum electrodes (3 cm long and 0.5 mm in diameter) aligned facing each other.

The flow-injection detection of the photogenerated nitrite is based on the oxidation of iodide by nitrite. The nitrite photogenerated by photodegradation of the nitrocompounds is detected biamperometrically by the iodine/iodide couple as indicating redox system. The triiodide formed resulting of the oxidation of iodide by nitrite yields a proportional analytical response against the injected nitrocompounds when it flow through the biamperometric cell with two platinum wire electrodes polarized at 100 mV. The method was applied to the determination of nitrocompounds in pharmaceuticals.

O12

FLOW-THROUGH VOLTAMMETRY OF COPPER IN NATURAL WATER USING GLASSY CARBON ELECTRODE

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Copper is widely distributed in nature and is one of the foremost contaminants of the environment especially in water, where it's content should not exceed mg/l [1].These is not surprising because copper together with its alloys are commonly used in various industries for making of utensils.

Anodic stripping voltammetry (ASV) 's potential for trace copper analysis have been shown [2]. The ASV in flow-through configuration is an ideal method for copper because it reduced contamination risks. Cu gives a sensitive stripping peak at 0.2 ± 0.05% V which was used to determine trace amounts of copper in natural water samples. The results of which as well as those of a certified reference material (no. 251) containing 0.090 ± 0.004% Cu will be discussed.

[1] Drinking water methods of analysis collection 12d Standortov, moscow (1984)
[2] JE. Tahn, AJ. Moronta and RA. Romero, Anal. Chim. Acta, 1990

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O13

NATURAL MONOCRYSTALLINE PYRITE AS ELECTRODE MATERIAL FOR POTENTIOMETRIC TITRATION OF ACIDS IN BUTYROLACETONE AND PROPYLENE CARBONATE

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In previous work the possibility of applying natural monocrystalline pyrite as sensor for potentiometric titration of acids in water was investigated [1]. This electrode was applied as indicator electrode for potentiometric titration of weak organic acids in γ-butyrolactone and propylene carbonate.

The pyrite electrode was prepared as explained following. A narrow glass tube was placed on a previously finely shaped piece of moncrystalline mineral pyrite, and mercury was poured into it. This was placed into a larger glass tube (Ø = 1 cm). Then, one end of copper wire for contact was immersed into mercury and larger glass tube was cemented with a mass for cold sealing based on methyl methacrylate. The contact with crystalline pyrite can be made by means of a silver paste. The area of the mineral in contact with the solution was 0.25 cm^2.

A modified calomel electrode was used as the reference electrode.

The behavior of the pyrite electrode as an indicator electrode was checked by titration of a series of organic acids of different strengths and various structure (benzoic acid, 1-nitroso-2-naphthol, antranilic acid, salicylic acid).

As titrating agent in the determination of acids, potassium hydroxide in methanol was used.

The potential in the course of the titration and at the equivalence point (TEP) was found to be rapidly established.

Our investigations have shown that the potential jumps at the titration end point obtained by using the pyrite electrode amounted to 120-220 mV/0,3 ml in γ-butyrolacetone and 120-270 mV/0,3 ml in propylene carbonate and were even higher than the potential jumps obtained by the application of the glass electrode.

[1] M. Antonijević, B. Vukanović, R. Mihajlović, *Talanta* **1992**, *39*, 809.

O14

pH-RESPONSE OF HYDROGEN-PALLADIUM ELECTRODE IN AQUEOUS AND NONAQUEOUS SOLUTIONS

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In previous papers [1][2] it is shown that hydrogen-palladium electrodes (palladium wire previously saturated with hydrogen obtained by the electrolysis of dilute sulphuric acid) were successfully applied as indicator electrodes in the titrations of acids and bases in water and nonaqueous solvents. The principal advantages of this electrode over a glass electrode lie in the following: this electrode can also be used in basic media, it has a small resistance and gives very stable potentials, and can be used in the titrations of small volumes.

The aim of the present work was to study the response on hydrogen-palladium electrodes in aqueous and some nonaqueous solutions.

In order to investigate pH-response in aqueous media, the potential against SCE in buffers, in the pH range 2-12, was measured. The slope of the E *vs.* pH line was 30 mV/pH unit. We also used procedure [3] to make comparative measurements with a glass electrode and a hydrogen-palladium electrode in so-called E°-titration (trishydroxymethylaminomethane, in sodium perchlorate media, is titrated by electrolytically generated H^+ ions [4]). The slope of the E *vs.* pH line was 29 mV/pH unit.

The response of hydrogen-palladium electrode in some dipolar aprotic solvents (acetone, methyl ethyl ketone, methylpyrrolidone) was investigated from the potential measurements in perchloric acid-sodium perchlorate solutions. The results indicate that the slopes of the potential response were sub-Nernstian in all the solvents studied.

The stability of the electrode potential with long time was investigated, too.

[1] R.P. Mihajlović, Lj.V. Mihajlović, V.J. Vajgand, Lj.N. Jakšić, *Talanta* **1989**, *36*, 1135.
[2] R.P. Mihajlović, Lj.N. Jakšić, R.M. Džudović, *J. Serb. Chem. Soc.* **1996**, *61*, 689.
[3] S. Glab, G. Edwall, A. Jongren, F. Ingman, *Talanta* **1981**, *28*, 301.
[4] R.P. Mihajlović, V.J. Vajgand, Lj.N. Jakšić, *Talanta* **1991**, *38*, 333.

O15

COULOIMETRIC-POTENTIOMETRIC TITRATIONS OF BASES IN ACETIC ANHYDRIDE BY APPLICATION OF QUINHYDRONE ELECTRODE

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In our previous paper [1] an application of quinhydrone electrode in coulometric-potentiometric titrations of bases in propylene carbonate is described.

This paper is aimed at investigating the application of quinhydrone electrode as indicator and generator one in the titrations of bases in acetic anhydride. The investigated bases (sodium acetate, potassium hydrogenphthalate, pyridine, triethylamine, quinoline, N,N-diphenylguanidine) were titrated coulometrically with H^+ ions obtained by the oxidation of the hydroquinone on the platinum anode. The quinhydrone added to the solution to be analyzed served both as the source of hydrogen ions, and together with the immersed platinum electrode as a quinhydrone electrode. By using hydroquinone for the coulometric generation of H^+ ions in acetic anhydride we have avoided preparation of standard solution, and by using quinhydrone electrode as indicator one we have avoided activation of a platinum electrode. A modified SCE was used as the reference electrode. The supporting electrolyte was 0,1 M solution of sodium perchlorate in acetic anhydride.

The relative error of the determination of bases was less than 1% for the concentration from 0,001 to 0,01 mol/l.

[1] Lj.N. Jakšić, R.M. Džudović, R.P. Mihajlović, Euroanalysis IX, Bologna, Sept. 7-11, 1996.

O16

SIMULTANEOUS DETECTION OF DOPAMINE AND URIC ACID IN AN EXCESS OF ASCORBIC ACID USING A NOVEL POLYMER MODIFIED GC ELECTRODE

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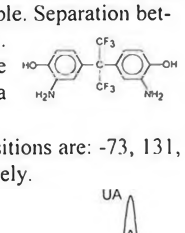
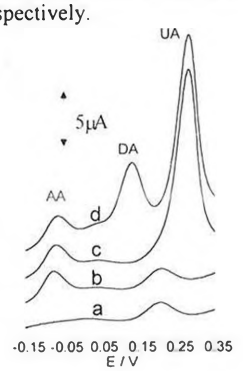
Electrode modification by electropolymerized film of poly-2,2'-Bis(3-amino-4-hydroxyphenyl)hexafluoropropane (see monomer structure shown) dramatically changes electrode properties towards biologically important analytes such as ascorbic acid (AA), dopamine (DA) and uric acid (UA). The modified electrode in extremely sensitive towards DA and cyclic voltammogram reveals that the reaction is highly reversible. Separation between anodic and cathodic peak is below 30mV. Excellent resolution of voltammetric signals of the tree analyte studied is achieved in DPV mode. Fig. 1. shows a series of DPVs for (a) background electrolyte, (b) 1mM AA, (c) b + 50μM UA, and (d) c + 0.5μM DA. Peak positions are: -73, 131, and 280 mV vs. Ag/AgCl for AA, DA and UA, respectively.



Relative sensitivity DA/AA is about 4000:1 and UA/AA about 30:1. Such sensitivity profiles in connection with high peak separations suggest potential usefulness of the modified electrode for the detection of sub-mikromolar levels of DA in real biological samples in which this compound co-exists with large excesses of AA and UA. On the other hand, however, the electrode sensitivity towards UA is high enough to allow its quantification. Analytical application for real biological sample was demonstrated on the determination UA in diluted human urea.



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O17

POLYEUGENOL MODIFIED Pt ELECTRODE AS VOLTAMMETRIC SENSOR FOR SELECTIVE DETECTION OF DOPAMINE IN THE PRESENCE OF ASCORBIC ACID

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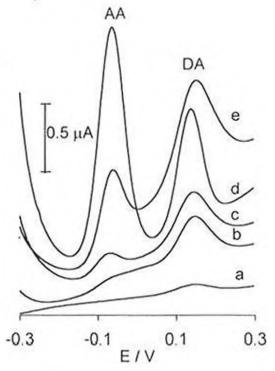
Platinum electrode was modified with electropolymerized film of 4-allyl-2-methoxyphenol (eugenol) by its oxidative polymerization from an alkaline solution by cyclic voltammetry. The modified electrode was than used to determine dopamine (DA) in an excess of ascorbic acid (AA) by differential pulse voltammetry (DPV). The peak positions as well as relative sensitivity DA/AA were affected by potential window applied for polymerization Fig. 1 shows a series of DPVs of a binary mixture containing 10mM AA and 0.2mM DA at electrodes prepared by monomer polymerization between 0 and (a) 0.7, (b) 1.2, (c) 1.4, (d) 1.65, and (e) 2.2 V, respectively. For the polymerization between 0 and 2.2 V the peak potentials recorded in phosphate buffer solution (pH = 7.4) were -61 and +152 mV vs. Ag/AgCl for AA and DA, respectively. After 5 min equilibrating relative sensitivity DA/AA was 164 and the current sensitivity for DA was 7.9 nA μM^{-1}. The detection limit for S/N = 3 is 0.1 μM. The high selectivity and sensitivity for dopamine was found to be mainly due to charge discrimination and analyte accumulation as was confirmed by observed dependence on solution pH. Chronocoulometric data reveal that DA is accumulated on the electrode as monolayer. The electrode is stabile, reversible and free of fouling problems.



O18

TEST TOOLS BASED ON NON-COVALENTLY IMMOBILIZED REDOX INDICATORS

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The non-covalently immobilized redox indicators are perspective reagents for determination of organic and inorganic analytes (reducing agents and oxidants). Retention of N,N-diethyl-p-phenylenediamine(DPPDA), Bindschedler's green (BG_, variamine blue, indophenol blue, 2,6-dichloroindophenol (DCIP), and 2,6-dibromoindoguaikol on reversed-phase silica gels (SG-Ph, SG-CN) and ion-exchangers (SG, SG-SO_3, SG-TA, Dowex 1x4,Dowex 50w4) has been investigated. Capacities depend on conditions and the nature of sorbents.

Spectrophotometric characteristics, dissociation constants and redox potentials of immobilized reagents have been studied. The considerable influence of the immobilization of reagents on the transient change in redox potentials and dissociation constants has been obtained. Reactions of immobilized reagents with various oxidisers and reducing agents have been investigated.

Length-of-stain indicator tubes (IT) and indicator powders for solid phase spectrophotometry determination (SPS) of iron(II) and chlorine in water have been elaborated.

Analyte	Indicator powder	Detection	Analytical range, mg/L	RSD
Fe(II)	DCIP/SG-CN	IT	0.1 - 3.0	0.08
		SPS	0.02- 0.5	0.04
Chlorine	DPPDA/SG	IT	0.05 - 3.0	0.05
	BG/SG-TA	SPS	0.04 - 0.8	0.08

O19

MOLECULAR DESIGN OF THE DIPHENYLAMINE AND PHENOTHIAZINE SERIES ANALYTICAL REDOX REAGENTS

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Electronic effects in the XCH_2COOH, CH_3X, n-$C_5H_{11}X$, C_6H_5X, 4-$H_2NC_6H_4X$, 4-$O_2NC_6H_4X$ molecules, as well as in 2,6-disubstituted pyridines and N-methylpyridinium cations, have been studied using the SCF MO LCAO CNDO/2, INDO, MINDO, MINDO/3, MNDO, AM1, PM3 methods. The dependence of electronegativity (determined by various experimental and theoretical methods and expressed against different scales), inductive parameter ι values, mesomeric dipole moments of substituents X upon the electronic structure indices has been stated. The possibility of a facilitated estimation of electronegativity, inductive and mesomeric parameters of atomic groups (including N-containing ones in aromatic amines) using 83 correlations has been shown. Involving the results of PM3 calculations the correlations of diarylamines redox potentials (E) with the first ionization potentials, of the pK_a values characterizing both the amines nitrogen protonation and the carboxy substituted reagents dissociation via COOH group with the proton affinities of the corresponding diphenylamines and COO^--containing anions, of the experimental values of the molecules dipole moments (μ) with the theoretical ones have been found. *A priori* E, pK_a and μ evaluation is of interest for molecular design of diphenylamine derivatives with given protolytic, redox, polar, analytical properties. The correlations have been found of the phenothiazines oxidation potentials with the first ionization potentials calculated using the MNDO, AM1, PM3 methods, which is important for constructing the phenothiazine series compounds with desirable redox characteristics.

O20

OXIDATION MECHANISMS OF SOME DIPHENYLAMINE DERIVATIVES - ANALYTICAL REDOX REAGENTS

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Oxidation kinetics of 5-sulphomethylamido-2-methoxy- and 5-sulphodiethylamido-2-methoxy-N-phenylanthranilic acids by potassium hexacyanoferrate (III) in NaOH media, of sodium diphenylamine(DPA)--4-sulphonate and N-methyl-DPA-4-sulphonate by ammonium persulphate in neutral aqueous and sulphuric acid solutions have been studied by spectrophotometric technique. The reaction has been stated to be first-order with respect to amine, oxidant and - in alkaline and acidic media - also to ^-OH and H_3O^+ ions, respectively. Rate constants and activation energies have been determined, their values are explained in terms of the influence of molecular electrostatic potential on reactivity. Using EPR method, tetraarylhydrazinium cation radical was found in the reaction mixture of sodium DPA-4-sulphonate oxidation (the EPR spectrum consists of a quintet with the line intensity ratio1:2:3:2:1). Oxidation mechanisms of diarylamines in alkaline and aqueous media are proposed. The processes have homolytic character. The elementary acts of the reactions include interaction of substrate molecules or anions with reacting particles of the oxidants, and the radical intermediates formed undergo dimerization, finally yielding a product of diphenoquinonediimine structure. The results obtained confirm the existence of essentially common features of the oxidation reaction of the DPA series with different substituents in aromatic rings and at nitrogen atom, proceeding in media varying in acidity, with diverse oxidants.

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O21

HOMOLYTIC COUPLING OF ORGANIC SUBSTANCES INCLUDING DIARYL AMINO COMPOUNDS - REDOX REAGENTS IN ANALYSIS: A QUANTUM CHEMICAL EXPLANATION FOR THE REGIOSELECTIVITY

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Homolytic dimerization processes are widely occurring radical reactions which are convenient as model ones for investigations of various compounds reactivity. By means of the INDO-UHF, MNDO-UHF, AM1-UHF, PM3-UHF methods we have calculated the spin density distribution on atoms of the radical intermediates of homolytic (oxidative and reductive) coupling reactions of 52 organic substances and their derivatives. The compounds under study were: diethylmalonate, acrylonitrile, diethyldithiocarbamate-anion, thiourea, N-phenylthiourea, toluene, *ortho*-, *meta*- and *para*-xylenes, styrene, naphthalene, anthracene, phenanthrene, aniline, N-methylaniline, N,N-dimethylaniline, diphenylamine, N-methyldiphenylamine, triphenylamine, phenol, phenolate-anion, thiophenol, thiophenolate-anion, nitrosobenzene, nitrobenzene, benzaldehyde, acetophenone, benzonitrile, benzoic acid, benzoate-anion, thiobenzoic acid in prototropic tautomeric forms and thiobenzoate-anion, pyridine, its N-oxide, quinoline, 8-hydroxyquinoline, 8-mercaptoquinoline and its zwitterion, acridine, N-methylpyridinium, pyrilium, thiopyrilium, pyrrole, carbazole, furan, thiophene, acridane, acridone, thioacridone, 5,10-dihydrophenazine, its N-oxide, phenoxazine, phenothiazine. General trends in the uncoupled electron density distribution have been formulated and the regioselectivities of the above mentioned processes substantiated. It has been shown that the spin density on atoms of radical intermediates obtained from the gas-phase quantum chemical consideration represents an effective reactivity index to predict homolytic coupling directions in solutions, which is of importance for analytical chemistry.

O22

ELECTROCHEMICAL IDENTIFICATION OF LEAD IN CERAMIC BODIES OF EARTHENWARE OF 17^{TH}-18^{TH} CENTURY

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Analysis of solid samples is of considerable interest in the field of consevation and restoration of works of art in which selective and sensitive methods for analyzing relatively small amounts of analyte are required. Chemically modified electrodes have evoked considerable interest in the past decade for analyzing scarcely soluble compounds. In particular, modified carbon paste electrodes (MCPE) have become widely used due to the simplicity and accessibility of the method of fabrication and the convenience of practical use.

A voltametric method has been developed to detect lead in a series of ceramic fragments produced in workshops in Manises in the 17^{th}-18^{th} centuries. The fragments were from wheel.thrown bowls and plates, a significant part of which were decorated with a cobalt blue pattern over a white glaze. The presence of lead in the ceramic body is due to diffusion of the glaze into the ceramic body during the melting-cooling process.

To determine the presence of lead, cyclic voltammograms at 100 mV/s of MCPE immersed into an acetic acid/sodium acetate buffer were recorded. MCPE were made throughly mixing graphite powder (15 mg), 1 mg of the powdered solid samples and paraffin oil (15 mg). Under our experimental conditions, a cathodic peak at -920 mV vs SCE appears in the initial cathodic scan corresponding to the Pb^{2+} to metallic Pb reduction. This is followed, in the subsequent anodic scan, by a stripping oxidation peak at -550 mV which is usable for semiquantitative estimates of the amount of lead in the samples.

The proposed method yields to a rapid and unambiguous determination of the weathering process of the glaze surface.

O23

STUDY OF STOICHIOMETRY AND STABILITY OF COMPLEXES FORMED BETWEEN 18-CROWN-6(18C6) LIGAND AND Pb^{2+}, Tl^{+}, and Cd^{2+} CATIONS IN DMSO-NM AND DMF-NM BINARY SYSTEMS USING SQUARE WAVE POLAROGRAPHY (SWP)

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The complexation reaction between Pb^{2+}, Tl^{+} and Cd^{2+} ions with macrocyclic ligand 18C6 was studied in dimethylsulfoxide (DMSO) -nitromethane (NM) and dimethylformamide (DMF) -nitromethane binary systems at 22°C by square wave polarography technique.The stoichiometry and stability of the complexes were determined by monitoring the shift in half-wave or peak potential of the polarographic waves of metal ions against the ligand concentration. The complexes formed between 18C6 with these metal cations in most cases were 1:1. The obtained results show that there is an inverse relationship between the formation constant of complexes and the donor number of solvents based on *Gutmann* donocity scale, and the stability constants show a high sensitivity to composition of the mixed solvent systems. A linear behavior observed for variation of log K_f of complexes *vs.* the composition of the mixed solvent systems. In all of the investigated systems, the Pb^{2+} cation forms a more stable complex than other two cations and the order of selectivity of this ligand for cations is: $Pb^{2+} > Tl^{+}, Cd^{2+}$.

O24

VOLTAMMETRIC DETERMINATION OF S-CONTAINING COMPOUNDS USING CHEMICAL SENSORS BASED ON METALLOPHTHALOCYANINES

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At present, voltammetric methods of analysis have attracted considerable interest owing to decision of environment monitoring problems. The numerous development are aimed on the design of various sensors based on chemically modified electrodes (CME) with catalytic properties.

Electrocatalytical activity of metallophthalocyanines immobilized on electrode compositions towards thiol oxidation was established. Among the 3d-transition metals catalytic effect is received only in the presence of Fe (II) or Co (II) complexes. At electrodes modified by NiPc and CuPc catalytic effect was not shown. The electrode reaction includes oxidation of phthalocyanine metal (II) to metal (III) on the electrode surface, accompanied by an oxidation reaction of the substrate in the solution. The similar mechanism is observed for thiourea and sulfide-ions oxidation on these CME. Catalytic activity of MPc is determined by the nature of the centre atom and decreases in the row: CoPc > FePc > NiPc > CuPc. Cu (II) complexes are only effective catalysts for the electrooxidation of organic sulfides (diethylsulfide, methionine) unlike mentioned above substrates. On the voltammograms one can see a significant increase of a peak current corresponding to the oxidation of complex CuPc only. This fact can be explained by the absence of thermodynamic condition of catalysis proceeding for other complexes ($E^0_{S/P} < E^0_{M(III)Pc/M(II)Pc}$).

On the base of received data electrodes modified by FePc or CoPc are recommended for voltammetric determination of thiols and thiourea and CME based on CuPc - for the determination of organic sulfides. The linear range for these compounds is observed in a wide concentration interval up to 10^{-8} mol/l. Electrodes based on metallophthalocyanines can be used for the analysis of real samples avoiding complex pretreatment with an acceptable level of selectivity.

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O25

ELECTROCHEMICAL STUDIES OF THE INTERACTION BETWEEN HEPPS pH BUFFER AND METAL IONS

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Hydrogen ion buffers are usually necessary for many biological and chemical studies, as is the case of speciation studies, which are usually carried out at a constant pH value. However, the choice of a pH buffer may constitute an important problem since many of them (inorganic or organic ones), traditionally used for speciation studies, are also complexing agents and may disturb the equilibrium state.

A new assemblage of organic compounds, derived from N-substituted aminosulphonic acids, was introduced by Good and collaborators since 1966 [1]. N-2-hydroxyethylpiperazine-N'-propanesulfonic acid (HEPPS) is one of these pH buffers, similar to N-2-hydroxyethylpiperazine-N'-ethanesulfonic acid (HEPES) largely used, with a higher buffering range (7.3 -8.7) but less studied.

The aim of the present work was to investigate the suitability of HEPPS for copper or zinc speciation studies by electroanalytical techniques. These studies were performed by differential pulse anodic stripping voltammetry and differential pulse polarography in the presence of the buffer up to 0.1 mol/l concentration. Additionally, glassy ion potentiometry was also used for calculating the copper-HEPPS stoichiometric stability constant.

The results obtained are presented and discussed.

[1]-Good NE, Winget GD, Winter W, Connolly TN, Izawa S, Singh RMM (1966) Biochemistry 5: 467-477

O26

A NEW APPROACH OF THE POLAROGRAPHIC BEHAVIOUR OF Se(IV) IN AQUEOUS SOLUTIONS

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The polarographic behaviour of Se(IV) was approached using polarographic techniques (d.c. polarography, tast-polarography, sinusoidal current polarography with sensitive phase, normal pulse polarography, differential pulse polarography), in aqueous medium (Britton-Robinson buffer, aqueous solutions of different supporting electrolytes). The influence of chemical system parameters (ionic strength, pH, supporting electrolyte, Se(IV) concentration) and of characteristic parameters of the techniques (the mercury column height, the amplitude and the frequency of the superimposed alternating signals, the angle of the detection phase) were studied in order to elucidate the nature of the different polarographic signals obtained by the employed techniques, but also to optimise these parameters for the quantitative determination of Se(IV) in the concentration range $1 \cdot 10^{-3}$ - $5 \cdot 10^{-8}$ mol·L^{-1} from different aqueous samples.

O27

ELECTROANALYTICAL BEHAVIOUR OF BILIRUBIN

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The electrochemical reduction of bilirubin is examined by different polarographic (direct current polarography, tast-polarography, differential pulse polarography) and voltammetric (cyclic voltammetry, square wave voltammetry) techniques, using as working electrodes the dropping mercury electrode (DME) and the hanging mercury drop electrode (HMDE), in aqueous medium (Britton-Robinson buffer, ammoniacal buffer, 0,1 M KCl). The i = f(ε) curves obtained by these techniques provide that bilirubin is reducible in aqueous medium on mercury electrodes. Cyclic voltammograms have shown that the reduction occurs in two stages (ε_{p1} = - 1.385 V, ε_{p2} = - 1.470 V vs. Ag, AgCl), the magnitude of the maxim currents of peaks and voltammograms shapes were strongly scan rate-dependent. The polarographic study of bilirubin has shown three reduction waves: the first, strongly irreversible, is placed at less cathodic potentials ($\varepsilon_{1/2}$ = - 0.750 V vs. Hg pool), the second reduction wave ($\varepsilon_{1/2}$ = - 1.175 V vs. Hg pool) is complicate by kinetic and adsorption phenomena and the last one is a reduction wave of "presodium" type ($\varepsilon_{1/2}$ = - 1.700 V vs. Hg pool).

Signals obtained by differential pulse polarography and differential pulse voltammetry were optimised with a view to quantitative determination of bilirubin in the concentration range of $1 \cdot 10^{-3}$ - $1 \cdot 10^{-7}$ mol·L^{-1}, with a detection limit of $5 \cdot 10^{-8}$ mol·L^{-1}.

O28

ELECTROCHEMICAL EXTRACTION OF Cu(I) AND Cu(II) ASSISTED BY A MACROCYCLIC TETRATHIAETHER LIGAND.

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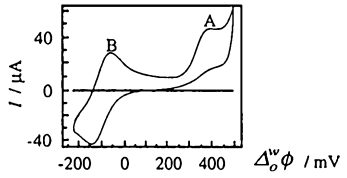
The electrochemical transfer of metal ions from aqueous solutions to organic solvents can be carried out by complexation at the liquidlliquid interface. At polarised interfaces, the transfer of the ionic species is associated with a faradaic current response. In the present work, the transfer of Cu(I) and Cu(II) assisted by the ligand 1,4,7,10-tetrathiacyclododecane is studied at the waterl1,2-dichloroethane interface.

The transfer mechanism of the copper ions was analysed by cyclic voltammetry, employing Li_2SO_4 and bis(triphenyl-phosphoranylidene) ammonium tetrakis(4-chlorophenyl)borate (BTPPATPBCl) as the supporting electrolyte for the aqueous and organic solutions respectively. The interface was polarised by a four-electrode potentiostat. Two voltammetric responses are observed for the transfer of both copper species in the presence of the organic ligand, as displayed in the figure. These two responses indicate that regardless of the initial oxidation state of copper, both ion species are present in the experimental conditions employed.



In the case of Cu(I), both voltammetric waves are observed during the first cycle. In the presence of Cu(II), the voltammetric wave A is the only feature during the first forward cycle, while wave B appears during the reverse cycle. These results suggest that Cu(II) is formed by disproportionation of Cu(I) in aqueous solutions. On the other hand, the generation of Cu(I) from Cu(II) seems to occur by homogeneous reduction of the Cu(II) complex by the anion $TPBCl^-$ in the organic phase. Interfacial complexation constants, stoichiometry and the effect of other organic supporting electrolyte are also investigated.

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A1

A GENERAL METHOD TO PERFORM NON COMPETITIVE IMMUNOASSAY FOR SMALL MOLECULES

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We are developing a new method to perform a non-competitive enzyme immunoassays for haptens, using cortisol as a system model. Mathematical modeling has shown that non-competitive assays are potentially more sensitive (i.e. having a lower analyte detection limit) than competitive assays, by orders of magnitude. However, till now, immunoassays for low-molecular-mass analytes continue to employ competitive formats because the analytes are too small to permit simultaneous binding of two antobodies (as in sandwich non-competitive method). Some attempts have been made to develop non-competitive assays for small molecules, but they are limited to same chemical structure or require the development of antimetatypes antibodies. We describe a general approach which allows to measure the analyte-bound antibody binding sites (as in non-competitive method) thus improving the sensitivity in small molecules determination. The model is based on the competition between analyte and a polydentate ligand (poly-L-lysine conjugate with cortisol, reaction ratio: 1 mole of cortisol per mole of lysine residue in the polypeptide) for the occupancy of the binding sites of an immobilized specific antibody. After the capture of both analyte and ligand, the addition of enzyme-labeled cortisol for a short time (30 min.) allows to remove the analyte molecules but, because of the different exchange kinetic, not the polydentate ligand. In this way, the measured signal presents a near linear correlation with the analyte concentration, determinig lower detection limits than competitive method in which there is inverse correlation. We report the characteristics of analyte and polydentate ligand interactions with the immobilized antibodies and a preliminary evaluation of a non-competitive assay for cortisol, showing at the same time that the model is sussessful and generally applicable to all small molecules,without limitation due to their chemical structure or need of affinity purification and labelling of anti-analyte antibody.

A2

DETERMINATION OF LITHIUM IM PHARMACEUTICALS FORMULATIONS BY ATOMIC ABSORPTION SPECTROMETRY

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Lithium is clinically used to treat manic and hypomanic states because of its stabilizing effect in manic depressive psychosis. The drug has an exceedingly low therapeutic index, and the plasma concentration must be frequently monitored [1]. This article describes the determination of lithium by atomic absorption spectrometry in four unlike pharmaceuticals formulations using an air-acetylene flame and lantanum as releasing agent.

Experimental conditions are studied such as samples digestion and interference elimination.

The reproducibility of the technique was good and it performed well in recovery test. The results are compared with those obtained by using a spectrophotometric method [2].

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A3

THEORETICAL AND EXPERIMENTAL ^{1}H, ^{13}C, ^{15}N, AND ^{17}O NMR SPECTRA OF 5-HALOGENOURACILS

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The 5-halogenouracils exhibit significant pharmacological activity and are used as an antitumor, antibacterial and antiviral drugs. Recently, we investigated their vibrational spectra both in argon matrix and in the solid state [1,2]. So far, the theoretical NMR spectra of 5-halogenouracils have not been studied, whereas the experimental studies were not fully complete for ^{15}N and ^{17}O nuclei. To improve the ^{13}C data we have measured all the carbon-proton and one-bond carbon-carbon spin-spin coupling constants which allowed to confirm the assignment of carbon signals. The influence of halogen substitution on the chemical shifts of ^{1}H, ^{13}C, ^{15}N and ^{17}O nuclei was tested and the linear correlations of chemical shifts with the halogen electronegativity for several nuclei were found. The halogen effect was studied by both experimental and theoretical *ab initio* methods. The calculations were performed using the polarization double zeta of Hansen and Bouman, and the polarization triple zeta of Sadlej basis sets.

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A4

VOLTAMMETRIC DETERMINATION OF AMOXICILLIN USING A CARBON PASTE ELECTRODE MODIFIED WITH POLY(4-VINYL PYRIDINE)

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Amoxicillin,[D - (-) - α - amino -p- hydroxybenzyl - penicillin trihydrate], synthesized from 6-amino penicillanic acid,is an orally absorbed,acid-stable,semisenthetic,broad-spectrum antimicrobial agent.

Polarographic investigations on penicillins have been indirectly performed e.g. as reduction of the chemically oxidised compounds or degradation products formed by acidic or alkaline hydrolysis or reduction of their derivatives.In recent years it was reported that some penicillins could be electrochemically oxidised on gold electrode based on the catalytic effect of gold oxides [1],and on rotating gold and platinum electrodes[2].

In the present study a voltammetric method developed based on the electrooxidation of amoxicillin on PVP modified carbon paste electrode.The voltammograms showed that the reaction was irreversible in the scan rate range of 10-100 mVs^{-1}.The limiting current was found to be linearly dependent on amoxicillin concentration in the range of $8x10^{-6}$-$1x10^{-4}$ M with a slope of $2.44x10^{4}$ μA/M,intercept of 1.05 μA,correlation coefficient 0.999.

The proposed method was applied to the tablet,capsule and oral suspension forms of amoxicillin.The results were compared with those obtained by USP XXII method by means of t-tests and the difference between the two methods was found to be unimportant.The voltammetric method was suitable for the accurate and sensitive determination of amoxicillin and it could be applied directly without any seperation step because the excipients present in the pharmaceutical forms of this compound did not interfere with the voltammetric analysis.

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A5

COMPARATIVE STUDY BY GC-MS ON DIFFERENT GENETIC LINES OF SOME ESSENTIAL OILS FROM CARROT FLOWERS

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GC-MS analysis of the essential oils from carrot flowers was carried out as three flower types: fertile flowers (hermaphrodite), "petaloid", and "brown anther" type androsterile flowers.

The essential oils were extracted by steaming for 4 hours. The flowers to be studied were picked up between the first and the fourth day of blossoming.

Comparative study of the chromatograms obtained by GC-MS showed significant differences in the composition of these essential oils. The presence under certain ratios of terpenic compounds in essential oils gives certain advantages or disadvantages during the flower pollination.

OV1 (50 m x 0.32 mm x 0.2 μ) separation column was used from GC-MS analysis. Identification of terpenic compounds was made by comparing each compound mass spectra with mass spectra in NIST and WILLEY Spectra libraries.

A6

EFFICIENT CHARACTERIZATION OF COMBINATORIAL CHEMISTRY LIBRARIES USING MASS SPECTROSCOPY (MS) AND CHEMILUMINESCENT NITROGEN DETECTION (CLND)

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Combinatorial chemistry offers pharmaceutical and biotechnical companies a quick and efficient tool to synthesis, test and develop a multitude of potential drug candidates. Due to the sheer number of compounds, characterization of combinatorial libraries is difficult and tedious. However, LC/MS and Chemiluminescence Nitrogen Detection (CLND) used together provide a **powerful, efficient,** and **reliable** mechanism to identify, quantitate, and characterize complex libraries and samples. Several examples are presented to illustrate the answer to two basic questions of concern for chemists: What is it? How much is there?

A7

MODERN ANALYTICAL METHODS IN NATURAL PRODUCT ANALYSIS

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The experiments described here involve the analysis of phenolics in plant tissue, eucalypt, by high performance liquid chromatography (HPLC), capillary electrophoresis (CE) and gas chromatography - mass spectrometry (GC-MS). The extraction process involves a quick microwave digestion followed by solvent-solvent extraction. The cell wall bound phenolics extracted from *Eucalyptus marginata* are tentatively identified by micellar electrokinetic capillary chromatography and/or RP-HPLC to be gallic acid ferulic acid and p-coumaric acid. The presence of these phenolics is then confirmed by GC-MS.

These experiments can be completed in isolation or form part of an extended laboratory exercise. The experiments form the base for a well constructed third year project especially for biology majors completing a minor in chemistry. Comparing the phenolic profiles of a number of closely related eucalpyts showed significant differences in the phenolics present. For example the phenolics released from the cell walls leaf tissue of Eucalyptus calophylla contain gallic acid but no ferulic or p-coumaric acid was evident.

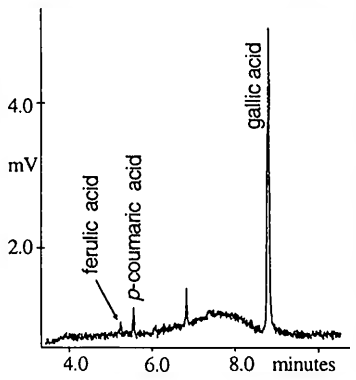

Figure 1. Electropherogram of phenolics extracted from *Eucalyptus marginata*

A8

THIORIDAZINE DETERMINATION WITH CHROM(III) COMPLEX ANIONS

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The last years research proved that the complex anions of the Cr(III), analogues of the Reinecke salt ($NH_4[(NCS)_4(amine)_2]$) where amine is aniline,toluidine,imidazole,etc.) are analytical reagents with a greater sensibility and selectivity for some N-organic bases determination.

In this paper we have studied the determination of the thioridazine-the newest against tuberculosis drug(3-methyl-mercapto-10,2'-[N-methyl-piperidyl-(2')-ethyl-(1')] phenothiazine).

Some new gravimetric,oxidimetric,complexometric and spectrometric methods for the thioridazine determination were described (the concentration range 10^{-3}-10^{-5}M) . The results were statistically evaluated. The method accuracy is influenced by the "amine" ligand.

The stability of the Thioridazine-H Rein combination was confirmed by the derivatographic study of this one.

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A9

USING HPLC FOR THE QUALITATIVE ANALYSIS OF BROWN MUTANT *TRICHODERMA VIRIDE* M 108 SECONDARY METABOLITES

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Brown mutant *Trichoderma viride* M 108 was prepared by using UV - irradiation of parental strain *Trichoderma viride* 8 - 7 Pers. ex S. F. Gray [1]. The cultivation on a modified liquid Czapek - Dox medium containing 3.0 % sucrose and 0.1 % yeast autolyzate (IMUNA, Šarišske Michaľany, Slovakia), pH before sterilization 6.0, was used for the production of secondary metabolites. Two of these pigments - yellow and orange metabolites were identified and spectroscopically characterized as anthraquinone derivatives, 1,3,6,8-tetrahydroxy-9,10-anthraquinone (metabolite B) and 1-acetyl-2,4,5,7-tetrahydroxy-9,10-anthracenedione (metabolite C) [2] (Fig. 1). Their structures were determined by analysis of UV/VIS, IR, mass, ^1H NMR and ^{13}C NMR spectra [2]. Compounds B and C did not exhibit antimicrobial activity in cross-streak tests. However, in rat mitochondria they function as uncouplers of oxidative phosphorylation [3].

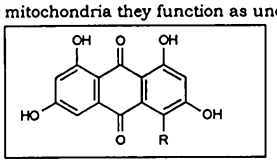

Fig. 1: Chemical structures of anthraquinones formed by brown mutant M 108 *T.viride*: 1,3,6,8-tetrahydroxy-9,10-anthraquinone (metabolite B) (R = H, R_F = 0,38) 1-acetyl-2,4,5,7-tetrahydroxy-9,10-antracenedione (metabolite C) (R = $COCH_3$, R_F = 0,26).

Chromatographic methods (TLC, PC, LSC, HPLC) were used for colour secondary metabolites separation and purification. The medium filtrate and mycelium extracts contained a wide range of metabolites of similar colours shade (it included colours shades from yellow to dark orange). The relatively close R_F (benzene : acetone, 3 : 1) values made the isolation of pure chemical compounds by previously used chromatography methods very difficult or impossible. The HPLC method was suggested to solve the problem. HPLC method with reversed phases (colum 56X C-18, diameter 7 µm, Tessek Prague, Czech Republic; methanol as mobile phase) was applied. Qualitative representation of secondary metabolites was depended on the growth of brown mutant in individual cultivation days. Measured values from both metods were compared with metabolite standards B and C.

Metabolites separated and purified by preparative TLC (benzene : acetone, 3 : 1) were analysed by HPLC, the purity of each of them was checked, the retention time of 7 of them was determined. Then the qualitative composition of filtrate and mycelium extracts from the growth process of brown mutant M 108 was examined.

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A10

CHEMILUMINESCENT DETERMINATION OF PHENYLEPHRINE HYDROCHLORIDE AND SALICYLAMIDE IN A CONTINUOUS-FLOW

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A certain number of chemiluminescent procedures are based on well-known reagents like luminol in which the light is produced by reaction with strong oxidants in presence of some activators (organic or inorganic). The complexity of the reaction allowed many indirect procedures for determination of substances which can influence the main reaction. An interesting analytical trend is to obtain chemiluminescent reactions with the direct oxidative treatment of the analyte.

This means a lot of empirical work dealing on the reaction of the analyte with a wide range of strong oxidants in different media. There is not clear rules to predict the chemiluminescent behaviour of a given molecule and the exceptions are frequent.

This communication is dealing with empirical screening of molecules of pharmaceutical interest to detect chemiluminescent reactions to be applied to field of pharmaceutical analyses. The work is done into the continuous-flow methodology trying to propose very simple manifolds; the sample volume is injected into a carrier and merges with the oxidative solution stream as close as possible to the flow-cell entrance. An alternative to FIA methodology is a manifold in which the sample solution is continuously flowing and merges with the reagent as is reported for the FIA procedure. Both manifolds require a coiled flow-cell in front of the photo multiplier tube.

Two positive chemiluminescent reactions were found. Oxidative reaction of phenylephrine hydrochloride and salicylamide proved to be suitable for the determination of those drugs. The most adequate oxidant resulted to be the potassium permanganate in sulphuric acid medium. The increase of temperature resulted in higher light emission. Both procedures are applied to determination of the active principles in pharmaceutical formulations.

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A11

FAST DETERMINATION OF TOXIC METALS IN HUMAN URINE, SERUM AND BLOOD BY GRAPHITE FURNACE ATOMIC ABSORPTION SPECTROMETRY

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Electrothermal atomic absorption spectrometry (ETAAS) is typically used for trace metal analyses in biological fluids using Zeeman-effect background correction. Thus, urine or blood samples could be analyzed for toxic elements contents for the biological monitoring of occupationally exposed persons. However, conventional methods have large analysis times due to the prior treatment of the sample which normally involves an acid mineralization step. When no mineralized samples are directly introduced into the atomizer, problems derived from the accumulation of carbonaceous residues appear. The removal of these residues could be carried out by the addition of nitric acid and hydrogen peroxide which destroys the organic matter during the heating cycle, decreasing both background problems and the build-up of carbonaceous residues.

In this communication, procedures for the direct determination of arsenic, lead and cadmium in human urine, serum and blood without previous mineralization of the sample are presented. The addition of nitric acid to the samples produces precipitation of the proteins and, consequently, two successive injections were carried out. The first injection (10 µl) consisted of the biological sample, 0.015% Triton X-100 and 0.1% phosphate. After a drying step at 220°C, a second injection (10 µl) of a solution containing 15% hydrogen peroxide and 0.65% nitric acid was performed and the total heating program was run. Platform atomization was used for all the elements. Calibration was carried out using aqueous standards for urine samples and by the standard additions method for both serum and blood. The methods proposed were applied to the determination of the contents of the metals in samples from different persons. The reliability of the procedures was checked by analyzing several certified reference materials.

A12

INCREASING PERFORMANCE IN MULTIPLE DRUG OVERDOSES BY USING GC-MS-SECI SYSTEM

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The certainly diagnosis in multiple drug overdose belongs to the Analytical Toxicological Laboratory. GS-MS with electronic ionization (EI) is usually used as a screenining method. When the identifying of drugs and/or their metabolites, which are present in multiple drug overdoses, cannot be performed only in EI, we have used another ionization techniques – selected ejection chemical ionization (SECI). We have used a GC/MS VARIAN SATURN 3 system with Septum Purge Injector (SPI) and Ion Trap Detector (ITD).

An EI analyze showed the presence of Metamizol and another three of its metabolites. The clinical state of the patient could not be explained only by the presence of Metamizol. The reprocessing of the sample by SECI - using butane - C_4H_{10} – for ionization, demonstrated the presence of Phenobarbital, who justified the clinical state of the patient, but it was screened in EI by the presence of the Metamizol - M (desalkyl -), an metabolyte of Metamizol.

The certitude diagnosis is done by the link between the clinical symptoms and the analytical diagnosis using GC/MS system – the mass spectra EI and SECI. Our experience in SECI permitted to create our computerized library MIC4H10, where a lot of spectra can be searched.

Key-words: Multiple drug overdose, GC-MS, EI, SECI.

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A13

HPLC AND HPLC-MS INVESTIGATIONS OF BUSPIRONE AND ITS RING-OPENED ANALOGUES

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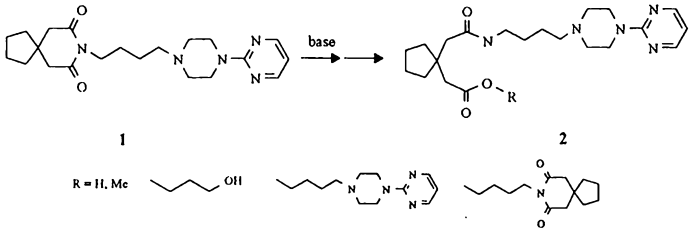
Buspirone (1) is a widely used anxiolytic agent. The spiroglutarimide ring in compound 1 is unstable under basic conditions and this provides an opportunity to prepare a series of ring-opened analogues (2).



These new compounds (2) have also considerable anxiolytic activity. The aim of our work was the HPLC and HPLC-MS investigations of 2.
The electron impact ionization (EI) fragmentation properties of these compounds were studied. Compounds 2 are unstable under EI conditions. Thermospray (TSP) mass spectrometry has proved to be a useful technique for analyzing these compounds. The ions formed under TSP ionization have been determined with positive and negative ion mode. The positive TSP mass spectra exhibit strong $[M+H]^+$ and/or $[M+NH_4]^+$ ions. The effect of the different HPLC and MS parameters for the TSP sensitivity was investigated and optimized.
The HPLC-TSP-MS method is suitable for measurements from biological matrixes.

A14

CYTOLOGICAL AND IMMUNO-CYTOLOGICAL ANALYSIS OF CEREBROSPIANL FLUID LEUKOCYTES: COMPARISON OF SEDIMENTATION AND CYTOCENTRIFUGATION TECHNIQUES.

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Objective: Cytological and immuno-cytological techniques are mainly performed in cerebrospinal fluid (CSF) by Sayk's sedimentation procedure and also by different cytocentrifuge techniques. To standardize preanalytical and analytical steps, both techniques were compared to find out an optimal procedure for cell analysis in CSF samples. Material and Methods: Fresh CSF samples (<2h after sampling) were analysed on polydimethyldiallylammonium chloride (PDDA) coated slides which were active for 3 weeks. Technique A was performed with Sayk's sedimentation chamber applying 1 ml native CSF sample (sedimentation time <30 min). Technique B was done with the Hettich centrifuge (Tuttlingen, Germany): CSF cells were concentrated by precentrifugation (20 min at 220xg); the cell pellet was resuspended with a bovine albumin solution containing a cell medium and fractionated into 0.25 ml portions for plastic cyto-cell chambers to sedimentate cells on slides for 5 min at 220xg followed by 820xg. Technique C: Immuno-cytology was done with the "Immunette" (ProMedeus Immuntechnologie, Offenbach, Germany) containing 10 tubes for 10 specimen preparations on PDDA coated slides (obtained by techniques A or B) to treat them with primary and secondary antibodies followed by colour staining. Mikroscopic evaluations of cell preparations were done at 200fold to 400fold, resp. 1000fold enlargements. Results and Discussion: PDDA coating of slides improved the cell yield. This was found with technique A with CSF samples of 0-5 leukocytes/μl: cell yield increased from 4% to 10%. Cell yields were higher by a factor of 5 with technique B thus causing altered differential counts of CSF leukocytes: Technique A showed relatively higher monocyte counts, technique B higher lymphocyte counts. Both techniques A, B brought good depictions of inflammatory and malignat CSF cells, but cells were larger and more dispersed with technique A when stained with technique C. Conclusion: Technique B with PDDA coated slides, representing the leukocyte composition of native CSF, gave higher cell yields of >45% and thus may be better qualified for CSF cytology and immuno-cytology than technique A.

A15

PROTEIN DETERMINATION IN CEREBROSPINAL FLUID (CSF): COMPARISON OF THREE METHODS

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Objective: In routine analysis of CSF total protein represents a parameter of blood-brain-barrier function. It was determined here by three routine methods: Method A, the biuret reaction, measures peptide bonds directly proportional to the protein content. This reference method is less practicable because CSF samples have to be concentrated. Method B, the pyrogailol red molybdate method, measures the increase in absorbance induced by binding basic amino groups of proteins to the red complex. Method C, the benzethonium chloride method, determines the turbidity with CSF proteins produced in alkaline solution. Material and Methods: For comparison, 95 fresh CSF samples, cell-free, were analysed with Method A: 0.25 mL sample were precipitated with 0.25 mL 1.2 mol/L TCA, dissolved in 0.5 mL biuret reagent and absorbance at 546 nm (d=2cm) was measured subtracting a reagent- and sample-blank (calibration with dilutions of Kontrollogen L (Behringwerke)). CV of imprecision: < 5%; inaccuracy: 3 to 10%. Method B: 0.015 mL sample were mixed with 0.500 mL Microprotein-PR reagent (Sigma) in a cuvette and absorbance at 578 nm or 623 nm (d=1cm) was measured subtracting a reagent- and sample-blank; calibration see Method A, resp. with standards (Sigma). CV of imprecision: < 7%; inaccuracy: 3 to 10%. Method C: 0.015 mL sample were analysed in 0.350 mL reagent in Hitachi 911 at 505 nm (and at 700 nm) using a 6 point calibration (Boehringer Mannheim). CV of imprecision: < 4%; inaccuracy: 3 to 10%. Comparison of the results of two procedures was done according to Passing & Bablok 1983. Results and discussion: Both manual procedures (methods A, B) were less precise than the automated one (method C), but all showed inaccuracies of the same range. Comparison with the biuret method A (x) no accordance was found with the results of method B measured at 578 nm (y = 1.12x + 66) and at 623 nm (y = 1.03x + 58). The results indicate blank problems, resp. higher values which cannot be explained by Ca and Mg ions, ascorbate, creatinine, glucose or uric acid in twofold concentrations as found in CSF samples. Comparing results of method C with those of method A also did not show accordance: y = 1.11x - 22, indicating higher values and blank problems. Conclusion: the fact that two of three protein methods did not yield comparable results with the biuret method in CSF samples, should be considered in the daily CSF routine analysis.

A16

Extraction of Essential Oils from the Medicinal Herbs

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Interest in plants has principally been for the isolation of essential oils, but to obtain other pharmaceutically active compounds has also been in concern. To extract natural products from plants important are non-toxicity, inertness and cheapness of the solvent and only few candidates can be chosen : water and carbon dioxide.
Simultaneous distillation/extraction with water (SDE), subcritical extraction with water (SHW) and supercritical fluid extraction techniques with CO_2 (SFE) are used for isolation of essential oil from plant material. SFE is receiving great attention in the isolation of chamomile oil, which is an example of a difficult to reproduce natural product due to presence of thermally labile compounds such as matricine. In this report the results obtained by using three techniques together with HRGC and GC/MS for studying of composition of essential oils from Estonian medicinal herbs were presented including chamomile (*Matricaria recutita L.*) and yarrow (*Achillea millefolium L.*). The individual compounds in oil extracts were identified by their retention indices (RI) on two columns using our RI data bank and GC/MS data. In this work SHW and SFE conditions were chosen to obtain a range of extracts rather than to achieve selectivity.
Extracts of the same product with different kinds of solvents produce different results owing to the selective solubility of each component in the fixed solvent. Because of that a universal extraction strategy for analytes and matrices will never be feasible but using sub- and supercritical fluids instead of different kinds of solvents the same fluid at different pressure and temperature is used with the same result. It was estimated that two hours distillation time should be sufficient for isolating volatile constituents from chamomile and yarrow by SDE. The optimisation of SFE extraction parameters (sample size, pressure, temperature, trapping) were evaluated. At moderate pressure of CO_2 the content of undesirable compounds in essential oil decreased and extracts obtained were qualitatively similar to SDE extracts.

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A17

DETERMINATION OF pK_a-VALUES OF *trans*-β-BENZOYL ACRYLIC ACID AND ITS *p*-SUBSTITUED DERIVATIVES

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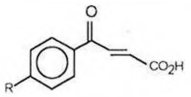
Acidity is the feature exerted by many substances, and frequently is a basis for their classification and for the rationalization of their chemical and biochemical behaviour. Acidity is important for the elucidation of reaction mechanisms, too. When the experimental pK_a determinations are difficult or impossible to perform, a theoretical evaluation of their values is very valuable. The most useful methods of pK_a prediction are based on the assumption that within particular classes of acids and bases substituent produce free energy changes which are linearly additive. In this particular case the series of *trans*-β-benzoyl acrylic acid and its *p*-substituted derivatives was studied and their pK_a values were determined spectrophotometrically. This series included acids with general formula:



R = *H-; CH_3-; C_2H_5-; $(CH_3)_2CH$-; $(CH_3)_3C$-; F-; Cl-; Br-*

On the basis of pK_a-values obtained, Hammett equation was established and ρ constant was calculated. Since *trans*-β-benzoyl acrylic acid and its derivatives exhibit antibacterial activity, the knowledge of their pK_a is of great importance for the investigation of the transport mechanism through biological membranes.

A18

Application of physicochemical methods for estimate biological membrane permeability

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In some cases blood ionic composition variation allows to conclude about state of vascular channel. We have displayed the variation of potassium-sodium ratio in venous and capillary blood at pathologic processes with use of ISE.

Na-selective glass electrode and K-selective cover-wire electrode based on tetraphenilborate potassium were used. Electrodes were conditioned in plasma during 30 min before experiments. Sodium content in plasma, serum and whole blood at infectious toxicosis was not differ from common value. Potassium content in venous blood was differ from the capillary blood and was significantly more then normal physiological value. It has been established that value of potassium-sodium ratio is connected with capillary permeability.

To estimate the cellular membrane permeability the turbidity spectrum method is proposed. The diameter of erythrocytes was measured with using of microscope. The turbidity spectrum was determined relatively to NaCl solution after probe selection and its dilution by physiological solution. Wave lengths correspond a adsorption minimum. Method allows to determine the average volume of erythrocytes, the relative and absolute refraction index, their concentration in blood, the content of dry substances, water in erythrocyte, its density. The given characteristics of peripheral blood erythrocytes allow to conclude about the homeostasis of vascular system, in particular at infectious toxicosis. The defined violations at infectious toxicosis in the period of full swing of disease have been revealed. Refraction index and density at the beginner period of illness were differ from these at period of reconvalescencion significantly. These violations were characterized by increasing of water content in erythrocytes.

A19

EVALUATION OF THE IMPORTANT CRITERIA IN RP IP-HPLC METHOD FOR THE DETERMINATION OF SOME PHARMACEUTICALS

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The evaluation of the important criteria for the reversed-phase ion-pair high-performance liguid chromatographic method was done on the determination of some water-soluble vitamins in some pharmaceutical dosage forms. It was introduced through the parameters for the validation of the method such as: linearity, selectivity, response factor of the detector, precision, accuracy, reproducibility, recovery and robustness. The validation was applied to the determination of vitamins: B_1, B_2, B_3, B_6, C and p-aminobenzoic acid in multi-vitamin coated tablets Beviplex® and Oligovit®.

The chromatographic LKB Pharmacia Gradient HPLC System consisted of a HPLC pump A and pump B 2150 LKB, LC controler 2152 LKB and Rapid Spectral "diode array" UV detector 2140 LKB. LDC Analytical Consta Metric HPLC System consisted of Consta Metric pump 3000 LDC, Spectro-monitor 3100 variable wavelenght detector and integrator LKB 2221.

Separation were performed on Supelcosil column LC-8-DB 250x4.6mm, with 5μm particles sizes. Sample were introduced through a Rheodyne injection valve with a 10μl sample loop. Hexanesulfonic acid sodium salt and triethanolamine in water-methanol (85:15 v/v) was used for Oligovit®, but the ratios for Beviplex® was (92:8 v/v) and (82.8:17.2 v/v). pH was adjusted to 2.8 with orthophosphoric acid. Phenol was used as an internal standard. The flow rate was 2ml/min and UV detection was performed at 280nm, at room temperature.

All the parameters for the validation of the linearity were determined: slope (a), intercept (b), correlation coefficient (r), standard deviation of the slope (S_a), standard deviation of the intercept (S_b), limit of detection (LOD) and limit of quantificatio (LOQ).

As all the mentioned parameters are in a good agreement of the statistical criteria of some analytical method, the authors propose this RP IP-HPLC method for the simultaneous quantification of the water-soluble vitamins in multicomponent pharmaceutical formulations.

A20

ATOMIC ABSORPTION SPECTROMETRIC METHOD FOR THE DETERMINATION OF PHOSPHORUS IN PLANTS MATERIALS USING BISMUTH-PHOSPHOMOLYBDATE COMPLEX

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Trace amount of phosphorus are usually determined by spectrophotometric methods based on the formation of the heteropoly-blue complex.

Atomic absorption spectrometry is often used in preference to spectrofotometric methods for the determination of trace amount of elements because of its sensitivity and free from interferences from associated metal ions. However, phosphorus is not easily determined by atomic absorption spectrometry as the resonance line of phosphorus lies in the extreme ultraviolet region.

Phosphorus has previously been determined an indirect AAS method by the formation of the phosphomolybdate complex using the molybdenum resonance line [1,2]. Molybdenum, however, is not easily atomised and require the use of hotter flame such as dinitrogen-oxide acetylene. The use of the dinitrogen-oxide flame is generally not favourable because of its toxicity and explosive nature.

In this paper an indirect method using the bismuth phosphomolybdate complex for the determination of phosphorus in plants materials is suggested.

As bismuth and phosphorus are present in 1:1 stehiometric ratio, the phosphorus content can be correlated with the concentration of bismuth. The condition for formation of the complex, its extraction with isobutyl methyl ketone and the determination of phosphorus in solution by utilising the 223,06 nm resonance line of bismuth, and by using an air-acetylene flame are discussed.

All the experiments were performed on a Perkin Elmer 3300 atomic apsorption spectrometer.

Plant material (0,3-0,5 g) were wet-ashed with 10 mL of concentrated nitric acid and 2 mL hydrogen-peroxide solution.

The interferences of various ions on the determination of phosphorus were investigated.

The results obtained by this method were compared with those obtained spectrofotometrically.

1. Ramakrishna, T.V., Robinson, J.W., and West, P. W., *Anal Chim. Acta., 45, 43, 1969*
2. Hurford, T.R., and Roltz, D.F., *Anal. Chem., 40, 379, 1968*

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A21

LENGTH-OF-STAIN INDICATOR TUBES FOR PHARMACEUTICAL AND CLINICAL ANALYSIS

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The use of length-of-stain indicator tubes for the determination of ascorbic acid and tin(II) in pharmaceuticals and nitrate, nitrite and copper(II) in urine and blood serum have been investigated. Human serum albumin or its microspheres with attached tin(II) is the base of new russian radiopharmaceutical preparations.

Reversed-phase silica gel (SG-CN) coated by Binschedler's Green was used as indicator powder to the ascorbic acid determination. The porous sol-gel powder doped with ammonium salt of molybdophosphoric acid and PAN were indicator powders for tin(II) and copper(II) consecuentially. The indicator powder for the nitrite determination is the mixture of sulphonic, chromotropic, and citric acids, and diazotization catalyst. The indicator powder for the determination of total content of nitrite and nitrate included also zinc powder as a reducing agent.

The analytical signal (the length of colored zone which is proportional to the concentration of analyte) is detected directly after the sample passage through the tube. The following ways of sample injection were used here: the solution flow upward through the tube by capillary forces; a home made pumping device was used in order to inject the sample through the indicator tube. The choose of the way of sample injection depends on the nature of an indicator tube.

Indicator tubes and indicator powders developed have been tested and accepted in various organizations of Russian Academy of Medical Sciences: Research Institute of Pediatry (determination of nitrate and nitrite in urine and blood serum), Medical Radiological Research Centre (analysis of Russian radiophrarmaceutical preparations).

A22

DERIVATIVE LINEAR VARIABLE-ANGLE SCANNING FLUORESCENCE SPECTROMETRY FOR THE DETERMINATION OF CLOSELY OVERLAPPED DRUG MIXTURES

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The simultaneous determination of salicylamide and salsalate in an organic medium is proposed. Salicylamide is a substance with some analgesic, anti-inflammatory and antipyretic properties, which character highly fluorescent in basic medium is well known. Salsalate is a substance with anti-rheumatic and anti-inflammatory properties, and there are little bibliography concerning its determinations and no fluorimetric methods are reported.

Although salsalate is a weak fluorescent compound, this shows a greatly increase of its fluorescent properties when an alkaline medium is provided to a salsalate chloroformic solution. At these conditions, the compounds present strongly overlapping spectra, and it is not possible to resolve their mixture by conventional fluorescence.

Synchronous scanning derivative fluorescence spectrometry is a very useful tool for resolving multicomponent mixtures. So that, the broad-band overlapping conventional spectra of salicylamide and salsalate are resolved by means of first derivative variable-angle synchronous fluorescence spectrometry. The measurements are performed in an alkaline medium, which is adjusted by adding 0.40 M pyrrolidine chloroformic solution to the organic phase. The method is applied for the simultaneous determination of salicylamide and salsalate at concentrations between 0.100 and 1.000 $\mu g\ mL^{-1}$ for both components, by means of absolute values of first derivative of variable angle synchronous scan at the emission/excitation wavelenghts of 410/299 nm for salicylamide and 440/307 nm for salsalate. The serum and urine are extracted with chloroform, by adding acetate buffer solution to provide a pH 4.8 in the aqueous phase. Finally, pyrrolidine chloroformic solution is added to organic phase, where both components are determined, without the need for re-extraction step into an aqueous phase.

A23

FAST DETERMINATION OF NAFRONYL IN PHARMACEUTICAL PREPARATIONS BY STOPPED FLOW / ROOM TEMPERATURE PHOSPHORIMETRY

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Nafronyl or naftidrofuryl oxalate develops peripheral and central dynamic-vessel action, having a direct effect in the autoregulation of cerebral circulation, without any influence on the cardiac conduct or hypotension effect. This can be used for certain sports to prevent cerebral and peripheral circulation insufficiency, as well as arteriopathies of lower members (cramps and spasms).

The phosporescence of this compound in the presence of sodium dodecyl sulfate has been studied by us and, recently a batch determination method using this micellar medium has been proposed. However, the procedure takes around 30 min to remove oxygen and obtain a stable signal. The stopped-flow mixing technique in combination with room-temperature phosphorescence has been only proposed for the determination of carbaryl and naproxen to date. The through mixing of the streams from the syringes favors the interaction of reactans, allowing the interaction of oxygen with sulfite ions and accelerating the necessary deoxygenation process.

The interaction of nafronyl with tallium(I) ions, in the presence of sodium dodecylsulfate and sulfite ions, produces a room-temperature phosphorescence emission that develops in a time of only 5 seconds. The linear calibration range form intensity and rate measurements, was 30-600 ng mL-1. The detection limits, calculated according to the Clayton criterium, were 19 and 20 ng mL-1, for intensity and rate measurements, respectively.

The recommended procedure was applied to the determination of a commercial formulation containing nafronyl: Praxilene. The assays results, expressed as a percentage of nominal content, resulting from the average of three determinations of three different tablets, are 99.1 ± 0.2% (intensity method) and 101.2 ± 3.6% (rate method).

A24

ANALYTICAL STUDIES CONCERNING THE FLAVONOIDS COMPOSITIONS OF HYDROALCOHOLIC EXTRACTS FROM PLANTAGO BY HPLC

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The use of hydroalcoholic extracts from medicinal plants in pharmaceutical and cosmetic products requiring a better knowledge of their composition determining the class of their compounds.

Analytical studies of a large number of Plantago and Calendulae extracts were made.

The previous steps of preparation were focused on braking the complex matrix of probes by using the extracts on solid phase state of C_{18} and C_6H_5 type.

The HPLC analyses were made in reverse phase detected by UV at 280 nm.

The identification and quantitative determination of these types of compounds were achieved from the resolution parameteres and by the help of calibration curves.

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A25

STUDY OF PROTOLYTIC EQUILIBRIA AND SOLUBILITY OF CLONAZEPAM AND LORAZEPAM

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Clonazepam and lorazepam belong to the class of 1,4-benzodiazepines, pharmacologically important tranquilisers. Chemically, these benzodiazepines are ampholytes (HA) with low intrinsic solubility of the neutral molecule. In homogeneous and heterogeneous systems of clonazepam and lorazepam, over the pH range 0 - 14, the following equilibria are possible:

Homogeneous system

$$H_2A^+ + H_2O \overset{Ka_1}{\rightleftharpoons} HA + H_3O^+$$

$$HA + H_2O \overset{Ka_2}{\rightleftharpoons} A^- + H_3O^+$$

Heterogeneous system

$$(HA)_S \overset{Ks_0}{\rightleftharpoons} HA$$

$$(HA)_S + H_3O^+ \overset{Ks_1}{\rightleftharpoons} H_2A^+ + H_2O$$

$$(HA)_S + H_2O \overset{Ks_2}{\rightleftharpoons} A^- + H_3O^+$$

The equilibrium constants of the above reactions were spectrophotometrically determined at 25 °C and constant ionic strength of 0.1 M (NaCl). On the basis of the values of these constants the distribution of equilibrium species and the solubility of clonazepam and lorazepam as a function of pH were calculated.

These investigetions are of great interest for the study of physicochemical properties and biological activities of the given benzodiazepines. In addition, the knowledge of the distribution of drugs in the physiologically pH range is necessary to understand the transportation models in the gastrointestinal and biological membrane.

A26

PURIFICATION OF DUGONG FERRITIN

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Samples of sediment, seagrass and dugong tissues were analysed for selected metals: Fe, Zn, Cu, Pb, Mn, Cd, Ni, Co, and Al . Iron in liver was the most interesting element found in relation to the samples analysed. The level of iron in dugong liver tissue is extraordinarily high, ranging from 13,000-70,000 $\mu g.g^{-1}$ dry weight[1]. Generally, iron is stored in the protein ferritin

Ferritins from liver of dugong were isolated and characterised. Ferritin was purified by a technique employing heat treatment and two-column gel filtration on Sephadex G-75 and Sephacryl S-300, followed by preparative polyacrylamide gel electrophoresis. Isolation of ferritin was monitored by determining iron to protein ratio. For reference, ferritin was also isolated from human liver and spleen.

Purity of the isolated ferritin was determined by analytical electrophoresis. The amino acid composition and subunit nature of the purified ferritin are within the normal range reported for the well-characterised human liver and spleen ferritins and horse spleen ferritin.[2]

[1] W. Chua-anusorn et al., Hyperfine Interaction, 1994
[2] P.M. Harrison et al., Biochem. Soc. Trans., 1987

A27

METALS IN DUGONG ORGANS

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The dugong, Dugong dugon (Müller) is the only herbivorous mammals species that is strictly marine. Ecologically, the dugong occupies an important position in the shallow water ecosystems along the subtropical and tropical coasts of the Indian and western Pacific Oceans. The dugong spends most of its time feeding the seagrass. The dugong is a large mammal that weights up to 400 kg and 3 m length [1]. The seagrass that constitutes the main source of nutrition to the mammal, may take in the elements from the sediment on which the seagrass is supported. The elements may be passed on to the dugong and incorporated into its body tissue. It was reported that the concentration of some metals such as Fe, Zn, Cu, Co and Ag in the liver of adult dugongs were extremely high compared with those reported for other marine mammals [2].

This paper presents the results of metals analysis on dugong samples, seagrass and sea sediments. Other organs of dugong are also included to verify and attempt to explain the previous finding. Fe, Zn, Cu, Pb, Mn, Ni, Co, and Al were analysed by ICP-AES.

The concentrations of Fe in all dugong livers are extremely high (13,000-71,000 $\mu g.g^{-1}$dry wt.). The levels of Zn are also high (1,500-2,800 $\mu g.g^{-1}$dry wt.). The level of Fe in spleen (7,600 $\mu g.g^{-1}$dry wt.), in heart (340 $\mu g.g^{-1}$dry wt.) and kidney (1,200 $\mu g.g^{-1}$dry wt.) are considerably high. Cd is mostly concentrated in Kidney (60 $\mu g.g^{-1}$dry wt.).

[1] G.E Heinsohn, et.al., Aquaculture ,1977
[2] G.R.W Denton, et. al., Marine Biology, 1980

A28

GAS-CHROMATOGRAPHY-MASS SPECTROMETRY SCREENING FOR INVESTIGATION OF SOME NATURAL HYDROALCOHOLIC EXTRACTS QUALITY

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Coupled analytical techniques as, in our case, Gas-Chromatography and Mass-Spectrometry (GC-MS), are more and more used for analytical approach of complex natural samples. The analytical studies were carried out on hydroalcoholic extracts of Plantago and Calendulae. First, some acid, basic and combined hydrolysis were proceeded to split large mass molecular compounds. Further, selective extraction with solvents of different polarities were conducted. The samples were silanised before being analysed by Gas-Chromatography.

For each fraction, separations were proceeded by Gas-Chromatography in stationary phase SE-54 (50 m x 0.32 mm x 0.2 µ). Detection was carried out by Mass Spectrometry.

A large range of chemical compounds from different classes as amino acids, hydroxiacids, carboxylic diacids, sugars, polyphenolic carboxylic acids were identified.

The obtained chromatograms are "finger print" like which give detailed information on the composition of these extracts.

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A29

COMPARATIVE RESEARCH OF THE COMPOSITION IN FATTY ACIDS OF SOME VEGETABLE OILS USED IN PHARMACEUTICAL AND COSMETIC INDUSTRY

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Many of cosmetic and pharmaceutical formulations for topical use include different vegetable fatty oils.

Their emollient, nutritive, dermo-restitutive healing properties are due to their complex composition of which we are mentioning fatty acids (mainly unsaturated), compounds of vitamin F, sterols, amyrin acids, liposoluble vitamins.

Of hereinabove mentioned ingredients we used as a criterium of comparison the product composition in fatty acids.

The paper describes a comparative analytical study on a series of oils already used in cosmetic and pharmaceutical industry like: sea burdock oil, sunflower oil, olive oil, wheat germ oil and a new oil obtained by extraction from butterfly chrysalis.

Research was carried out by Gas Chromatography by comparing with various reference samples of fatty oils.

A30

A RAPID METHOD (HPLC) OF IDENTIFICATION AND DETERMINATION OF POLYPHENOL CARBOXYLIC COMPOUNDS IN HYDROALCOHOLIC EXTRACTS FROM HERBS USED AS RAW MATERIALS IN PHARMACEUTICAL AND COSMETIC INDUSTRIES

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Analytical studies were carried out as hydroalcohol extracts from Plantago, Calendulae and hazelnut buds.

Herbs extracts are more and more used to produce cosmetics and pharmaceuticals for topical use especially due to their complex chemical composition rich in biologically active principles.

An important class of biologically active compounds are also the polyphenol carboxylic acids.

The paper describes the analytical studies conducted with the view to processing and enriching the samples in compounds of interest (by extraction in liquid and solid phase) and the analysis conducted by Liquid Chromatography on reversed phase with hydrocarbonate stationary phase with insertions of phenyl groups, SUPELCOSIL 3DP type.

The detection was proceeded in UV at 280 nm.

Quantitative estimations were carried out for polyphenol carboxylic compounds present in the investigated samples based on previously plotted calibration curves.

So called "typical chromatograms" have been obtained for each studied extract; that is the ratios between the concentrations of these compounds (polypheol carboxylic acids) are within a well defined range %.

The results enable finding eventual forgeries with other cheaper types of extracts, more easily to be obtained.

A31

SUBSTITUENT EFFECT ON PROTOLYTIC CONSTANTS OF SOME NEW OXIMES-ACETYLCHOLINESTERASE REACTIVATORS

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Newly synthesized oximes, mono and bis imidazole derivatives, which promise to be more effective acetylcholinesterase reactivators than standard antidotes used, were investigated by spectrophotometric and electrochemical methods. The investigations of protolytic processes are very important for understanding of their behavior in biochemical systems. The electrochemical investigations confirmed the existence of overlapping equilibria, obtained by spectrophotometric method. Dissociation constants of those oximes were also obtained by numerical treatment of overlapping equilibria, using Lavendberg-Marquart least square method, and compared with the same for some similar compounds found to be very effective acetylcholinesterase reactivators. The distribution of ionic forms of the investigated oximes, as a dependence of pH values, was calculated from the obtained values of dissociation constants. The obtained results indicated that a lot of oxime anions will be available at physiological pH (7.4) and a relative increased ability to reactivate inhibited acetylcholinesterase could be expected.

A32

STUDY OF CHEMICAL COMPOSITION OF THE VEGETAL WAX OBTAINED UNDER THE HIPPOPHAE RAMNOIDES PROCESSING

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The paper shows the results of the studies conducted to find the chemical composition of the waxes obtained under Hippophae Ramnoides processing.

This composition was studied by various physical and chemical methods which are presented in this paper.

These methods indicate the presence of several bioactive substances as: α–, β-amyrin acids, carotenoids, liposoluble vitamins (D, E, F) phospholipids, phytosterols.

This complex composition full of natural bioactive compounds recommends Hippophae Ramnoides wax to be used in cosmetic and/or pharmaceutical industry.

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A33

NEW APPROACHES TO XENOBIOTIC'S BIOIDENTIFICATION IN FRESH WATER

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It is known that many of the currently used methods of bioassay provide only the integral evaluation of the pollutant's effects on different biological objects but not the determination of toxicants a origin. It is well known from the field of classical toxicology that with use of different pharmacological agents (antidotes) it is possible to decrease the toxic effect of the poisons. These drugs are widely applied when employing experimental animals (mice, rats, etc.), but it has not been used at all for hydrobionts, some of them have very high sensitivity to xenobiotics. As a background of discussed method, we have chosen a big amount of anticholinesterase (antiChE) compounds, different heavy metals, organochlorine pesticides and cyanides. The experiments were carried out with using of *Daphnia magna* and Medicinal leeches. The toxicity of xenobiotics was determined by the value of CL_{50}, a concentration of the compounds causing death to 50% of hydrobionts during incubation with toxicants for 24 hours. The antagonists of poisonings were added to the incubation mixture simultaneously. We discovered that in experiments with *Daphnia magna* and Medicinal leeches some M-cholinolytics (atropine, amyzile, cyclodole, etc.) reduce a toxic effect of antiChE compounds (organophosphates and carbamates). In the case of heavy metals poisonings the chelating agents (BAL, EDTA, Trilon B, sodium thiosulphate) were effective, for certain organochlorine poisonings - anticonvulsive drugs (diazepam, phenobarbital) and for cyanide poisoning - sodium nitrite, glucose. As far as these antidotes have a specific treatment action only against definite classes of pollutants, we have worked out the sensitive method for the xenobiotic's bioidentification. Such new pharmacological approach with use of hydrobionts as test-object have made possible to perform the general identification of different classes of xenobiotics.

A34

SIMULTANEOUS DETERMINATION OF PSEUDOEPHEDRINE AND DEXBROMPHENIRAMINE BY DERIVATIVE UV SPECTROPHOTOMETRY

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Simultaneous determination of pseudoephedrine sulphate (**PES**) and dexbrompheniramine maleate (**DPM**) by direct UV spectrophotometry is impossible, since they have overlapped spectra.The derivative UV spectrophotometric method proposed is based on the measurement of the first derivative spectra at 264.0 nm for **PES** and at 281.6 nm for **DPM**, respectively. $dA/d\lambda$ values at mentioned wavelengths arises only from the drugs mentioned and are free from interference of each other.

Stock solutions were prepared in 0.1 N HCl. Standard solutions containing 225-1050 μg/ml of **PES** and 10-60 μg/ml of **DPM** were prepared separately by diluting with the same solvent. The calibration equations are for **PES** : $y = -6.7\ 10^{-4}\ x - 1.3\ 10^{-4}$ ($r = 0.9998$) and for **DPM** : $y = -7.1\ 10^{-3}\ x - 5.6\ 10^{-5}$ ($r = 0.9996$) , respectively.

For the assay of DİSOPHROL ® containing 120 mg **PES** and 6 mg **DPM**, tablet powder calculated was dissolved in 0.1 N HCl. The solution was shaken for 30 min and filtered through a membrane filter (0.25 μ). After appropriate dilution, the first derivative spectra of the solution was measured at 264.0 nm and 281.6 nm against solvent blank.

The mean percentage recoveries of the drugs in standard mixtures were 100.4 % and 100.8 % and the assay results of the commercial preparation was 120.0 ± 0.7* mg and 6.1 ± 0.2* mg (*standard deviation) for **PES** and **DPM**, respectively. The results were compared statistically with a HPLC method and the difference was found to be not significant at $p = 0.05$.

A35

SIMULTANEOUS DETERMINATION OF PSEUDOEPHEDRINE AND DEXBROMPHENIRAMINE BY RATIO SPECTRA DERIVATIVE SPECTROPHOTOMETRY

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A new spectrophotometric method for the simultaneous determination of pseudoephedrine sulphate (**PES**) and dexbrompheniramine maleate (**DPM**) was proposed, since zero-order spectra of these drugs are overlapped. The absorption spectrum of the mixture between 230 - 290 nm is obtained and divided by the corresponding absorption spectrum of a standard solution of one of the components (divisor). Analytical signals of the first derivative of the ratio spectra obtained were measured at 244.2 nm for **PES** and 252.2 nm for **DPM**, respectively. Measurements at chosen wavelengths are free from interference.

Standard solutions containing 225-1050 μg/ml of **PES** and 10-60 μg/ml of **DPM** were prepared separately in 0.1 N HCl. As divisor, solutions containing 225 μg/ml of **PES** and 10 μg/ml of **DPM** were used, separately. The calibration equation of **PES** is $y = 5.2\ 10^{-4}\ x + 7.9\ 10^{-5}$ ($r = 0.9997$) and of **DPM** is $y = 7.1\ 10^{-3}\ x + 6.4\ 10^{-3}$ ($r = 0.9998$).

The mean percentage recoveries of the drugs in standard mixtures were 100.3 % and 100.5 % and assay results of DİSOPHROL ® tablets containing 120 mg **PES** and 6 mg **DPM** were 119.9 ± 0.8* mg and 6.0 ± 0.1* mg (*standard deviation) for **PES** and **DPM**, respectively. The results were compared statistically with a modified HPLC method and the difference was found to be not significant at $p = 0.05$.

A36

MICROMETHODS BASED ON THE ENERGY DISPERSIVE XRF FOR CLINICAL APPLICATION

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Methods for the element determination in blood and urine are widely used for clinical purposes. The element contents of the materials such as puncture biopsies, smears, scrapings and microlitre quantities of different body fluids are studied far rarer due to the lack of adequate micromethods for the analysis of similar samples. A system of micromethods based on the energy dispersive XRF was developed, tested and successfully used in Medical Radiological Research Centre. Micromethods are realised by means of portable and operationally reliable devices including radionuclides such as ^{55}Fe, ^{109}Cd, ^{241}Am, etc. as sources of exciting radiation. Characteristic rays are registered by a Si(Li) detector of 25 mm^2 to 100 mm^2 crystal area. The 25-year experience ensures to emphasise the most important achievements in the field of XRF application in medicine which are out of competition with the other analytical techniques.

In vitro instrumental XRF micromethods for the native element analysis are used to determine: — P and Ca in the material of puncture biopsy of the bone destruction focus for the purpose of differential diagnostics of skeleton benign and malignant diseases; — Zn in puncture biopsy material of the prostate indurated area for the purpose of differential diagnostics of adenoma and cancer; — Zn in the drop of the prostate secretion under conditions of out-patient elderly male examination to select subjects with increased risk of prostate cancer; — Fe, Cu, Zn, Br, and Rb in the mucosal biopsy samples taken at intracavitary endoscopic studies for the purpose of differential diagnostics of benign and malignant tumours; — Cu in the material of liver puncture biopsy to diagnose Wilson disease, — Fe in the blood drop for anaemia diagnostics; — I in puncture biopsy material of thyroid nodules for the purpose of tumour nature to be diagnosed.

In vitro instrumental XRF micromethods for exogenous element analysis are used to determine: — Br, as a stable exogenous marker, in the microsamples of saliva and blood for estimation of the extracellular water space; — I in the microsamples of blood to study and control the pharmacokinetics of iodine-containing radiographic contrast agents.

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A37

DETERMINATION OF TRACE METALS IN MEDICAL HERBS BY THE ICP-AES METHOD

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Many new synthetic medicines are widely available and employed nowadays. Nevertheless a so called natural medicine attracts a great attention. Medical herbs and their mixtures are used by millions people all over the world both for cure and prevention of many diseases. Nevertheless studies of trace elements in the medical herbs have been published rarely in comparison to analyses of other plant materials.

In the present study trace elements in the herbs and in their water extracts (infusion of herbs) have been determined. *Folium Menthae piperitae*, *Anthodium Chamonillae* and a mixture of some herbs have been investigated. The element concentrations were measured by the inductively coupled plasma atomic emission spectrometry method (ICP-AES). About 20 trace elements (e.g. Al, B, Ba, Cu, Cd, Cr, Mn, Ni, Pb, Ti, V, Zn) and matrix elements (Na, K, Mg, Ca) have been investigated. Two sample digestion procedures (a classical treatment in mineral acids with addition of H_2O_2 and a digestion in a high pressure microwave system) were used and compared. In addition to the trace metals, matrix elements were determined and interelement effects were investigated. Recovery examinations for selected elements were carried out. Importance of choice of analytical lines of some trace metals for quality measurements has been analysed. Metal concentrations determined here in the medical herbs and their water extracts have been discussed taking into account a medical point of view.

A38

APPLICABILITY OF THE ICP-AES METHOD TO STUDY A HEMODIALYSIS TREATMENT INFLUENCE ON BLOOD SERUM CONCENTRATION OF TRACE ELEMENTS

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Knowledge on trace element concentrations in biomedical media is very important for a variety of purposes. In the medical sciences such an information is crucial for initiation and evaluation of therapeutic treatment in deficiency or excess situation. Whole blood and serum blood belong to the most important clinical samples due to a special role of blood in human organism. In the present study concentrations of some trace elements (Ba, Sr, Al, Si, Cu and Zn) and Mg and Ca in blood serum of chronic renal failure (CRF) patients have been investigated. The serum was collected from patients at three different steps of medical treatment by means of hemodialysis procedure. The serum levels of trace elements in patients affected by advanced chronic renal insufficiency still on conservative treatment and then, in the same patients, 30 days after the beginning of regular hemodialysis treatment (both before and after the HD procedure) were examined. Healthy subjects (a control group) were taken for comparison. A high pressure microwave system was used to digest blood serum samples with the aid of concentrated nitric acid. The inductively coupled plasma atomic emission spectrometry (ICP-AES) method was applied here to determine the trace elements. Matrix effects in the analysed samples were investigated. The Wilcoxon sum test was used for statistical analysis of data. Both element concentrations and correlation between the elements were observed to be affected by the medical treatment for some elements. Applicability and limitations of the ICP-AES method to the blood serum analysis have been discussed.

A39

ANTAMANIDE - A POTENTIAL ANTI-CANCER SERUM

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Antamanide is a non-toxic antagonistic cyclic decapeptide from fungus Amanita phalloides. It is immunosuppressive (Intr. Appl. PCT. Pat. no. WO91/04269, 1991), and has been treated for interleukin-mediated edemas (US Pat. no. 5,278,143, 1994), and (US Pat. No. 5,466,667, 1995). It protects human lymphocytes against the toxin phalloidin (1).

When a normal cell by an idiomorphological process (2) is transformed into a parasitic cell, by penetration of the cell-membrane and utilization of amino-acids, then cancercell may start an uncontrolled proliferation (3). Cancercells are liberating a toxin, which is able to penetrate the normal cell-membrane (4). Antamanide protects the normal cell-membrane, however it loses its antagonistic effect after 2 hours. The mechanism is unknown. Antamanides composition of essential amino-acids and its nutritional value may be a key in the protective action of the normal cells.

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B1

FLOW INJECTION ANALYSIS FOR DETERMINATION OF MERCAPTOACETIC ACID AND OTHERS -SH COMPOUNDS WITH A NEW CHEMILUMINESCENT REACTION

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A new sensitive flow injection system with chemiluminescent detection was developed for mercaptoacetic acid determination. The analysis system is based on a new chemiluminescent reaction of mercaptoacetic acid with luminol in the presence of potassium ferricyanide. Several parameters that influenced the performance of the system are studied and discussed : flow rate, length of the dispersion delay, configuration of FIA system, carrier composition, pH, luminol concentration, ferricyanide concentration. The calibration graph was linear from $0.5 \cdot 10^{-2}$ % to $6.0 \cdot 10^{-2}$ % mercaptoacetic acid with correlation coefficient r = 0,9987. Relative standard deviation (rsd) for n = 10 was 2,37 %. The proposed analysis method allows a throughput of 60 samples per hour. The use of this system for the determination of some others -SH compounds (cysteine, mercaptoethanol, glutathione) was investigated.

B2

SPECTROPHOTOMETRIC DETERMINATION OF Cu(II) WITH SEQUENTIAL INJECTION ANALYSIS.

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A sequential injection system was designed for the spectrophotometric determination of Cu(II) in natural waters and effluents. Since the determination of Cu(II) has not yet been studied using spectrophotometry as method of detection with sequential injection analysis, the study was subsequently conducted. The determination of Cu(II) was conducted by reaction with sodium diethyldithiocarbamate (NaDDC). This reagent was chosen for the colour reaction as NaDDC is very selective for determining small quantities of Cu(II). Previous determinations of Cu(II) with NaDDC included the extraction of the formed product into an organic phase before the determination could be conducted. The current approach did not include extraction into an organic phase, but the direct measurement of the formed product in an aqueous medium as was done previously by Wang and co-workers [1]. Masking of possible interfering ions was accomplished by introducing a zone of EDTA/tri-ammonium citrate. The sequential injection manifold was optimized for maximum sensitivity and repeatability. Both the physical and chemical parameters of the sequential injection system were optimized. The physical parameters studied included the flow rate, holding coil and reaction coil dimensions, reagent-, sample- and masking agent zone volumes and the order in which the three zones were drawn up. The chemical parameters studied were: pH and reagent and masking agent concentrations.

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B3

SOLID-PHASE EXTRACTION COUPLED ON-LINE TO A FLOW INJECTION APPROACH FOR THE RAPID ENRICHMENT AND DETERMINATION OF MERCURY IN BIOLOGICAL SAMPLES AND SEA WATERS

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In the last decade, the determination of low levels of heavy metals in sea water has received special attention as a way to assess the early impact of human sources on the marine environment. Although ICP-AES has been widely applied to the determination of trace elements, sometimes suffers from problems with signal suppresion and clogging of the sample introduction system when the sample contains dissolved solid at concentration greather than 0.2% m/v. On the other hand, for extremely low analyte concentrations a preliminary preconcentration is commonly also used.

Preconcentration tecniques have been used in asociation with FI to determine trace heavy metals in sea water, after either ion exchange or chelating resin concentration because of their selectivity. Synthesis of chelating resins having good selectivity is subject of continuous interest and importance. This paper described a new FI assembly with on-line solid-phase extraction for mercury determination. Synthesis of a new chelating resin (silica gel funcionalized with methylthiosalicylate) (TS-gel) and its characterization by elemental analysis, IR spectrum, and XPS has been made. An automatic method is described for the determination of mercury in biological samples. The manifold used involve a chelating resin microcolumn charged with TS-gel , where the preconcentration of mercury take places,included within the sample loop of an injection valve of a FI system coupled on-line with ICP-AES. The metal was eluted from the column using a solution of 5% thiourea and mixed on-line with $NaBH_4$, mercury vapour was generated directly and separated via a gas-liquid separator.

Several physical and chemical variables affecting the FI system and preconcentration and determination of Hg were optimized. The calibration graph, obtained with a 60 s loading time at a sample flow rate of 8 ml min^{-1}, was linear over the range 5-1000 ng ml^{-1} of Hg(II). The accuracy of this automatic method was examined by the analysis of certified reference materials and sea waters.

B4

DETERMINATION OF TRACE AMOUNTS OF COPPER USING A FLOW-THROUGH SPECTROPHOTOMETRIC SENSORS

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Automatic methods based on flowthrough sensors offer interesting assets such as simplicity, rapidity, low cost and flexibility.

The current trend in applications of immobilization is towards placement of the reaction unit in the detection systems, which measures the change in the immobilized reagent or in the surrounding solution on reaction with the analyte.

Copper forms a stable yellow complex with 1,2-cyclohexanodione dithiosemicarbazone (CHDT). Several FI systems are described for determination of copper with this reagent, and retention of the coloured complex in the flow cell. C_{18} was used as sorbent material in the flow cell. The retention process is monitorized spectrophotometrically at 462 nm, at which the complex exhibits maximum absorption. The product was removed from the sorbent by DMF as eluent and the support was regenerated.

The different chemical variables involved in the process, as well as flow injection and spectrophotometric variables have been optimized using the univariate method.

The effect of various foreing ions on the determination of copper by the proposed method was examined under the optimun working conditions.

The calibration graph was linear up 50 ng ml^{-1} of Cu. The method provides better sensitivity and selectivity than in the batch procedure.

Also, by FI the sampling rate is greather, and it permits to process a higher number of samples per hour.

The proposed method was succesfully applied to the determination of copper in real samples with good agreement.

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B5

SCHLIEREN EFFECT CORRECTION IN FLOW DETERMINATION OF NITRITE AND NITRATE WITH PROFLAVIN SULPHATE

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An automated flow assembly is used to spectrophometrically determine nitrite and nitrate with good detection limits. The nitrate is reduced photochemically to nitrite by a low pressure mercury lamp. The samples are multi-inserted in phosphate buffer (pH = 6.8) containing an appropriate photolysis activator by means of a solenoid valve, flow through a long photoreactor and then merge a hydrochloric stream of proflavin hemisulphate. Finally, the absorbance is monitored at 328 nm.

Due to the radial refractive index gradients formed in the flow cell during samples travelling through it, the peaks recorded at low levels of analytes have a strange shape. This phenomenon is called Schlieren effect in the literature and is corrected usually by performing measurements at two wavelengths. However, this method of correction was wrong in this case. Thus, an original method having a solid theoretical support has been applied to analyse different kind of samples. It involves the subtraction of a smoothed record obtained for a blank solution from the ones of the samples.

The algorithm we propose here to eliminate the consequences of the Schlieren effect proves to be very accurate in connection with the standard addition method and with a previous cleaning step of the difficult samples by ionic exchange.

B6

DETERMINATION OF SULPHURIC ACID IN PROCESS STREAMS USING SEQUENTIAL INJECTION TITRATION

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Volumetric titrations are one of the most widely used techniques in the field of industrial process monitoring. The batchwise mode of performing titrations are time-consuming, labour intensive and reagent consumption is high. Most automated titrators are still based on batch operations and are therefore difficult to employ as process analysers. The introduction of continuous flow injection (FIA) titrations in 1977 overcame many of the above mentioned problems. Although many of the developed FI titration systems are used in process monitoring the high reagent consumption is one of its big disadvantages. Sequential injection analysis (SIA) is considered to overcome this drawback.

An SI titration system was developed for the titration of sulphuric acid with sodium hydroxide. In the proposed SI titration system the continuous base stream of the FI system was replaced by two base zones on each side of an acid sample zone in a distilled water carrier stream. The base zones contained Bromothymol Blue as indicator and the endpoint was monitored spectrophotometrically at 620 nm. The flow rate of the carrier stream, zone volumes of the acid and base and the concentration of the base were optimised. The SI titration system was applied to the analysis of sulphuric acid in process streams.

B7

IMMOBILIZATION OF CATALASE, HORSE RADISH PEROXIDASE AND UREASE INSIDE A POLYMERIC GEL

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Of the various immobilization methods available at present, entrapment of biocatalyst in synthetic polymer gel are quite advantageous due to the enzymes stability and to the fact they can be used in continuous processes. [1-3]

The entrapment of catalase, horse radish peroxidase and urease has been realized inside a polymeric gel obtained from poly-(amidehydroxy-urethane) (PAHU) and calcium acetate. The complex formation was found to proceed stoechiometrically M/PAHU=1:2 by turbidimetric titration. The resulting gel was characterized thermogravimetrically and by IR spectrometry.

Immobilization was achieved by conducting the complexation in teh presence of the enzyme which was found to be incorporated in the ramified network of the polymeric gel.

The characteristics of the reactivity and stability of the immobilized enzymatic product as to the native enzyme have been followed up function of the concentration ratio PAHU/Ca^{2+}, time, pH.

It was found that the optimum pH range of immobilized enzymes was wider than that of the native enzymes and self life of the enzymes was increased and they can be used repeatedly. It could be noticed that fixed catalase showed a higher thermal stability. The high value of Michaelis Menten constant (KM) for each enzyme can point to decreasing of the accessibility of the substrate at the active center and a possible conformational of chemical change of the enzymatic macromolecule.

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B9

A SOLID PHASE EXTRACTION SYSTEM WITH POLYURETHANE FOAM FOR NICKEL DETERMINATION BY CONTINUOUS FLOW ANALYSIS

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Polyurethane foam (PUF) has been used as sorbent to a wide variety of inorganic and organic compounds from different media by conventional methods, however it does not have been used in flow injection analysis(FIA). The first application of PUF in FIA was done recently by Jesus et al[1], to preconcentrate zinc and separate it from interferent metals, during zinc determination in biological matrices.

The present paper describes the use of a solid phase extraction system using a PUF column to separate interferences in the nickel determination by FIA with spectrophotometric detection. The separation is based in the retention of interfering ions as thiocyanate complexes on PUF column. Nickel does not form complex with thiocyanate and can be determinate with the 4-(2-pyridylazo)-resorcinol (PAR) as chromogenic reagent. In this way parameters such as: effect of the thiocyanate concentration and pH on nickel separation efficiency, sorption capacity of the PUF column, influence of the flow rates, PAR concentration and pH effect on the chromogenic reaction, minicolumn recuperation after separation, analytical characteristics and others were studied. The results demonstrated that nickel 0.50 $\mu g\ ml^{-1}$, can be quantitatively separated from iron and copper(200$\mu g\ ml^{-1}$), zinc(150$\mu g\ ml^{-1}$), cobalt(80$\mu g\ ml^{-1}$) and lead(5$\mu g\ ml^{-1}$) using a minicolumn containing 0.125 g of polyurethane foam. The detection limit was 77 $ng.ml^{-1}$ and the RSD was 2.63 %. A dynamic range from 0.27 to 5.00 $\mu g.ml^{-1}$ achieving a sample throughput of 30 samples per hour. The method was applied to determine nickel in certified brasses. The results showed accuracy satisfactory.

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[CNPq, FINEP, CAPES]

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B10

NICKEL AND ZINC DETERMINATION BY SOLID PHASE SPECTROPHOTOMETRY EXPLOITING DIFFERENT SORPTION RATES IN A FLOW INJECTION SYSTEM

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Solid phase spectrophotometry (SPS) associated with flow injection system (FI) has growing popularity due to its simplicity, high analytical throughput and low detection limits achieved. In this technique a solid matrix, which can be recovered with a chromogenic reagent, is employed to concentrate the analyte, and the absorbance is directly measured employing a simple spectrophotometer. In this work, FI-SPS system was applied to determine nickel and zinc concentration in copper based alloys based on the different sorption rates of these ions on the 1-(2-tiazolylazo)-2-naphthol (TAN) immobilized on a C_{18} bonded silica support. The Zn^{2+} sorption rate on the solid support is constant for flow rate ranging from 0.6 to 2.0 mL min^{-1}, but this fact is not observed for Ni ions. This cationic species shows na exponential reduction of sorption rate when the flow rate is increased. A flow system based on manual injector was developed to determine these ions by employing sequential injection of the same sample aliquots (625 µL) in two different flow rates (0.6 and 1.5 mL min^{-1}). The absorbance was measured at 598 nm, where both immobilized complexes present the maximum absorption. This process was applied to determine zinc and nickel in copper alloys in the range from 0.1 to 2.0 mg L^{-1} with good precision (RSD < 2%) and the sample throughput was 20 h^{-1}.

(CAPES, CNPq, FINEP, FAPESP)

B11

ON-LINE PRECONCENTRATION WITH INDIFFEENT COPRECIPITANTS IN FLOW INJECTION ANALYSIS

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The flow injection analysis is the best way for the environmental monitoring of natural waters. Among the different techniques of preconcentration, a filtration is not attractive procedure usually. The new way of high effective on-line microfiltration preconcentration in spectrophotometric flow injection analysis has been developed. The main idea consists in usage of special organic coprecipitation substances, which promotes to get a poorly soluble in water precipitation containing the element to be determined. The concentrate was filtered through on-line column filter and, further, was dissolved in the dose of dipolar aprotonic solvent. The simple one channel flow system with two periodically turned on peristaltic pumps was the best for mentioned hyphenated technique.

The determination of micro amounts of phosphorus existing as orthophosphates using microfiltration preconcentration – dissolution in flow analysis will be reported as an example. The orthophosphates were converted into the molibdovanadiumphosphate anions in strong acid media. The ones were precipitated as associates with cationic dyestuffs of different chemical origin. It was found that addition of indifferent coprecipitants rules to the good coprecipitation. The microfiltration column was packed with the polyprophylene fibres. Using the developed mehod, phosphorus in natural water was determined.

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B12

SPECTROPHOTOMETRIC DETERMINATON OF AMMONIA IN A CONTINUOUS-FLOW ASSEMBLY

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The frequent presence of ammonia in a wide variety of analytical samples of the environmental, clinical and industrial types, among others, has fostered the development of a large number of methods for its determination. Some FIA methods for ammonia are based on the Berthelot reaction; other isolate the gas by diffusion through a permeable membrane and use a conductimetric, spectrometric or potentiometric detector. As far as immobilized reagents are concerned, FIA methods for ammonia are mostly of the enzymatic type supporting the enzyme in controlled pore glass beads. There is one reference to the use of immobilized AgCl solid; the reactor preparation procedure is seemingly scarcely reproducible as it involves filling a column containing glass beads with freshly prepared AgCl once washed and dried at 110°C.

In this communication the silver is immobilized as AgCl on polyester resin; the silver released from the reactor forms a complex of high molar absorptivity, *viz.* [Ag(*o*-phen)2]'BPR, with Bromopyrogallol red (BPR) and *o*-phenanthroline. The immobilization procedure is fairly expeditious, simple and non-specific, and has found a new use for water-soluble solid reagents commercially available as fine powders - which hinders their direct use owing to the low working pressures involved - *viz.* as materials for making solid-phase reactors in a variety of configurations. The proposed method is quite selective for the types of samples studied; pharmaceutical formulations and commercial fertilizers.

Calibration graphs were linear over the range 1-20 mg/l NH_4^+. The limit of detection (S/N = 3) turned out to be 0.35 mg/l NH_4^+. Sample throughput was 48 h^{-1}. The study of interferences included both substances that may accompany ammonium ion in pharmaceutical preparations, and the typical cations and anions present in fertilizers.

B13

PHOTOCHEMICAL DERIVATIZATION OF DRUGS IN A CONTINUOUS-FLOW ASSEMBLY

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The analytical potential of photochemical reactions arises from the inherent advantages of this type of reaction over the reactions with chemical reagents. These advantages are most relevant when they are implemented with the FIA methodology, mainly due to simpler manifolds required, and the quick and economic procedures. The advantages of the photochemical reactions over its counterparts with chemical reagents are various. The reagent is the light (the photon) and its nature can readily be changed by modifying the working wavelength ("selectivity" by change of reagent); the reaction conditions are also readily changed by modifications on the power lamp ("sensitivity" by changing the concentration of the reagent) or the reactor configuration. On the other hand, there are many light-sensitive compounds including among them a certain number of pharmaceuticals. These reasons make it interesting to develop methods for the determination of pharmaceuticals with the aid of the coupled FIA-photochemical reactors.

This communication reports the results of a FIA procedure for the on-line photochemical derivatization of diethylstilbestrol with application to analyses of pharmaceutical formulations. In our laboratory, the spectrophotometricand fluorometric flow-injection determination of several drugs was achieved with the drug derivatized on-line photoreaction [1][2].

The proposed assembly is a mono-channel manifold in which the light source is nesting in the way from the injection valve and the spectrophotometric detector. The sample, injected in a carrier stream of aqueous dipotassium hydrogen orthophosphate flowing at 3.2 ml/min. The sample is irradiated as it flows through a PTFE tube (168 cm) helically coiled around the UV lamp and it resulted in a relevant change on the spectral properties of the drug. The monitorization is carried out at 330 nm wave-length. Experimental parameteres like the media or sample and carrier, type and power of the irradiation sources and flow assembly (sample volume, carrier flow-rate and reactor length) were carefully tested. The calibration graph was linear up to 60 µg ml^{-1} of diethylstibestrol with correlation coefficient 0.9990 and the reproducibility of the method, in RSD (%) was 2.6. The influence of the compounds which can be found in the pharmaceutical formulations accompanying the drug were also studied. The procedure was applied to the determination of diethylstilbestrol in some pharmaceutical formulations.

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B14

FLOW-THROUGH POTENTIOMETRIC DETECTOR FOR DYPIRONE DETERMINATION IN PHARMACEUTICAL PRODUCTS BY FIA

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The quality control of pharmaceuticals envolves the quantification of the active drug as well as other associated products. According to official monographs [1], dypirone is usually determined in acidic medium by using an iodometry at a controlled temperature. This is a time-consuming and lack of precision method. Owing to the large working range of ion-selective electrodes (ISE) and as FIA provides a practical way of performing on-line prior treatment of samples (pH/ionic strength adjustment), potentiometry coupled to FIA is an advantageous analytical procedure for the chemical control of drugs in pharmaceutical preparations [2]. A plastic tubular ISE membrane was prepared for dipyrone flow analysis in pharmaceuticals. The ISE membrane was applied directly on a non conductive graphite support and was based on dipyrone tetraoctylammonium (2.1 %w/w), dibutylphtalate (71.4%w/w) and PVC (26.5%w/w). Under limited dispersion flow conditions the ISE presented a linear response between $7x10^{-4}$ and $1x10^{-2}$ mol/L with a slope of 61 mV/dec . The reproducibility was ± 0.2 mV and the sampling rate about 60 /hour. The analytical usefulness of the constructed tubular detector was assessed by perfonming FIA determinations in some pharmaceutical preparations commercially available in Brazil. Results with a variation coefficient less than 2% were obtained.

Acknowledgements: This work was supported by LAFEPE, FACEPE, CNPq and UFPE

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B15

SAMPLE PREPARATION IN SEQUENTIAL INJECTION ANALYSIS. SPECTROPHOTOMETRIC DETERMINATION OF TOTAL PHOSPHORUS IN FOOD SAMPLES

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A sequential injection (SIA) procedure involving in-line sample preparation is proposed. A natural suspension or a slurry is transported together with nitric acid towards a home-made digestion bomb placed inside a microwave oven for subsequent digestion. The sample zone is stopped inside the oven and, after digestion, directed in reverse flow towards a holding coil and then towards detection. The formed air bubbles are efficiently wasted, thus avoiding the need for a debubbler unit, and the digestion bomb acts also as a mixing device promoting easy homogenization regardless of the number of required reagents.

As application, the spectrophotometric determination of total phosphorus in foodstuffs based on the molybdenum blue method was selected. The proposed system is very robust and yields reproducible measurements, (r.s.d. usually < 3%) for 20.0 - 400.0 mg L^{-1} P-PO_4. Results are in agreement with a conventional spectrophotometric procedure involving manual sample digestion.

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B16

SEQUENTIAL INJECTION SYSTEM EMPLOYING A SOLENOID VALVE . SPECTROPHOTOMETRIC DETERMINATION OF NICKEL IN STEEL ALLOYS

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Keywords: Sequential injection analysis; nickel determination; steel alloys

A flow system employing a six port solenoid valve to implement a Sequential Injection Analysis (SIA) approach is described. Assembling the flow set up with this device, reagent solutions should be sampled and added to the sample zone in a random way. The ability of the designed flow system to handle three reagent solution, was investigated in order to develop a spectrophotometric procedure for determination of nickel in acidic solution of steel alloys. A 486 microcomputer furnished with electronic interfaces and running a software wrote in the Microsoft Visual Basic 3.0 was employed to control direction of rotation and speed of the peristaltic pump, to switch the solenoid valve, and to perform data acquisition. In order to evaluate its ability spectrophotometric determination of nickel in steel alloys using dimethylglyoxime as chromogenic reagent was selected. This method require a oxidizing medium (peroxydisulphate solution), and a masking reagent for iron (triethanolamine solution), then, the proposed system should be able to handle four different solution. Once established the better operational condition, *i.e.*, pumping flow rate, time interval to switch on solenoid valves to load into the flow network holding coil aliquots of sample and reagents solution, etc., in nickel in acidic solution of steel alloys was determined. Results compared were well with that obtained by atomic absorption flame spectrometry. Others profitable features such as, a relative standard deviation of 1,7 % (n=6), an analytical throughput of 50 determinations per hour, a reagent consumption of 2.3 mg dimethylglyoxime, 12 mg peroxydisulphate per determination were also obtained.

CNPq, JNICT, FAPESP, PRONEX

B17

USE OF FLOW INJECTION MULTI-SITE DETECTION FOR BLANK SIGNAL COMPENSATION: SPECTROPHOTOMETRIC DETERMINATION OF AVAILABLE IRON IN SOILS

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Some spectrophotometric determinations involve the previous measurement of a blank signal, if samples intrinsically absorb at the set wavelength. Therefore, two measurements have to be performed for each sample, before and after the addition of the colour reagent.
In this work we describe a flow injection system using multi-site detection [1] to compensate the sample blank signal. A serial monitoring of the signal corresponding to the blank and the sum of the blank plus the analyte signal was achieved by relocating the detector in two different sites of the manifold, yielding two sequential signals for each sample. This approach was applied to the determination of available iron in soil extracts. This spectrophotometric procedure is based on the formation of a complex produced by the reaction between iron(II) with 1,10-phenanthroline, after reduction of iron(III) to iron(II) by ascorbic acid. In the manifold developed for this determination, the sample was mixed with a buffer and a reducing solution, and was directed to a flow cell to measure the blank signal. The colour reagent was subsequently added in a confluence, and the injector-commutator was switched to relocate the flow cell to allow the reading of the resulting plug. The net sample absorbance was obtained by subtraction of the two signals, after correction of the different dispersion values between the two measuring sites. The results obtained with this methodology were comparable to those obtained by the manual procedure. Relative standard deviations better than 4% were obtained, with a sampling-rate of 30 h^{-1}. The detection limit was 0.08 mg L^{-1}.

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B18

A FLOW INJECTION SYSTEM FOR GRAVIMETRIC DETERMINATION OF PHOSPHORUS IN FERTILIZERS

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A flow injection procedure based on precipitation of phosphorus as magnesium ammonium phosphate is proposed for phosphorus determination in fertilizers. The in-line formed suspension flows through a sintered glass mini-filter, the precipitate is accumulated on it and weighed inside the main flowing stream.

Sample and reagent solutions are simultaneously injected into two merging streams, and an ammonium hydroxide solution is added to the sample zone, before the main reaction coil. After sample measurement, an acidic solution is injected to promote solubilization of the precipitate which is wasted through the mini-filter. Influence of reagent concentrations, temperature, surfactant addition and available time for development of the precipitation reaction/crystal growth were investigated.

The proposed system is very stable and handles about 20 samples per hour which means; 120 æg Mg required per determination. Results are precise (r.s.d. < 2.3 %) and agree with those obtained by the spectrophotometric official method.

B19

COMPARISON OF FLOW AND SEQUENTIAL INJECTION SYSTEMS FOR FLUORIDE ASSAYS IN TOOTHPASTE AND BOREHOLE WATER, USING A F^--SELECTIVE ELECTRODE.

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The F^--selective electrode is an ideal detecting device for the determination of fluoride in flow systems, due to the accuracy of the analytical information obtained as well as to its low response time. The hydrodynamic properties of flow systems assured that the working pH is maintained at a constant value of 5.50 by using TISAB II. At this pH value, the fluoride-selective electrode is free of interferences, and can therefore successfully be used for the on-line determination of the fluoride anion in the manufacturing of toothpaste and in the on-line monitoring of borehole water. Flow injection and sequential injection systems are well-known as process analysers. This advantage was used in the designing of systems for fluoride anion assays. The results obtained for both FIA and SIA concepts will be highlighted comparatively.

B20

SOLID-PHASE REACTORS IN FLOW INJECTION SYSTEMS.

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FIA was originally conceived as a means of converting an analyte in a sample through reaction into a measurable species in a homogeneous medium. While this continues to be a norm in FIA work, there are an increasing number of procedures that involve solid-phase reactors because of their high versatility and potential. Incorporation of solid-phase reactors into the conduits of FIA systems involves normally reagents embedded on a solid-phase and having the sample-carrier zone flow through or over the reactor in order to facilitate reaction at the solid-solution interface. The use of solid-phase reactors incorporated into FIA manifolds may offer certain advantages. The reagent consumption is greatly reduced and the system is simplified with fewer junctions for blending of reagent -, sample - and carrier streams. Redox -, complex-formation - and enzyme reactors are amongst the most popular systems currently employed with the latter by far the most popular. The different types of solid-phase reactors, immobilization strategies, the function of the bed-reactor, advantages and disadvantages and some applications are outlined.

B21

DETERMINATION OF NITRITE, NITRATE AND BORON IN LIQUID FERTILIZERS WITH ON-LINE SEQUENTIAL INJECTION PROCESS ANALYSIS.

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The use of chemical analysers in the process control strategy represents a significant shift in the thinking of many process control engineers. Increasing pressure on the chemical manufacturing industry to produce higher quality products, in an economically viable and environmentally acceptable manner, increases the requirement to maintain strict control of plant conditions throughout the production process.

Sequential injection analysis, launched in 1990, is a technique that has a great potential especially for on-line measurements and in the monitoring of the environment, due to the simplicity and convenience with which sample manipulations can be automated. This technique was applied in the development of process analysers for the determination of nitrite, nitrate and boron in the manufacturing of liquid fertilizers. The proposed systems were evaluated with regard to response linearity, accuracy, precision, sample interaction, interferences and sampling rate and the results obtained will be outlined.

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B22

SIMULTANEOUS DETERMINATION OF TRACE AMOUNTS OF IRON(II) AND IRON(III) USING DPASV IN A FLOW-THROUGH CONFIGURATION ON A GC ELECTRODE.

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Simultaneous determination of iron(II) and iron(III) complexes of pyrophosphate can be done in a basic medium at a pH of 9.The peak potentials used were -0.8 and 0.5 V for Fe^{3+} and Fe^{2+} respectively. Linear calibration plots over a wide range were obtained. Detailed iron couple cyclic voltammetry studies, sample handling procedures, possible interferences and analytical applications of the method on real samples will be outlined. Evaluation of the method regarding detection limits and precision will be given.

B23

QUALITY CONTROL OF RESIDUAL CHLORINE IN WATER BY FLOW INJECTION ANALYSIS

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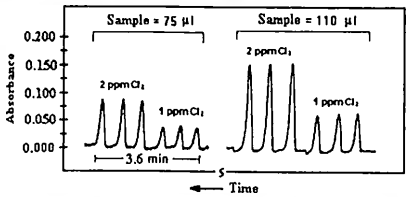
A rapid and reliable quality control procedure is described for residual chlorine determination in water samples by spectrophotometric-FIA. The chlorine is measured on the absorbance of the yellow complex formed through the orto-toluidine oxidation in hydrochloric acid medium [1]. A volume of 75 µl was injected for a sampling rate of 160 samples per hour. Carrier and reagent flow rates were measured; the effect of their ratio was controlled and a precision better than 0.5 percent was found. The sample volume influences the signals as a dispersion characteristic, rather than due to chemical kinetics [2]. The peak detection as a function of flow and analytical parameters was optimized by means of the simplex method. Chlorine concentration values in standard solutions against absorbance peaks height were fitted by least-squares with a determination coefficient equal to 0.999. The precision of the chlorine concentration determination was improved by weighted least-squares fitting. For a set of 300 samples, the confidence interval was of 95 %. The concentration of chlorine was determined in the range of 15 – 2250 ng.



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C1

FAST HPLC- SEPARATIONS ON POROUS STATIONARY PHASES

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The requirements in HPLC today are shifting more and more to faster separations. For instance, in process monitoring, environmental analysis, quality control in pharmaceutical industry and combinatorial chemistry a high sample throughput is a must. Fast separations can be achieved by using short columns packed with small particles.

This poster demonstrates that analysis times in gradient separations can be dramatically reduced even on porous supports. A decrease of the column length and an increase of the gradient steepness lead to faster analysis with only an insignificant loss in the performance of the separations.

Shorter analysis times are resulting in a higher productivity of the HPLC devices as well as to a higher mass sensitivity of the analytes. These are important facts particularly in environmental analysis where analytes often are present in small quantities only and, therefore, are hard to be determined.

The concept to increase the speed of analysis is demonstrated in two examples: (1) the separation of water soluble vitamins and (2) the determination of phenols included in EPA- methods 604 and 625.

(1) For the separation of the water soluble vitamins a ProntoSIL AQ column was used. This column shows an excellent performance and peak shape for all applications where the eluent has to contain a high amount of water.y

(2) For the separation of the phenols a new column of ProntoSIL line was applied. This support was especially designed for this application.

C2

GAS CHROMATOGRAPHY AND THERMODYNAMICS OF XYLENES AND ETHYLTOLUENES SEPARATION ON 4-[(4-CHLOROBENZYL)OXY]-4'-CYANOAZO-BENZENE LIQUID CRYSTAL

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Investigation of liquid crystals as stationary phases in packed and capillary columns were presented by G.M. Janini and other workers [1-3]. Difficult separations of geometric isomers of polyaromatic hydrocarbons and m-, p-, o- isomers were performed on liquid crystals in nematic, smectic or in solid state temperature range.

In this work, the separation of m-, p-, o- xylenes and m-, p-ethyltoluenes was studied on packed column with 2.5% 4-[(4-chlorobenzyl)oxy]-4'-cyanoazobenzene on Chromosorb W HP 100-120 mesh. Temperature domain for the separation of m-, p-, o- xylenes was found to be 125-85°C, and for m- ethyltoluene and p- ethyltoluene 160-85°C, both at cooling. By GC measurement, some modifications of transition temperatures between mesophases have been observed, most probably, due to influence of support on the liquid crystal.

Specific retention volumes, activity coefficients at infinite dilution and partial molar excess free energies were determined for xylenes and ethyltoluenes, at different temperatures. These values were compared to those of other compounds: alcohols, n- alkanes and ketones.

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C3

SEPARATION OF LORAZEPAM ENANTIOMERS BY MICELLAR ELECTROKINETIC CAPILLARY CHROMATOGRAPHY WITH BILE SALTS AND MALTODEXTRINS AS CHIRAL SELECTORS

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Enantiomers are isomeric forms of the same compound which differ only in their spatial orientation but their physical properties are identical. In this work we proposed the separation of the enantiomers from lorazepam by using sodium cholate and maltodextrins as chiral selectors. Bile salts are natural, anionic and optically active surfactants found in biological components. The most commonly bile salts used in MEKC enantiomer separation are sodium cholate, sodium deoxycholate, sodium taurodeoxycholate and so on. It is believed that solutes enter between the layers of the micelle which form helically shaped agglomerated in solution.

Some 1,4-benzodiazepines were sucessful separated by MEKC using bile salts[1]. At low temperature (20°C), peak splitting due to enantiomer separation of lorazepam was found. This behaviuor was eliminated by rasing the temperature up to 33°C. However, if it want to improve the enantiomeric resolution a temperature lower than 20°C and/or different electrolite composition sould be employed in the MEKC separation.

The most characteristical chemical parameters: buffer composition, differrent bile salts and percentage of maltodextrins or starch are studing. Actuality, we are employing starch as chiral selector because it is less expensive and it permits to work at 25°C without a decrease in resolution. Rather, the electropherograms present high level of baseline noise.

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C4

PHARMACEUTICAL, MEDICAL AND BIOTECHNICAL APPLICATIONS BY CHEMILUMINESCENT NITROGEN DETECTION (CLND)

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Pharmaceutical, medical, and biotechnical analysis involves the separation power of High Pressure Liquid Chromatography (HPLC) and Supercritical Fluid Chromatography (SFC). Of the numerous detectors available for both HPLC, SFC, many rely upon chromaphores, either initially present on the target compounds, or placed on the target compounds by derivatization. If high purity standards are not available for each target compound, the detector response can only be roughly estimated. In biological matrices, purification of a compound may require weeks or even months of careful, labor intensive work to obtain enough compound to calibrate the detector. A truly equimolar detector responds the same for all compounds and offers an alternative method for rapid quantitation. The Chemiluminescent Nitrogen Detection (CLND) can easily and efficiently quantitate nitrogen-containing compounds. Since over ninety percent of all pharmaceutical compounds produced in the last 10 years have a least one nitrogen, a universal nitrogen detector rapidly quantitates most pharmaceutical and biotechnical compounds in crude and purified samples. Examples of the analysis of antibiotics, liver extracts, polyamino acids, and other applications will be discussed. Applications of paired detectors such as HPLC-MS-CLND and HPLC-UV-CLND will also be presented.

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C5

APPLICATION OF PYROLYSIS-GAS CHROMATOGRAPHY TO THE CHARACTERIZATION OF NATURAL RESINS USED IN ANCIENT PAINTING FROM VALENCIAN COMMUNITY (SPAIN)

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Pyrolysis-Gas Chromatography (Py-GC) is a quick and straightforward way of analyzing solid materials. Pyrolysis fragments large molecules such as natural polymers produces smaller volatile compounds which may be analyzed by GC. This fragmentation is reproducible, and it produces a chromatogram that is characteristic for the macromolecules which were pyrolyzed. Its application in conservation has been severely limited due to the compositional complexity and extremily limited sample size of the materials presented for examination. Similarly, the ausence of reliable reference compounds for identification of major materials in works of art has led to achieve comparative studies on actual artifacts. The use of Pyr-GC let us obtain chromatograms of aged samples of terpenoid resins (Copal, Dammar, Mastic; Shellac, etc) usually used as varnishes and coating films. This subject deals with the first step of this contribution. The method proposed in this paper consists on the extraction of a small sample of protective layer using a glass wool swab soaked in an appropriate solvent. The glass wool is inserted into a quartz tube to be pyrolyzed (Pyroprobe 1000, CDS Analytical). Different temperatures of pyrolysis are applied secuentialy (400°C, 600°C, and 800°C) with and without a methylation agent (tetramethylammonium hydroxide). The pyrolysis products are isolated in a gas chromatograph (HP-6890) using a capillary column (HP-1710, 30mx0.25mm, film thickness o.15(m). The suggested method has been applied successfully to the identification of natural resins of mediaeval panel paintings from the Valencian Community in Mediterranean coast.

C6

Stacking from the Sample Stream in Capillary Electrophoresis

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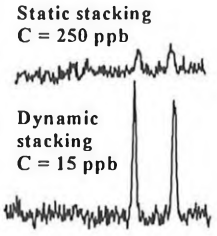
Recent developments in non-conventional sample introduction in capillary electrophoresis (CE) have focused on the possibility of forcing the sample stream to pass the separation capillary inlet. In the work described here, the development and testing of a pneumatically driven computerised sampler for CE is described [1] . In all other systems, the sample is said to be introduced by well-known electrokinetic phenomena during the time when sample is resident at or passes the capillary inlet. It is also possible that, since sampling requires periodic flushing of the input channels by sample solution, simply the pressure applied to the sample solution could introduce sample.

In our experiments, this feature of stream samplers was accompanied by a reduction of detection limits if the sample solution conductivity was lower than that of the running buffer. This effect results from a column-head, field-amplified, sample stacking phenomenon and it occurs over the entire volume of the input channel. We observed also that detection limits could be improved further if the stacking was performed from the flowing sample stream (*dynamic stacking*) compared with the situation when the sample is stagnant during the stacking (*static stacking*) (see Figure). Overall, the detection limits can be reduced by more than two orders of magnitude compared to the common methods of stacking from a stationary sample. The detection limits achieved for two alcylbenzylamine cations were 1.25 ppb (5 nM) using UV detection. The mechanism responsible for the improved detection limits obtained by dynamic stacking may be that sample is drained off otherwise from the input channel.



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C7

FRITLESS CAPILLARY ELECTROCHROMATOGRAPHY

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Capillary electrochromatography (CEC) has become a widely accepted analytical technique with high resolving power. In order to retain the stationary phase in a CEC capillary, frits are usually fabricated by locally sintering a narrow band of the reversed phase packing with a heating filament.

Frit preparation is one of the crucial steps in the fabrication of CEC capillaries, since the sintering procedure may induce changes in the surface characteristics of the stationary phase. This can cause local differences in the electroosmotic flow and result in the formation of air bubbles.

Here the applicability of capillary electrochromatography in a fritless column is demonstrated. The inlet side of the capillary was tapered to retain the packing material. No frit was required at the outlet side, taking into account that the reversed phase material is negatively charged, and thus, maintained by the electrical force when voltage is applied.

Both porous and non porous ODS materials (3µm and 1.5µm) were tested and compared . The stability of the column was investigated in a wide range of mobile phase compositions, varying the acetonitrile content, the pH value, and the ionic strength. Highly efficient separations were achieved, in a repeatable manner.

Aiming towards coupling of CEC with MS, the capillary was successfully tested without pressurization at its ends.

C8

SEPARATION OF (±)-METIPRANOLOL AND ITS ADMIXTURES BY CAPILLARY ZONE ELECTROPHORESIS

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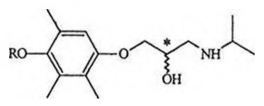
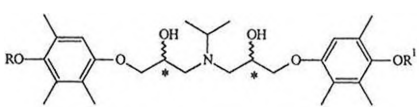
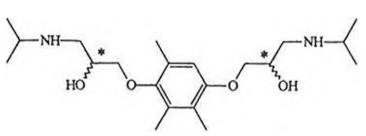
(±)-Metipranolol (1), an aryloxipropanolamine produces an antihypertensive effect by blocking adrenergic receptors. Separation of 1 and its admixtures 3 - 6 was studied by capillary zone electrophoresis (CZE). All studied compounds were resolved in a plain acidic buffer, however, addition of cyclodextrins was necessary to enhance resolution of peaks of 1 and 2 in samples with mass ratio of 1 : 2 above 20. (±)-1 was separated into its enantiomers by crystallization of diastereomeric salts with R- or S-mandelic acid or the enantiomers were synthesized from the appropriate chiral epoxides. Because separation of enantiomers of 1 by CZE was only partial and substantially higher was that of compound 2 , the enantiomeric purity of 1 was determined after its hydrolysis and subsequent analysis in a bare silica capillary (40 cm x 50 µm), 80 mM triethanolamine/acetic acid, pH 5.7, 20 mM carboxymethylated β-cyclodextrin, 25 kV and 17°C. Also diastereo-isomers of 3 and 6 were resolved under these conditions.



1 R = CH_3CO
2 R = H



3 R = R1 = CH_3CO
4 R = H R1 = CH_3CO
5 R = R1 = H



6

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C9

STUDY OF COMPLEXATION REACTIONS BETWEEN DICYCLO HEXANO-18-CROWN-6 AND Mg^{2+}, Ca^{2+}, Sr^{2+} AND Ba^{2+} CATIONS IN MIXED SOLVENT USING CONDUCTOMETRY METHOD

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The interaction between Mg^{2+}, Ca^{2+}, Sr^{2+} and Ba^{2+} cations with DCH18C6 ligand was studied in water/acetonitrile (AN) binary system using conductometric method. The obtained data show that in all cases the stoichiometry of complexes is 1:1. The formation constants of 1:1 complexes were measured at different temperatures. The value of enthalpy and entropy parameters ($\Delta H°_c$ and $\Delta S°_c$) of complexation reaction were obtained from temperature dependence of formation constants by using the *van't Hoff* plots. The results obtained show that the values of $\Delta H°_c$ and $\Delta S°_c$ depend on the solvent compositions and all of the complexes are entropy stabilized. The $(DCH18C6.Ca)^{2+}$ complex is enthalpy stabilized, but other complexes, *i.e.* $(DCH18C6.Mg)^{2+}$, $(DCH18C6.Sr)^{2+}$ and $(DCH18C6.Ba)^{2+}$ are enthalpy stabilized.

The order of selectivity of DCH18C6 ligand for alkaline earth metal cations in different percents of AN with the exception of 64.0 mole percent of AN is:

$$Ba^{2+} > Sr^{2+} > Ca^{2+}, Mg^{2+}$$

but in 64.0 mole percent on AN the stabillity of complexes is reversed:

$$Ba^{2+} < Sr^{2+} < Ca^{2+}, Mg^{2+}$$

In general the stability of complexes depend on the solvet composition and in the case of Mg^{2+} and Ca^{2+} cations the complex formation constants of the appropriate complexes increase with increasing of AN in binary systems, but in the case of Sr^{2+} and Ba^{2+} cations the stability of their complexes decreases with increasing the concentration of AN in AN/H_2O binary mixtures.

C10

SYNTHETIC POLYPEPTIDES WITH MOLECULAR RECOGNITION PROPERTIES OBTAINED BY TEMPLATE POLYMERIZATION IN AQUEOUS MEDIUM

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In the last years the scientific community devotes a lot of strenghts to developing new synthesis of artificial structures with molecular recognition toward specific ligands neglecting the traditional organic synthesis and choosing alternative technique such as the molecular imprinting.

We studied the feasibilty of oligopeptide mixtures with binding properties toward the steroid hormone estradiol, using the technique of template polymerization. This approach is completely new as we worked in aqueous medium without the formation of a rigid structure.

The mixtures of aminoacids were polymerized in aqueous enviroment in presence of a condensing agent and of the templating molecule, estradiol. After the complete removal of the steroid hormone from the oligopeptide mixtures by ion-exchange chromatography, we characterized the oligopeptide mixtures by HPLC, spectrophotometric techniques and competitive immunoassays. Beside we obtained by ion-exchange chromatography three fractions of the oligopeptide mixtures with different binding and chemical properties.

All the mixtures are characterized by a mean molecular weigth in the range 1-2 KD corresponding to amonoacid sequences of 8-16 units.

We evaluated the effect of the polymerization conditions, as reaction time and initial aminoacid mixture composition, the experimental conditions of the competitive immunoassay, as pH and ionic strenght, and the binding specificity on the affinity constants. All the binding measurements were compared to analogous ones performed on oligopeptide mixtures polymerized in absence of estradiol.

The experimental results shows the presence of a specific molecular recognition behaviour of all the template oligopeptide mixtures with affinity constant up to 10^9 M^{-1}.

C11

MIXED STATIONARY PHASE POLYMETHYLSILOXANE - ACRYLIC ACID: SEMIEMPIRICAL QUANTUM CHEMICAL AND GAS CHROMATOGRAPHIC CONSIDERATIONS

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By means of the SCF MO LCAO PM3 method the standard heats of formation, entropies, free energies of formation, and the molecule dipole moment for acrylic acid (AA) in the *s-cis* and *s-trans* conformations, as well as for the system $(CH_3)_3SiOSi(CH_3)_2OSi(CH_3)_3$ representing a fragment of polydimethylsiloxane OV-1, have been calculated. It has been shown that the AA conformers are of practically equal probability from the viewpoint of the ΔH_f and ΔG_f values. The enthalpy reaction profile of the *cis-trans* isomerization has been obtained. An evidence has been provided that the rotation around the ordinary C-C bond is fairly free, the barrier (ΔH_f and ΔG_f) not exceeding 1.3 kcal/mol.

Molecular spatial parameters, molecular flexibility and polarity of AA proposed as an additive to OV-1 as gas chromatographic (GC) stationary phase (SP) appear to work well in fitting the corresponding SP characteristics. The modified SP formed demonstrates a complementary GC behaviour in the cases of test hydroxylic compounds used. Using packed columns with OV-1 certainly modified with appropriate amounts of AA, a simplified GC technique for the rapid determination of benzoic and heptanoic acids in aqueous solutions has been elaborated.

C12

PHARMACEUTICAL AND PETROLEUM APPLICATIONS BY SULFUR CHEMILUMINESCENCE DETECTION (SCD)

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Sulfur analysis is a necessary and sometime difficult analysis in both the petrochemical and pharmaceutical industries. Many different separation methods and detectors have been developed to identify and quantitate sulfur. Until now, sulfur analysis has been limited to Supercritical Fluid Chromatography (SFC) or Gas Chromatography (GC). Antek Instruments, Inc first introduced Sulfur Chemiluminescence Detection (SCD) in the early 1980's as a GC and SFC detector. This presentation introduces a proven technology (SCD) adapted to a powerful separation technique (HPLC). While many of these methods rely on chromaphores, either initially present on the target compounds, or placed on the target compounds by derivatization to identify and quantitate the compound of interest, SCD is specific to sulfur, thus is not compound dependent. Detectors based on chromaphores require high purity standards available for each target compound, so that the detector response can be calibrated. In complicated matrices such as petroleum products or biological matrices, isolating enough material to calibrate the detector may take weeks or months. The SCD offers rapid quantitation of sulfur containing compounds. Due to the equimolar detector response, sulfur can be quantitated without regard to the structure of the target compound. In many cases, a single, readily available, sulfur standard can be used to calibrate the detector, and allow rapid identification, and quantitation of all sulfur containing compounds in the sample. Examples of the analysis of antibiotics and high temperature sulfur compounds in crude oil will be discussed.

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C13

ADVANCED MICROFABRICATED POLYMER DEVICES FOR ANALYTICAL APPLICATIONS

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In the last years, the Laboratoire d'Électrochimie has shown expertises in the microfabrication of analytical devices by photoablation of polymers. This interesting technique allows the micropatterning of surfaces with different properties. The control of the machining parameters allows the generation of different charges, cristallinities, roughness or even conductivity. Simple mechanisms have also been developed for the patterning of proteins and electrodes on polymer surfaces with micrometer resolution.

These elements have been integrated in µfluidic networks for different bioanalytical purposes. Capillary fill enzyme assays with electrochemical detection are performed as an element of a fast immunoassay. Electroactive surfaces in a correct geometry (placement of anode, cathode and reference electrode) allows electrochemical measurements with microscopic characters (thin layer cell) with a minimal IR drop.

Acidic surfaces integrated in µchannels allow the generation of electroosmotic flow when placed in a high voltage field. The surfaces exhibit a zeta potential growing with the pH, as the surface is deprotonated. Polylysine could be used in order to inverse the electroosmotic flow. The fabrication of network parts like cross or double T injectors allows the dispensing of 100 pL on separation columns. A large effort has been made in the control of the current/mass uncoupling. Control of the geometries and surface charges allows the mass current to be extracted from the high voltage area in order to be dispensed in the electrochemical cell or in a µwell. The coupling of these elements enables the injection, fast separation and on line detection of electroactive species on a microchip.

Separation of biomolecules on µ-devices has also been a field of great interest due to its fast and high throughput characteristics. This is of special interest for proteome analysis which involves the fast and reliable separation and identification of numerous of proteins. We present here first results on the separation of model protein mixtures in photoablated polymer devices in free flowing solution. Different immobilized pH values were established in the capillaries using polyacrylamide gels and immobiline reactives.

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D1

OPTIMIZATION OF THE COMBINATION ION CHROMATOGRAPHY / MASS SPECTROMETRY USING AN ELECTROSPRAY INTERFACE

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Over the years, investigations into improved detection techniques have remained an important area of research in ion chromatography (IC). The progress made so far has resulted in advances in detection sensitivity, selectivity and convenience. Universal detection by a bulk property detector based on conductivity measurements is still the preferred mode, but new applications might benefit from detection techniques that also provide information about identity, structure or elemental composition of the analytes. Therefore, mass spectrometric detectors, which became quite important in HPLC even for routine applications, are also attractive in IC for positive identification of inorganic and low-molecular-mass organic ions.
Currently, the most powerful interface between IC and MS is the electrospray interface. Although this interface has become quite popular for HPLC applications, its use in IC ist not yet fully exploited. Therefore, a systematic investigation has been carried out to compare the performance of this detection technique with suppressed and non-suppressed IC. In both cases, mobile phases containing up to 20% organic solvents and flow rates in the range between 50 and 200 µl were used; the low flow rates require the splitting of the eluent after the column or the use of microbore and capillary columns.
An optimized non-suppressed system was established on the basis of a citrate electrolyte as mobile phase; for anion separations, the detection limits were at about 1 ng in the MS. Suppressed systems improved the detection limits by a factor of 2 to 3.
In addition to IC separation techniques, electrochromatography was investigated in combination with MS detection. Addition of a liquid phase at the end of the capillary (sheath flow) resulted in a considerable versatility with respect to eluent compositions compatible with the MS. A critical comparison of detection limits for MS detection in IC and electrochromatography has been carried out for anionic as well as cationic species.

D2

ASSESSMENT ON THE APPLICABILITY OF TWO-STEP LASER MASS SPECTROMETRY FOR THE ANALYSIS OF PESTICIDES

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Two-step laser mass spectrometry (L2MS [1]) offers unique advantages such as the redundancy of sample preparation and very low detection limits. We attempt to make use of these specific benefits in applying L2MS to the field of environmental analytical chemistry.

After desorption of the analytes with an IR laser pulse, resonance enhanced two-photon ionization (1+1 REMPI) is performed with a tunable UV laser. The efficiency of this ionization mechanism greatly varies from analyte to analyte, and is of crucial influence on the limit of detection (LOD). Whereas the photoionization ion yield has been investigated in detail for PAHs, it remains uncharacterized for most other environmental pollutants. Therefore, we currently determine ion yields of various pesticides relative to Benz(a)anthracene (BaA), a well characterized analyte with a LOD around 1 attomole, by a concomitant ablation from PVC membranes [2]. Initial results indicate that for a set of naphthyl-pesticides, namely Carbaryl, Naphthyl Acetic Acid, and Naphthyl Acetamide, ion yields are about five times lower than for BaA. Other pesticides, such as Carbofuran, Warfarin, and Isoproturon, exhibit much lower numbers (<< 1 %). Still other pesticides are hardly ionizable with nanosecond laser photoionization in the mid UV (e.g., Atrazine, Metamitron, and Metsulfuron methyl). However, ion yields might be increased by using shorter ionization laser pulses. Conclusively, the determination of ion yields is a straightforward tool to judge the feasibility of L2MS for the analysis of individual environmental pollutants. Clearly, L2MS has the potential for the trace analysis of PAHs and pesticides with similar ion yields in various kind of environmental samples.

The data obtained is useful for the application of L2MS to the analysis of aqueous water samples in combination with modified Solid Phase Micro Extraction (SPME), Solid Phase Extraction (SPE) using extraction disks, or by direct analysis of frozen water samples, as currently pursued in our laboratory.

[1] Voumard, P., Zhan, Q., and Zenobi, R. 1993. Rev. Sci. Instr. 64 (8), 2215-2220.
[2] Haefliger, O.P., and Zenobi, R. 1998. Rev. Sci. Instr. in press.

D3

TIME-RESOLVED ANALYSIS OF PARTICLE-BOUND AROMATIC COMPOUNDS IN URBAN AIR USING TWO-STEP LASER MASS SPECTROMETRY

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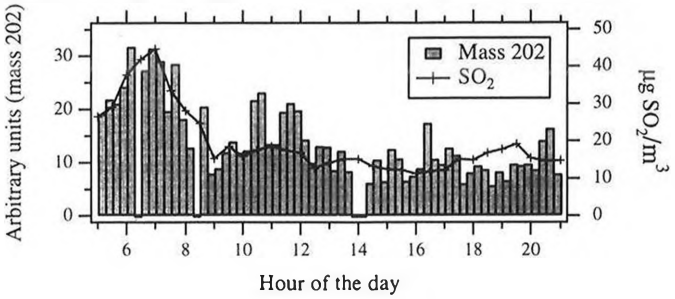
Two-step laser mass spectrometry (L2MS) is used for the direct analysis of selected compounds in complex mixtures such as environmental samples. Two lasers are used to perform desorption and soft ionization followed by time-of-flight mass analysis in a mass spectrometer. The mass spectra are dominated by intact parent ions of the analytes. Major advantages are the detection limit in the attomole range and minimal or no need for sample preparation.We report here on the application of L2MS to the time-resolved analysis of polycyclic aromatic compounds (PACs) adsorbed on urban aerosol particles. 1 cm^2 pieces of quartz fiber filter mounted on specifically designed filter holders were used for both sampling (20 L/min) and measurement in our L2MS instrument immediately thereafter. Temporal variations were recorded with a time resolution of 15 minutes. The figure below shows for example the development of the ion signal at mass 202 (pyrene, $C_{16}H_{10}$, and isomers) recorded downtown Zürich on February 3rd, 1998. The similarity with the curve measured for SO_2, which is known to be generated by local heating, may suggest that this is also an important source of PACs.



D4

NEW FRAGMENTATION PROCESS OF CARBONYL COMPOUNDS WITH A δ-SILYL GROUP IN MASS SPECTROMETRY

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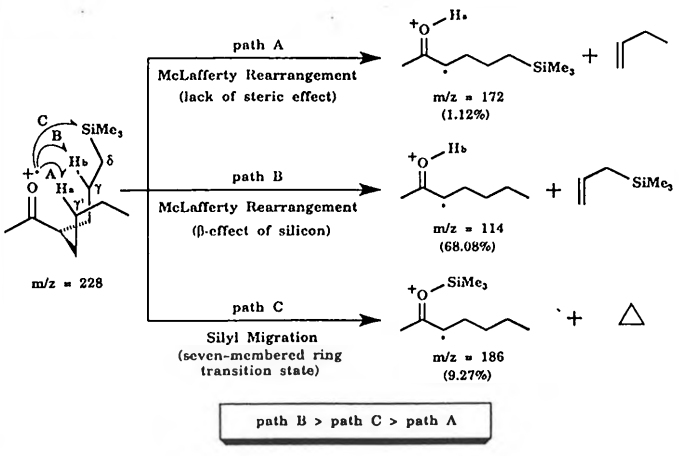
Electron-impact induced fragmentations in the gas phase were performed in mass spectrometer on δ-silyl aldehydes, ketones, thioketones, carboxylic acids, and acetates. All of these compounds showed significant silyl migration through a seven-membered ring transition state. For ketones and acetates, this silyl migration process may overwhelm the McLafferty rearrangement, which involves a six-membered ring transition state. Its feasibility is greater for acyclic than cyclic carbonyl compounds. The migration proceeds easier for a smaller than a bigger silyl group.



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D5

MS SPECTRA IN THE ANALYTICS OF ACETYLENIC γ-GLYCOLS

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Studies of a series of 15 sym. and asym. diols with various substituents ($R_1R_2C(OH/D)C{\equiv}C(D/HO)CR_3R_4$, Ph, p-halogen Ph, alkyl, H), both OH as well as OD, were carried out to determine the analytical usefulness for rapid differentiation - of the mode of substituent distribution at 1,4 position of a butine system, structure of substituents. Attention has been drawn on the processes: OH (OD), H_2O (D_2O) elimination and decarbonylation, especially in the initial stages of fragmentation.

General conclusion - already simple fragmentation permits to establish the type and number of substituents, and the distribution results from the decomposition regularities observed.

Some of the relationships observed - initial fragmentation, proceed analogously for diols of a predominant number of phenyl substituents (H_2O/D_2O elimination, decarbonylation accompanied with 2×Ph rearrangement), - in diols with two alkyl groups (also three, four), the fragmentation starts from the elimination of one such group (then - H_2O/D_2O, CO), - an effect of the deformation of angles in the molecule by the bulky groups on the fragmentation takes place, - the diol acetylenic bond has the ability of keeping Ph, Me, H.

D6

DETERMINATION AND CHARACTERIZATION OF CHEMICAL ADMIXTURES FOR CONCRETE BY MASS SPECTROMETRY (LC/ESI-MS, MALDI-TOF AND TOF-SIMS)

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Superplasticizers (high range water reducing admixtures) such as sulfonated naphthalene formaldehyde condensates (SNF) are widely used to improve the flow properties of fresh cement mixes and to produce low water/cement ratio concretes of high strength. Determination of the composition of these compounds is a crucial step towards understanding how admixtures work and how their properties can be improved. Simultaneously, suitable chemical analysis allows to determine admixture content of concrete samples as well as to study how superplasticizers are leached from concrete. Data on characterization of commercially available superplasticizers as well as on concrete samples containing superplasticizers using methods such as electrospray mass spectrometry (ESI-MS), liquid chromatography/electrospray mass spectrometry (LC/ESI-MS) and time-of-flight mass spectrometry (MADLI-TOF, TOF-SIMS) will be presented. Applying these techniques to sulfonated naphthalene formaldehyde condensates (SNF), individual oligomers can be separated and analyzed [1]. Simultaneously, by-products such as mono- and disulfonated naphthalene sulfonate monomers can be detected easily. It will be demonstrated that concretes containing SNF can be identified quickly by LC/ESI-MS. Currently, further analytical methods such as GC/MS, TGA, TG-MS and GPC are investigated. The combination of these analytical approaches will allow to carry out studies geared towards determination of the mechanism of action and the fate of admixtures in fresh concrete.

[1] M. Kohler, N. V. Heeb and P. Schmid, Tagung „Bauchemie" der Gesellschaft Deutscher Chemiker (GDCh), München, 1997.

D7

APPLICATION OF THE LEAST-TRIANGLE METHOD FOR CALIBRATION IN ATOMIC-EMISSION ANALYSIS

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The least-square method (LSM) has been applied for the calculation of linear calibration in atomic-emission analysis (AEA), despite its instability to the presence of outliers and the distortion of the initial data. This is explained by the computational simplicity of the method. If together with LSM we use the "jack-knife" method, the computational procedure becomes more resistant, but this leads to increasing of iterations and the enlargement of the time consumption. Other statistical methods of the estimation can be used too [1].

The least-triangle method (LTM) was applicated as the alternative of LSM for the calibration of AEA impurities in the reference standard materials of metallic silicon. LTM is used as the criterion of minimisation of the sum of the oblong triangle squares. The method is simple enough for calculations.

Settlings were fulfilled for the analytical lines of Fe, Ti, Al, Ca in the arc spectra (spectrograph DFS-458, automatic microdensitometer IFO-462).

The results received by LSM and LTM are compared.

The LTM-estimates proved to be more resistant to the errors of measurements.

[1] Robustness in Statistics, 1979, Academic Press, London

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E1

DETERMINATION OF PHENYL-MERCURY BY COLD VAPOR ATOMIC ABSORPTION SPECTROMETRY AFTER PRECONCENTRATION WITH LIVING *ESCHERICHIA COLI*

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A method to determine phenyl-mercury (Hg-Ph) in water samples, containing other mercury species, is proposed. This novel method makes use of living cells for preconcentration prior to the determination of mercury by cold vapor atomic absorption spectrometry (CVAAS). The extraction/preconcentration procedure consists of putting a *Escherichia coli* strain into contact with a culture medium suplemented with different mercury species. By allowing a maximum growth of the bacterial cells to be reached, an equilibrium between the analyte in the solution and in the extractive solid phase is established. Then, discarding the supernatant, the concentration of the organo mercury compound is determined directly in the biomass pellet by CVAAS. The extraction procedure was optimized by controlling the composition of the culture medium, the seeding density, and the growth time.

A theoretical model based on a saturated concentration-depending rate and intended for mathematical modelling the Hg-Ph uptake by the living bacterial cells was developed. The theoretical model fits in well with the experimental data. This relationship can also provide a feasible quantification of the extraction process before and after the adsorption equilibrium is achieved, whenever the agitation conditions and the sampling time are controlled. The interference effects from other mercury species were also studied.

Acknowledgment
The financial support of CICYT (Spain) by means of the Grant AMB 96 0385 is gratefully acknowledged.

E2

EXTRACTION-SPECTROPHOTOMETRIC DETERMINATION OF CADMIUM, LEAD AND THALLIUM IN SOIL

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Implementation of the new, ecologically imperfect technologies and the intensive chemicalization of agriculture and transport have contributed to the pollution of the environment with toxic heavy metals.

Therefore, the development of simple and reliable methods of determination of toxic metal ions content in soils becomes an actual and important task.

The methods developed by us are based on the ability of cadmium, lead and thallium to produce the intensively dyed ionic associates (IA) in the presence of the acidoligands and cyanine dye -2-[1-(5-dimethylamine-tienil-2)vinil-2]-1,3,3-trimethyl-3-N-indolenine chlorid (DTVTI).

The influence of acidity, nature and concentration of halide ions, DTVTI, solvent and other factors on the formation and extraction of IA has been investigated.

The composition of IA and its structure have been determined by various spectrophotometric methods, as well as, by studying the IR spectra of the extracted compounds.

The extracted IA corresponded to the general formula $[CdI_3]^-R^+$, $[PbBr_3]^-R^+$ and $[TlCl_4]^-R^+$ (where R^+ is a cationic DTVTI). The optimal condition for IA Cd: pH 1-4 (solvent: toluene + TBP); for IA Pb: pH 0,2-1 (solvent: toluene + TBPO) and for IA Tl: pH 0-5 (solvent: toluene).

The absorption spectra have been measured under the optimum conditions of IA formation and extraction. The principal chemical-analytical characteristics of the dyed IA extracts have also been calculated. The molar absorptions for various IA are about $(0,9\text{-}1,3).10^5$.

On the basis of the experimental data, the highly sensitive and selective methods of Cd(II), Pb(II) and Tl (III) extraction and spectrophotometric determination in solutions of different types of soils doped with Cd, Pd and Tl were examined.

E3

ELECTRON PROBE X-RAY MICROANALYSIS OF LITTLEST MINERAL COMPONENTS OF SNOW COVER

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The snow cover is an informative indicator for investigation and monitoring of polution of atmospheric precipitation, air, surface waters and soils. The determination of phase and chemical composition of mineral components of solid sediments as massive grains (above 10 microns) and small fractions (1-5 microns) are important analytical tasks in the study of snow cover.
One of perspective methods for solving these tasks is X-ray microanalysis with electron probe (EPXMA). However, the methods of EXPMA devised for massive homogeneous objects are practically unuseful for the analysis of particles, which in size are comparable or smaller than the area of X-ray generation. It's necessary to modify the theory of EPXMA.

In this work has been considered the method of EXPMA for determination of chemical composition of small particles, which in size are comparable with the area of X-ray radiation generation. The sizes of particles are accounted by size-factor. The modified by authors biexponential model for the function of distribution of characteristic X-ray radiation with depth was applied for account of matrix effects. The joint correction factor for the absorption and atomic number effects with account of a size factor were introduced into the procedure of calculation of contents of determined elements.

The validity of correction of this method was evaluated using results of determination of chemical composition of small grains, comparable in size with the area of X-ray generation and massive grains of minerals, of known chemical composition. The investigations were performed using devices Superprobe-733 and Camebax SX-50. The two methods of calculation of contents of determined element (the suggested method and known PAP-method) were compared with stehiometric composition and composition of massive samples. The account of size-factor allows to reduce the error of determination of composition from 35-45% relative percent to 5-22% for smallest (1-4 microns) particles. The results of suggested method are comparable with well-known ZAF and PAP methods.

E4

COMPARATIVE METHODS FOR TRACE ANALYSIS

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Using analytical spectrometry methods, atomic absorption spectrometry and atomic emission spectrometry with inductively coupled plasma, was determined the content of four elements: Cadmium, Copper, Lead and Zinc. The samples were collected in period March- October 1996, from Danube in the point of contact with Black Sea (Sulina) and different points of the border of Black Sea (Midia, Mamaia, Constantza- harbor, Agigea, Costinesti and Vama -Veche) [1].

To concentrate the elements from water sample, we utilized solvent extraction of complex compounds, using tandem systems of complexes agents: APDC (ammoniumpyrrolydine dithiocarbamate) and DDDC (diethylammonium diethyldithiocarbamate) and as solvent we utilized methyl isobutyl ketone (MIBK).

Quantitative determination of the elements' concentrations were performed using an atomic absorption spectrometer Jarrell ASH 850 and an atomic emission spectrometer (ICP-AES) a SPECTROFLAME device. The concentration level of these elements indicates the influence of the Danube as a collector on the pollution of the Black Sea Coast. The biggest concentration of the studied elements was observed at Sulina, the place were the Danube enter into the sea. Considering the necessity of finding correct, sensitive and rapid analytical methods in order to detect the metals content belonging to the environment sample, the results obtained by using the two analytical methods have been statistically processed using the paired "t" test [2].

The obtained "t" test values have been compared with the critical value form tables (2.18 for 12 liberty degrees). No significant differences between the two measurement sets have been noticed, the two methods presenting similar degrees of accuracy.

[1] Birghila S., Proceedings "Mediterraneanchem", Taranto, C_2, P_{01}, 1995
[2] Chirila E., Carazeanu I., Mincu A.T., Analele Univ. "Ovidius" (Chimie), III, 25-32, 1992

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E5

THE ROLE OF PHENOLICS IN DISEASE RESISTANCE OF EUCALYPTS

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Phenolics contribute to a number of different metabolic functions in plants, the nature of which depends on the molecular structure and compartmentation. They have been associated with adventitious root production, defence against herbivores, and disease resistance. In particular, they have been shown to be related to *Phytophthora cinnamomi* resistance in jarrah (*Eucalyptus marginata*) clones [1] and clearly their thorough analysis needs development. This work reports on analysis of phenolics from eucalypts and a possible role in resistance jarrah leafminer (*Perthida glyphopa*), oviposition and larval feeding.

Extracts from several eucalypt species including *E. marginata, E. calophylla, E. todtiana, E erythrocorys, E. rudis* and *E. tuart* were analysed by high performance liquid chromatography (HPLC). Extracts from eucalypts susceptible to leafminer attack (*E. marginata, E. erythrocorys, E. rudis and E. tuart*) all possessed a common phenolic, most likely a proanthocyanidin, however, this was absent from *E. calophylla*, a field resistant species.

In addition, *E. marginata* displays varying degrees of resistance to leafminer [2]. A number of *E. marginata* trees of varying resistance were studied with regard to phenolic production. Plant extracts analysed by HPLC and spectrophotometrically to determine the total level of phenolics showed that the more detailed analysis obtained from HPLC showed clear differences between trees that were not obvious observable from total phenolics analysis.

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E6

SIMULTANEOUS DETERMINATION OF IRON, COBALT, NICKEL, COPPER, ZINC AND CADMIUM BY UV-VISIBLE SPECTROPHOTOMETRY WITH MULTIVARIATE CALIBRATION

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In this paper a method for the simultaneous spectrophotometric determination of the divalent ions of iron, cobalt, nickel, copper, zinc and cadmium based on the formation of their complexes with 1,5-bis(di-2-pyridylmethylene) thiocarbonohydrazide (DPTH) is proposed. This ligand is a good chromogenic reagent. It can react with various metallic ions to form stable complexes with high sensitivity, but unfortunately these reactions are usually not selective enough. Fe(II), Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) react with DPTH to form different complexes but the absorption curves overlap severely. It is impossible to determine these elements simultaneously by conventional spectrophotometric methods. The resolution of mixtures of these metallic ions was accomplished by several chemometric approaches. A comparative study of the results obtained for simultaneous determination in mixture by using principal component regression (PCR) and partial least-squares regression (PLS-1 and PLS-2) for absorbance, first-derivative and second-derivative data is presented. With the aim of investigating the possibility of determining Fe(II), Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) in mixtures, the optimum working conditions were studied under the conditions previously established for each metal ion. A sodium acetate buffer solution of pH 4.0 was selected. The effect of DPTH concentration was also investigated, a reagent concentration of 2.8×10^{-4}M was chosen. Under these optimum working conditions, the spectral region between 400 and 510 nm was selected for analysis. The optimum number of factors (latent variables) to be included in the calibration model was determined by cross-validation. In all instances, the number of factors for the first PRESS value whose F-ratio probability drops below 0.75 was selected as the optimum.
This procedure allows the simultaneous determination of cited ions in biological materials. Good reliability of the determination was proved.

E7

DETERMINATION OF MONO- AND DICARBOXYLIC ACIDS IN THE ATMOSPHERIC AEROSOL PARTICLES BY ION CHROMATOGRAPHY

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Mono- and dicarboxylic acids are important components of atmospheric particulate matter. Their determination is usually accomplished by derivatization to obtain alcoholic esters which are analysed by HRGC. This treatment is quite tedious and time-consuming; therefore we have developed an ion chromatographic method allowing to semplify and shorten the whole analytical procedure. It is based upon the direct injection of the analyte solution into a Dionex AS-11 column, followed by elution at a gradient program and monitoring by conductivity detection. The atmospheric acidic fraction was obtained by extracting particulates by soxhlet, using a benzene-methanol mixture as solvent; after solvent evaporation, the extract was redissolved with iso-propanol, filtered through a PTFE membrane (0.2 um pore diameter) and then diluted with water.

The proposed method was particularly suitable to determine the most polar components (i.e. light monocarboxylic and dicarboxylic acids), although long-chain monocarboxylic acids could not be detected at the selected operative conditions.

Aerosol concentrations of organic acids observed in different world areas (i.e. urban, forest and remote) will be presented and discussed.

E8

METAL DETERMINATION IN WATER, SEDIMENTS AND PLANTS FROM AN ARTIFICIAL LAGOON USING ICP-AES

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The original natural equilibria appear today seriously altered by anthropogenic interventions. This situation requires, at least, a careful control of the hydrological and sedimentological equilibria. Utilization of ICP-AES for environment samples' analytical characterization allows the detection of some trace elements and the possibility of biogeochemical transformations taking place as well. Original results deal to determinations of total Cadmium (Cd), Copper (Cu), Chromium (Cr), Lead (Pb), Zinc (Zn) and Nickel (Ni) concentrations in water, sediments and plants (young and mature) from an artificial lagoon. This lagoon (about 500'000 square meters) is in Constantza District, on the Romanian Black Sea Coast, and is the final stage of a complex water treatment plant.

Analyses were performed using a "Spectroflame P" apparatus provided by *Spectro Company*, in following conditions: Ar of 99.99% purity as support of torch plasma and as carrier gas with the flow at 1L/min; the radiofrequency generator's power 2.5 kW and frequency 27.12 MHz; the plasma's temperature 8'000-9'000°K [1][2]. Solid samples (sediment and plant) were dried and dissolved with sulfuric acid and hydrogen peroxide in a digestion unit "Digestahl" at 440°C. The mean of obtained concentration's values is presented in the *Table*.

Sample / Metal concenuration	Pb	Cd	Cr	Cu	Zn	Ni
Water µg/L (ppb)	0.6	25.5	0.0	0.1	1.0	8.1
Plants µg/g (ppm)	31.49	0.69	21.68	17.35	32.85	19.45
Sediments µg/g (ppm)	9.16	0.78	25.14	13.34	24.36	26.36

As expected, sediments and plants contain higher metal concentration (ppm) than water (ppb) due to the bioaccumulation and to the other physico-chemical processes. Lead, Copper and Zink are in higher concentration in plants than sediments, comparing with Cadmium, Chromium and Nickel. Also, there are metals (Ni and Zn) which have been found in higher concentration in the young plants than in mature ones.

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E9

SAMPLING QUALITY IN THE ENVIRONMENTAL MONITORING

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A sampling experiment was accomplished in the frame of the Czech Ministry of Enviroment project (no. VAV/340/2/97) „Monitoring of foreing substancesiv the food chain."
As a plant matrix used for sampling a bulk feed - clover was selected.. Samples were taken on the basis of randomized selection in autumn 1997 in relatively non-polluted area of Bohemia. Homogeneity of large filed (200x200 m) was tested by taking 100 samples alongside the field diagonal with respect to multielemental analysis. Samples were treated under the clean room condition by the following way: each sample was dried, homogenized in cryogenic mill, duplicates of samples were decompsed under pressure in microwave oven and analyzed by inductively coupled plasma mass spectrometric method (ELAN 6000). Content of various elements (Cr, Ni, Cu, Zn, As, Se, Mo, Ag, Cd, Tl and Pb) was determined and interpreted by the use of two multivariate analysis: principal component analysis (PCA) and multivariate analysis of variance (MANOVA). Two parts of combined uncertainty were identified: sampling uncertainty and measurement uncertainty. Measurement uncertainty is approx. 10% of whole uncertainty. Linear discriminat analysis of result show sampling field is not homogenous with the respect of all elements.

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E10

DETERMINATION OF HEAVY METAL CONTENT IN WOOD-ROTTING FUNGI IN THE CZECH REPUBLIC

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Accumulation of heavy metals by fungi has been known for several decades and it has been studied mostly from the viewpoint of possible risks in connection with edible or market species. Terrestric fungi (e.g. *Amanita* or *Agaricus* spp.) were found to contain high concentrations of heavy metals. The main source of metals in these fungi is soil. Contrary to them, wood-inhabiting fungi take up heavy metals mostly from dry or wet atmospheric deposition. Therefore they can serve as sensitive and versatile tools for biomonitoring of atmospheric pollution by anthropogenic metals.

Wood-rotting fungi usually form tough and hard fruit bodies, the homogenization of which is not easy. In our case, a kryogenic mill was used for sample homogenization and a microwave oven for mineralization.

In the present work, contents of Ag, Al, As, Be, Cd, Cr, Cu, Mo, Ni, Pb, Se, Tl, and Zn in fruit bodies of four fungal species (*Fomitopsis pinicola*, *Ganoderma applanatum*, *Piptoporus betulinus*, and *Stereum hirsutum*) collected in medium-polluted sites were determined by AAS or ICP-MS. In all cases, the data did not exceeded the values described for fungal samples from heavy polluted regions in the Czech Republic [1]. The use of ICP-MS (Elan 6000) allowed determination of individual isotopes among studied metals. Only in the case of chromium, significant difference between concentrations of isotopes ^{52}Cr and ^{53}Cr was found. The results are in compliance with available data for metal content in atmospheric deposition.

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E11

HEAVY PETROLS BY AAS

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Transition metals [M] in organic surroundings, namely complexes of V, Ni, Cu and others with porphyrenes M ← N,N , aminoacids M ← N,O , thioacids M ← O,S = all are components of natural fuels: crude oils, shists, coals. Fuels content more than 30 metals (10^{-2} - 10^{-12} mass.%) and for M redox equilibria such as $V^{4+} \longleftrightarrow V^{5+}$ or $Cu^{1+} \longleftrightarrow Cu^{2+}$ exist [1].
AAS-methods are commonly used for the determination of M in crude oils and heavy fractions. High T° by decomposition, high viscosities by solvation and big molecular masses = all create difficulties with probing. Electrothermal AAS provides here advantages in comparison with flame AAS [2].
For completely removing the organic matrix in Coces, Pitches, Asphaltenes and other heavy residues, we used as solvents MIBC, DIBC, MEC for diluting, solving, extracting. The conditions, required for determination in heavy petrols V, Ni, Cr, Pb and others, especially the volatile [M] as first and last ones were used [2]. We hope, the study will help to clear up the degrees and passes of M-contamination, as well as the distribution of them in soils and waters by drilling and burning of oils. And it may recommend us the proper ways of protection -- how to neutralise or even how to prewent today metalic contamination of the Environment [3].

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E12

CHARACTERIZATION OF ORGANO-METALLIC COMPLEXES FROM SPODIC AND ANDIC SOILS FROM THE ROMANIAN NORTHERN CARPATHIANS

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The organic and organo-mineral compounds as the main components of the basic systemic structure of the soil act as ecological determinants in the nutritional processes of the ecosystem. The organic matter has an important ability to complex with metal ions and hydrous oxides which affects the availability of nutrients to plant roots and biological systems, influences the physical proprieties of soils and plays a prominent part in the genesis of soils.

The paper present an extended study of the organo-metallic complexes and the humus composition of the main types of andic and spodic soils from the northern part of Romanian Carpathians. The research was carried out on 22 soil profiles. The authors studied different types of spodic soils from brown podzolic soils to podzols and also different types of andic soils from acid brown andic soils to typical andisoils.

The research methodology included four steps: the extraction of different humic fractions and the organo-metallic complexes using 0.1 M $Na_4P_2O_7$ at pH=10; separation by acidification to pH=1.5 of the main humic fraction (fulvic and humic acids); hydrolysis and insolubilization of silica; determination of total organo-metallic complexes, humic acid complexes and fulvic acid complexes. The organo-metallic complexes with Pb(II), Cr(III), Cu(II), Zn(II), Mn(II), Co(III), Cd(II) were also analyzed.

The research put into evidence the fact that the studied soil profiles are very rich in organic mater and the main fraction present is the one of the fulvic acids. It also resulted that the studied area is a polluted one, especially with Pb which is mainly complexed with fulvic acids fraction.

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E13

Spectrophotometric Determination of Gold in Water by Liquid-Liquid Extraction using Amiloride Hydrochloride

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Amiloride hydrochloride has been used satisfactorily for the spectrophotometric determination of gold (III). The developed method is based upon the formation of gold aureate ($AuCl_4$-) ion and the resulting species at pH 7-10 is then extracted with amiloride hydrochloride in 2-methylcyclohexanone. The absorbance of the produced ion-associate in the organic phase is then measured at 360 nm. The composition and stability constant of the ion-associate have been investigated. Gold (I) species is also determined after its quantitative oxidation to $AuCl_4$- in chloride media (pH < 3) with bromine water. The molar absorptivity, the Sandell's sensitivity and the optimum concentration range evaluated by Ringbom's plot for the formed associate have been critically determined. The proposed method has been successfully used for the determination of trace amounts of gold species present in industrial waste water and liquid waste.

E14

A Case Study on the Determination of Some Heavy Metal Ions in Soil Around Al-Ain Cement Factory

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The present study dealing with the determination of trace elements Cd, Pb, Zn, Cr, Mn, Ni and Cu in soil around Al-Ain cement factory, United Arab Emirates with the help of AAS technique. The study with conducted with soils from the vicinity of the factory to evaluate the extend of contamination by these metals. The investigation has been extended over a period of one year during 1996-1997 at various distances in the Cardinal origins of the factory. The results indicated that the trace elements in the soil of different mandals in the vicinity of the factory in the command areas were found high as compared to non-command areas in the district. However, the tested soil samples around the factory have metals (Cd, Pb, Cu and Ni) concentrations below the permissible levels reported by WHO. The greater quantities of various pollutants might be the result of rapid weathering process and the increased human activity in terms of cultivation, industrial waste brackets, traffics and consequential erosion of soil.

E15

Spectrophotometric Determination of Tungsten and Iron in Water by Solvent Extraction of their Anionic Thiocyanate Complexes with Amiloride Hydrochloride

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A rapid, sensitive and selective simultaneous spectrophotometric method for the determination of tungsten (VI) and iron (III) has been developed. The method is based upon the selective extraction of the ion associates of their anionic thiocyanate complexes with amiloride hydrochloride at pH 5-9 in 2-methylcyclohexanone and measuring the absorbance of the extracts at 360 and 520 nm. The molar absorptivities, stability and the compositions of the formed ion associates of tungsten and iron were determined. The Sandell's sensitivity and the Ringbom's plot of both metals ions were determined. The potential interference have been examined and the method was applied for the analysis of iron and tungsten in the natural and treated waste waters.

E16

THE ANALYSIS OF ULTRA FRESH BAIKAL WATER BY ICP-MS

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Using of ICP-MS method allows to obtaine complete information on element composition of ultra fresh water. The opportunities of direct determination of some elements in Lake Baikal water are evaluated. The determination was carried out on ICP mass-spectrometer "VG-Plasma Quad" of English company "VG Instruments".

For Na, K, Ca, Mg, Sr, S, Cl, Li, Ba, Al, Zn, Cu, U, Pb, Cd the standard additions method by ICP-MS concentration are measured and the detection limits are determined. For these elements the comparison of results obtained by the multielemental analysis and the analyses on the appropriate individual element are carried out.

This method gives opportunities of creation of natural Baikal water standard sample, which can be used for monitoring of elements on all volume of Lake Baikal, and also for the analysis of other fresh and drinking waters.

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E17

DETERMINATION OF Cu AND Ni IN SOIL EXTRACTS AFTER SEQUENTIAL EXTRACTION PROCEDURES BY AAS

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Metal toxicity depends on chemical association in soils. Determining the chemical forms of metals in soils is important for evaluation of their mobility and bioavailability. To study the distribution in a solid phase, the methods most widely used are based on extraction techniques with different chemical extractants used in a single step and in sequence.

In sequential extraction procedures, several fractions are usually diferentiated as: exchangeable fraction; carbonate fraction; reducible fraction (metal bound to Fe and Mn oxides); oxidizable fraction (metal bound to organic and sulfuric compounds); residual fraction.

The purpose of this work is to apply a five - step sequential extraction procedure, originally designed for sediment analysis, to soils. The extractant solutions were: 1 mol/l ammonium acetate, 1 mol/l hydroxylammonium chloride 1:1 in 25 % acetic acid, 0.1 mol/l hydrochloric acid, 0.5 mol/l sodium hydroxide and 8 mol/l nitric acid.

The amounts of analytes released by the sequential extraction procedure plus dissolution procedure using HNO_3 and HF at elevated pressure of the residue remaining after extraction were compared to total contents of analytes in soils.

The concentrations of analytes were determined in the soil extracts by FAAS and ETAAS methods. Accuracy was assessed comparing the sum of the contents of copper and nickel in soil extracts with the total certified values used CRMs of soils. The overall recovery rates for nickel was 84 - 105 % and for copper 105 - 114 %.

The five step sequential extraction procedure for speciation of heavy metals, where the metal fraction bound to the organic matter can be distinguished is compared to the Tessier's procedure, originally designed for the speciation in sediments, from which several sequential extraction schemes has been developed for soils.

E18

EVALUATION OF HEAVY METAL LABILITY EN POLLUTED SOILS USING A SHORT SEQUENTIAL EXTRACTION PROCEDURE

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High levels of metals are usually found in areas close to mining activities, smelting factories and traffic roads. The assessment of the environmental risk requires not only the knowledge of the total amount but also the evaluation of the more labile metal fractions in soils.

The sequential extraction provides detail information allowing the differentiation between several association forms. Among the various sequential procedures available the most used is that proposed by Tessier et al.(1979) [1].

A short sequential procedure that allows determining the more readily labile fractions has been attempted in our laboratory [2]. The mobile (extracted by 0.01 mol L^{-1} $CaCl_2$) and the mobilisable (extracted by 0.005 mol L^{-1} DTPA) were the sequential fractions evaluated using this short procedure.

The proposed method have been applied to a wide number of soils with different source of metal pollution (mining, industry and traffic). Different percentages of labile metals (mobile plus mobilisable fractions) were found in these soils. For Cd, Cu, Cr, Pb and Zn significant correlations between the labile contents and the easily extracted exchangeable and carbonate forms of Tessier's method have been found.

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E19

PHOSPHATE ROCKS SOLUBILISATION WITH *BACILLUS MEGATERIUM*

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A large variety of microorganisms (bacteria, fungi, yeasts or algae) can participate in metals'solubilisation and/or concentration from raw materials or solutions.

The purpose of this paper is to emphasize:

A. The ability of ***Bacillus megaterium*** (that we have called "**nonspecific bacterium**") to solubilise the phosphate rocks, an aspect still not mentioned in the literature of the field.

The "nonspecific baterium" leaches Fe, Ca and P at higher extraction rates (0.171; 4.72; 5.02 $g.l^{-1}$, respectively) while the trace elements are leached at lower extraction rates (Cu - $3.6.10^{-3}$; Co - $1.75.10^{-1}$; Zn - $6.4.10^{-2}$ $g.l^{-1}$, respectively). These results were obtained for 0.1 g phosphate rock employed in the experiments. The bacterium growth and the solubilisation yield decrease significantly with increasing the amount of rock. The importance of the bacterial metabolism is also discussed.

B. The kinetics of the solubilisation processes was characterized in the first 14th hours from the beginning of the experiments by favourable yields for Fe and Co, while for Cu and Zn the solubilisation was very slow (in the same period of time) probably as a result of the bacterium adaptation to the environmental conditions.

The process of calcium solubilisation is interesting if taking into consideration that the concentration values in solution constitute a perfect straight line with a positive slope, in the five moments of determinations.

By comparing the solubilisation results of specific (***Th. ferrooxidans***) and nonspecific (***B. megaterium***) bacteria, we can assert that the process of phosphorus solubilisation proceeds similarly for the two classes of bacteria.

E20

SPECTROMETRIC ANALYSIS OF FREE- AND BOUND-EDTA AND HEAVY METALS USED IN ADSORPTION MODELLING EXPERIMENTS

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The adsorption of free- and bound- metal ions (metal complexes) as well as of ligands onto various hydrous oxide type sorbents have been extensively modelled using EDTA as the model ligand. When the mixture solution is equilibrated with the sorbent, one is faced with the problem of determining either metal complex+free ligand (MY^{2-}+H_2Y^{2-}) or metal complex+free metal (MY^{2-}+M^{2+}) in the aqueous filtrate.

The developed method utilizes Vis- and AA-spectrometry widespread in common laboratories, eliminating the need for HPLC and UV techniques that require higher operational cost, expertise and contaminant-free media. The procedure is described below for the possible constituents of equilibrated solution (with the sorbent):

(i) Filtrate composed of (MY^{2-}+H_2Y^{2-}) mixture: Add a known excess of $Fe(NO_3)_3$ to convert all metal-EDTA complex to FeY^-; evaporate to dryness and take up the residue in acidic KSCN solution. Spectrophotometric determination of SCN^--bound Fe(III) enables the calculation of (MY^{2-}+ H_2Y^{2-}) by difference. Measure (MY^{2-}) separately by analyzing an original aliquot by AAS.

(ii) Filtrate composed of (MY^{2-}+M^{2+}) mixture: Convert all metal-EDTA into FeY^- as described in (i) by adding a known excess $Fe(NO_3)_3$, and measure SCN^--bound Fe(III). Calculate original (MY^{2-}) by difference. Find total metal (MY^{2-}+M^{2+}) in the filtrate by AAS.

Since surface complexes on the hydrous oxide sorbent are much more difficult to desorb and analyze, the simple procedure developed here is applicable to sorbent equilibrated solutions enabling adsorption modelling.

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E21

INDIRECT SPECTROPHOTOMETRIC DETERMINATION OF MICROAMAUNTS OF CYANIDE

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Both the high toxicity of cyanide and its widespead industrial applications make it necessary to determine it at very low concentration levels. A number of methods for the determination of cyanide ions have been proposed for various applications Cyanide can be determined by spectrophotometry [1] fluorimetry [2] or electrochemical methods [3] directly or after it is distilled. The aim of this work was to develop simple and rapid method for cyanide determination in water. The method is based on the oxidation of cyanide with chlorine (Cl_2) and the residual chlorine is determined by the color reactions with o-tolidine (3,3'- dimethylbenzidine). A linear calibration graph (4-36.10^{-6} M CN) is obtained under optimum reaction conditions at room temperature and pH 12. The stoichiometric mole ratio of chlorine, Cl_2, to cyanide is 1.The effective molar absoptivity for cyanide with o-tolidine ise 4.7.10^{4} at pH 1.6. The lower limit of determination is 2.10^{-7} mol/ 1 or 5.2 ppb. The effect of other ions was examined and it was observed that the determination of cyanide was not significantly affected by the presence of thirty ions. The results were satistically compared by t and F-tests.

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E22

Selective Optical Fire-Alarm Sensors

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A nitrite-selective solvent polymeric optode membrane based on the cobyrinate ionophore NI 1 (Fluka AG) and the chromoionophore ETH 5418, was shown to be sensitive to nitrite concentrations in the range between 0.5 mg L^{-1} and 5000 mg L^{-1} (ppm NO_2^-) in aqueous solutions [1]. The detection limit was found to be at 0.24 mg NO_2^- L^{-1} in aqueous solutions. The membrane reaction is based on coextraction of nitrite ions and protons. The absorbance of the chromoionophore at the wavelength of 660 nm varies with the degree of protonation and is related to the nitrite concentration in the aqueous phase.
The same membrane composition was applied to gas phase analysis of NO_x. However, the concentration of the active components was increased and an internal reflection element was used. No additional reagents were needed. The detection limit of these membranes was in the low ppb range for gas phase analysis. Therefore these membranes were found to be perfectly suitable for fire-alarme sensors. The NO_x-selective membranes were investigated in test fire cabinets versus various reference materials. They showed to respond reversibly to NO_x production even under conditions where the temperature raised to 60 to 120 °C.
The limiting conditions of the application of ion-selective optode membranes in fire-alarm sensors and the sensor design will be presented. The mechanism will be discussed. Analyte-selective optode membranes are generally a good choice for gas phase analysis owing to exceptionally low energy consumption, no need of reagents and low production costs.

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E23

STUDY OF ELEMENTAL DISTRIBUTION IN THE GYPSUM ORNAMENTS OF THE HELSINKI CATHEDRAL

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The gypsum ornaments of the Helsinki Cathedral that were investigated in this study, have been varnished and painted several times during 150 years to stand rain and other weather conditions. However in many places of ornaments, there were crevices and holes in the layers of paint and the gypsum under,the damaged layers of paint was largely deteriorated.

The gypsum ornaments of the Helsinki Cathedral were examined in this study by chemical, structural microscopic (polarisation and fluorescence microscopy) as well as and microbiological methods (stereo, fluorescence, confocal laser scanning and scanning electron microscopy; as well as cultivation on agar-plate).

This presentation focuses on the results of the chemical analysis. Results of pH, total carbon, inorganic carbon, nitrate and phosphate of gypsum ornaments will be presented. Also quantitative principal elemental composition of gypsum ornaments analysed by X-ray fluorescence spectroscopy (XRF) and the elemental composition of the layers of paint analysed by microanalysis (SEM/EDS) will be given. Laser ablation ICP-MS was also used in the studies.

On the base of chemical analysis the elemental distribution of gypsum ornaments is quite homogenous, only some metal and carbon concentrations vary in different samples. Total carbon, nitrate and phosphate concentrations decreased from the surface of gypsum ornament to the inner parts of gypsum ornament.

E24

THE ATOMIC ABSORPTION SPECTROMETRY OF MAIN AND TRACE METALS IN SILICEOUS SOIL

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Soil is a complex chemical environment causing the interference in Atomic Absorption Spectrometry. In the total analysis of soil the sample is brought into solution by full destruction and dissolvation of silicate structure of soil. The main disadvantage of total analysis is the high concentration of salt in the solution causing serious interference in AAS analysis. The alternative way is the pseudo-total analysis. The silicates are attacked by acid and the metals included in the inner structure of silicate stay indissoluble. The pseudo-total analysis is accepted in the agricultural and environmental investigation. In this paper several acids were used to analyse metals in the soil where the silicates occupied 75 - 98%. The mixture of HNO_3 and H_2O_2 was the most efficient for the analysis of Pb, Cu, Zn, Mn, Cd, Fe, Ca and Mg. The solubility of silicate determined colorimetrically was in the range of 0.2 - 0.4 % of total silicate. At the sample of 0.5 g the concentration of silicate in solution was 15 - 40 mg/L. The effect of chemical interference of the dissolved silicate up to 250 mg /L was investigated in the solutions containing 1.6 mg/L each of the elements Cd, Cu, Pb, Mn, Zn, Mg, Ca and 8.0 mg/L Fe. Lanthanum nitrate as the interference buffer was added. The concentration of nitrate (1M) and sodium ion (0.25 M) was kept unchanged.

In AAS-F the interference of silicate with the metallic elements was detected in the solution where dissolved silicate exceeded: 5 mg/L - Ca; 10 mg/L - Mn,Zn; 40 mg/L - Mg; 50 mg/L - Fe. The silicate interference with Pb is low. The interference of silicate with Cu and Cd in AAS-F is not detected. Silicate has serious interference with Pb (10 ng/mL, 283.3 nm) in AAS-GF, causing strong background effect. The background effect for cadmium (4 ng/mL, 228.8 nm) was lower. The determination of the elements succeeded by dilution of the working solutions and using the lanthanum salt addition. Serious difficulties were met in the determination of low concentration of trace elements.

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E25

Comparison of Coating Materials for Infrared Evanescent Wave Sensors Utilizing a Sequential Injection Calibration System (SICS)

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Monitoring of chlorinated hydrocarbons (CHCs) and other volatile organic compounds (VOCs) in various matrices is an important task for modern environmental analytical chemistry. Especially for on-line analysis of industrial effluents and screening of possibly contaminated sites rugged and rapid sensor systems would be appreciated. Due to the nature of these analytes, sensors based on common electrochemical, optical or acoustical transducer types show significant limitations in sensitivity, selectivity or stability.

Mid-infrared evanescent wave spectroscopy (IR-EWS) represents a promising alternative sensor principle, which can be realized with common Fourier transform infrared spectrometers (FTIR) or infrared tunable diode laser systems. The benefit of this rather sophisticated approach is the inherent molecular specificity of IR spectroscopy. Hence, for the analyte recognition layer rather simple but stable materials such as polymers can be chosen, which need to provide only broad analyte selectivity.

So far only few polymers have been described as coating materials for this kind of sensors, which may be due to the experimental effort necessary to accurately characterize and compare the sorption and diffusion properties of numerous materials for several analytes.

Repeated calibration experiments have been carried out with different VOCs in order to compare enrichment properties and sensitivity. A computer controlled sequential injection calibration system (SICS) was established which enables unattended continuation of complete calibration cycles (e.g. overnight), thus providing a statistically useful amount of data within reasonable time. The aim was to develop a general procedure for systematic comparison of potential coating materials usable in IR-EWS sensor systems.

This study is embedded in the EU project EWALD (ENV4-CT97-0475), which aims at the development of an optimized IR tunable diode laser sensor system for VOCs in waste water.

E26

INFRARED SPECTROSCOPIC STUDY OF REACTION PRODUCTS OF BIOGENIC HYDROCARBONS

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Plant emissions of volatile organic compounds consisting mainly of isoprene, mono- and sesquiterpenes, play an important role in atmospheric chemistry. These unsaturated compounds are very reactive towards atmospheric oxidants such as ozone. Because of their lower volatility, the oxidized products most likely undergo a gas-to-particle conversion forming an organic aerosol. In spite of their possible influence on the radiation balance of the atmosphere, most of the species present in the particles are not fully characterized yet.

The most widely used method to analyse such unknown compounds is mass spectrometry. However since it does not provide all necessary structural information for identification, infrared spectroscopy could be an attractive supplement, if its unfavourably low detection power is overcome. The drawback of GC/IR in comparison to GC/MS can indeed be reduced to about one order of magnitude by employing a cryocondensation interface (Biorad Tracer), i.e. by depositing the eluent on a liquid-nitrogen cooled target.

We are studying the gas-phase reaction of α-pinene and ozone. For this purpose a reaction chamber was constructed and built to collect reaction products. Gas-phase reaction products are sampled on adsorption tubes and detected by Thermodesorption-GC/Cryocondensation-IR. Particle-phase products are collected on boron-silica filters. For separating the components of the extract, LC is applied and in order to achieve identification in a similar way as before, an LC/Thermospray-IR interface was developed. Results from both detection schemes will be presented.

E27

STUDY OF THE STABILITY OF PHOSPHORUS PARTITIONING IN A SEDIMENT SAMPLE

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The main problem in the use of sequential extraction procedures to determine bioavailability/mobility of sediment phosphorus lies in the lack of selectivity of the extractants used, so the fractions obtained are operationally defined. This fact do not allow the results to be compared or the procedures to be validated. Taking into account this lack of comparability and quality control, the European Commission (within the Standards, Measurements and Testing Programme) has launched a programme the aims of which are to harmonise, to validate sequential extraction procedures for the determination of extractable contents of phosphate in sediments, and the production of a Certified Reference Material. At this stage it is necessary to demonstrate the feasibility of the preparation of material that fulfils the basic requirements of a CRM, for homogeneity and stability for the sequentially extractable P contents.

In this work, we present the studies of homogeneity and stability for a sediment sample with a high organic matter content (50%). The sample was collected, air-dried, sieved at 90 μm, homogeneised and bottled. Major components were determined by XRF. The homogeneity and the stability of the material (this one over a period of four months at 4°C and 40°C) was studied appliying a modified Williams procedure.. Moreover, the total phosphorus content was determined by a total attack validated procedure. Phosphorus determination was performed by two tecniques, ICP-OES and visible spectrophotometry, and the results obatined were compared. The results show good level of homogeneity and the stability of the P distribution with time is demonstrated.

E28

LEVELS OF VOLATILE ORGANIC COMPOUNDS (VOCs) IN A RURAL ZONE

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The interest for the Volatile Organic Compounds (VOCs) in the last years, is reflected in the increment in the number of published works that approach the topic. This study, part of a vaster project, tries to relate values of different VOCs, with the levels of ozone found in the area of study.

In this work we present the results obtained in 43 samples carried out in two stations of environmental contamination control belonging to an environment vigilancy net of a Power Station (1400 Mw), located in two small mounts (550, 640 meters altitude). 29 different compounds were determined, including alkanes, benzene and their alkyl derived, light polycyclic aromatic hydrocarbons, organochlorine compounds and natural origin compounds (α-pinene, β-pinene and isoprene).

1,2,4 trimethylbenzene presents the highest concentration (over 12 μg/ m^3), followed by the tetrachloroethylene, with a concentration near to the 4 μg/ m^3 and the toluene with a little more than 2 μg/ m^3.

It can be observed that the aromatic compounds represent more than the 70% of the total composition, the contribution of alkanes and chlorine compounds being a little over 10%.

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E29

DETERMINATION OF PERMETHRIN IN INDOOR AIR WITH AN ELISA

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Synthetic pyrethroids like permethrin are an important class of insecticides and have been used as active ingredients against various household or garden pests e.g. houseflies, mosquitoes and fleas. They are used as sprays, powders, in solutions for wood treatment, mosquito coils, on carpets and on impregnated paper for electro-evaporators - all mainly intended for indoor application.

Thus, pyrethroids are more persistent in indoor areas than outside. This could lead to permanent health hazards to occupants of contaminated houses.

In our research group we developed a method for determination of permethrin in indoor air. The particle bounded permethrin was actively sampled on a glass fibre whereas the gaseous permethrin was trapped on Tenax®. The sample devices were eluted with methanol, afterwards diluted with water and quantitatively detected using an enzyme linked immunosorbentassay (ELISA). An ELISA is an established technique for on-site determination of pyrethroids. Being based on the use of specific antibodies and highly active enzyme labels, it ensures specificity and sensitivity corresponding to the current practical requirements.

All preliminary examinations and validation of the ELISA were performed using the high performance liquid chromatography (HPLC). Here we had to develop and optimise a fast and simple method for sample preparation and as well as the parameter for UV detection.

Furthermore, several other pyrethroids like cypermethrin, tetramethrin etc. were examined, which are also often used in commercial products. Here our main interests were to determine whether or not cross reactivity between the antibodies and the different pyrethroids exists.

In this presentation the performance and efficiency of the sampling technique is demonstrated. To validate the procedure, samples were taken from different contaminated carpets. The results were determined and compared using an ELISA and the HPLC.

E30

DETERMINATION OF CHLORIDE AND COD IN WATER : RESULTS OF INTERLABORATORY STUDIES IN YUGOSLAVIA

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In order to achieve a better quality of water analyses in Yugoslavia long term interlaboratory project was initiated at the Faculty of Chemistry of Belgrade University. The first laboratory intercomparison in 1995 included determination of chloride (Mohr method, Yugoslav standard) and chemical oxygen demand (ISO 6060:1989) of tap water. Two year later the same parameters were determined for natural water. Samples were prepared by addition of corresponding components to the water of the river Danube near Belgrade, just after the mouth of the river Sava.

Twelve to eighteen laboratories from water supply organizations, medical and public health institutions, pharmaceutical, chemical and allied industries, research institutes, universities, etc, were included in these interlaboratory studies. About half of laboratories participated in both interlaboratory studies in 1995 and 1997.

In spite of fact that the more complex sample was used in 1997 (river water) very good agreement was obtained for most laboratories. The increased content of iron (9.7 mg/L) in one set of samples did not disturb considerably the agreement among laboratories in determination of chloride. Corresponding standard deviations were in the range 1-2 mg / L.

Additional efforts are required in some laboratories in order to improve their analytical work. These interlaboratory studies are important for the improvement of laboratory practice, accreditation of chemical laboratories and introduction of quality system based on ISO 9000 standards.

E31

DETERMINATION OF SOME TOXIC ELEMENTS AND THEIR DISTRIBUTION IN ENVIRONMENTAL SAMPLES

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The bio-toxicity and mobility of toxic elements in the environment depends predominatingly on their specific chemical form or types of binding rather than on the total element contents. Bioavailable toxic elements are accumulated from the soil by plants as well as animals and via the food chain may influence negatively the human health. This is the reason why by the analyses of environmental samples the emphases are put on the reliability of results of the applied analytical methods.

Three atomic spectrometry methods (FAAS, ETAAS, ICP AES) for the determination of toxic elements (Cd, Cr, Ni, Pb, V) in soils (fluvizemic carbonate in alluvial sediments), soil extractants (nitric acid, EDTA, acetic acid), plants (lucerne) and biota (soil organisms Lumbricids) were used and evaluated. The samples were collected in localities close to the refinery of Slovnaft Bratislava and Danube river in Slovakia.

In the present work, study of matrix influences on accuracy of determination of toxic elements in investigated samples and the statistical evaluation of the results were performed. However, the matrix effects, coexisting elements interferences , and sometimes insufficient sensitivities for some elements have limited the application of FAAS and ICP AES methods. The reliability of the measured data were tested with a wide variety of environmental certified reference materials, provided by the Canada Centre for Mineral and Energy Technology (CANMET), Community Bureau of Reference, Brussels (BCR) and Slovak Institute of Metrology, Bratislava (SIM). The matrices, considered in this study, were soils (CRM SO-2, SO-4, CANMET), soil extractant (CRM 483, BCR), plant (CRM Lucerne 12-2-03, SIM) and biota (CRM Bovine muscle 184, BCR) samples.

E32

INVESTIGATION OF PHOTOCHEMICAL REACTIONS OF AIR POLLUTANT GASES USING FT-IR SPECTROSCOPY

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The modern Fourier transform infrared spectroscopy (FT-IR) is one of the most powerful techniques in detection of atmospheric pollutants.

An FT-IR spectrometer (Bio-Rad FTS-185) has been used for monitoring the photochemical reactions of N_2O, NO_2, CO and CH_4 trace gases. A special multi-pass gas cell equipped with a mercury radiation source (185 and 254 nm) has been adapted to the FT-IR spectrometer [1]. For the detection of the spectra a conventional Peltier cooled DTGS detector has been used at spectral resolution of 2 cm^{-1}. Quantitative analyses were carried out with the aid of the Digilab interactive substration routine, using a set of digitized quantitative reference spectra.

Gas mixtures close to the "natural" concentrations dominating in the lower part of the atmosphere have been studied for modelling of photochemical "smog" formation and acidification processes.

Ozone formation was performed by UV-radiation and the O_3 concentration was stabilised after 40 minutes of exposition. Concentrations of H_2O and CO_2 were increased and the amount of NO_x, CH_4 were diminished during 40 minutes exposition time, while CO showed no concentration changes. Reaction of CH_4 was initiated only after 1 minute of irradiation. The possible chemical reactions will be discussed in this paper [2, 3].

Acknowledgement
We would like to express our thanks to Bio-Rad Digilab GmbH (Germany) for the supporting of this project.

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E33

A CHEMOMETRIC STUDY OF THE WATERS OF DANUBE RIVER ALONG THE ROMANIAN TERRITORY

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The Danube, one of Europe's main rivers, covers 1,075 Km of the Romanian territory, forming Romania's border with Bulgaria and Yugoslavia.
Interpretation of the huge amount of data obtained by a permanent monitorization of the Danube's waters involved multivariate chemometrical methods -factor analysis and cluster analysis [1,2]. Our paper employed the data collected, ten months a year, along seven years of observation (1990-1996).The samples taken over have been subjected to very strict chemical analyses, a total number of 19 variables being studied as follows: pH, organic carbon, hardness, residues, suspensions, alkalinity, carbonates, nitrites, nitrates, etc.
For a thorough analyses, both chemical and instrumental methods (such as flamphotometry, electroanalytical and turbidimetric procedures) have been applied. The dendograms' interpretation (based on Euclidean metrics) evidenced the stability of all variables subjected to observations for seven years. It was only the pH (and the variables correlated with it) that showed variation along one of the years of observation, which may be explained either through the influence of some climatic factors or through certain polluting effects. Finally, significant correlation could be established between the Danube water's composition and the living conditions of some fish species.
The paper discusses both the dendograms obtained by processing data from each of seven years of monitorization, and the scatterplots.

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E34

ANALITICAL APPLICATION OF EXTRACTION IN Ni (II) - NITROSONAPHTHOLE - CYANINE DYES SYSTEM

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Complex formation of Ni (II) with nitrosonaphthols (HA) and cyanine dyes (R^+) has been studied by means of spectrophotometric method. It has been found that in neutral and alkaline solutions chelate complexes of MA_3 type are produced. The are readily extracted with R^+ in the form of extensively dyed ion associated (IA) into lowepolar organic solvents. The influence of medium acidity, nature and concentration of nitrosonaphthols, cyanine dyes, solvents and other factors on complex formation and extraction of IA has been studied.

Maximum yield of IA is observed while using 1-nitrso-2-naphthole as HA, dimethyliindocarbocyanine (DIC) and dimethylidodicarbocyanine (DIDC) as a cyanine dye and toluene (or benzene) as an organic solvent.

The optimal medium for nickel IA formation and extraction is pH 7,5-10. The IA composition and structure have been determined by various spectrophotometric methods as well as by studying IR-spectra of the compounds extracted. The ratio metal: ligand: cyanin dye is egnal to 1:3:1, the extracted IA corresponding to the general formula $[MA_3]xRxS$ (where S is an organic solvent). The extraction power of solvents in the series benzene>toluene>o,p,m-xylol> ethylbenzene> butylbenzene>CCl_4 >>hexane, octane, heptane. Spectrophotometric parameters of IA metals with high value $(0,7\text{-}1,5)\times10^5$ of molar absorption coefficients have been calculated from electronic absorbtion. On the basis of the data obtained highly sensity and selective methods of nickel extraction-photometric determination the traces (DL 10^{-2} mg/l) of these metal in drinking water and electroplating wastes are suggested.

E35

DETERMINATION OF LEAD AND CADMIUM IN SOFT AND DURUM WHEAT BY DERIVATIVE POTENTIOMETRIC STRIPPING ANALYSIS

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Lead and cadmium play a primary role between heavy metals, since, owing to their metabolic inertness, they are permanently retained giving rise to the bio-accumulation, phenomenon that causes severe consequences for human health1. FAO/WHO fixed aa allowable weekly intake of 0.4-0.5 ppm of cadmium and 3 ppm of lead for the adult2,3. The determination of lead and cadmium in soft and durum wheat is important owing to the both nutritional interest and incidence in the diet of these foodstuffs. Flame and graphite furnace atomic absorption spectrophotometric techniques, as well as electroanalytical such as pulsed techniques, are frequently used4-6.
In this paper potentiometric stripping analysis (PSA) was employed. PSA is a relatively new electroanalytical technique first proposed by Bruckenstein and Bixler7 and further developed by Jagner and Graneli8. PSA is a two-step technique. The first step (preconcentration) is an electrolysis of the solution containing the ions of the metals under examination, which are amalgamated on a mercury-coated glassy carbon electrode. The second step (stripping) is a chemical re-oxidation of the deposited metals. When the potential (E) and time (t) data are digitally converted into dt/dE and dt/dE is plotted against E, the sensitivity of the method can be increased and the resolution improved. Accuracy of the method is 98-101% with a standard deviation of 3-5%. The detection limit is of the order of 0.1 ppb for both analytes, depending on deposition time. In the samples so far examined the concentrations were up to 200 ppb for cadmium and up to 400 ppb for lead.

E36

CATALYTIC TITRATIONS BY THE APPLICATION OF IODIDE-CATALYSED MANGANESE(IV)-ARSENIC(III) INDICATOR REACTION IN ACID SOLUTIONS

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The catalytic titration method was first described by Yatsimirskii and Fedorova [1]. They titrated silver(I) with iodide and detected the end-point by the application of iodide-catalysed cerium(IV)-arsenic(III) indicator reaction, while the change of the indicator substance (cerium(IV)) concentration was followed photometrically.

In our earlier paper[2] a new catalytic-potentiometric titration method for the determination of silver (I) by the application of the iodide-catalysed manganese(III)-arsenic(III) indicator reaction in the presence of sulphuric acid, was developed.

The results of our preliminary investigations in this work have justified the study of conditions for the application of the iodide-catalysed manganese(IV)-arsenic(III) indicator reaction for the catalytic titrations of silver(I) in the presence of sulphuric acid. The effect of sulphuric acid and of concentrations of some anions (ClO_4^-, NO_3^-, Cl^-, Br^-, SCN^-), of the molar ratio of manganese(IV) to arsenic(III), respectively, in the titrated solution, as well as the effect of the titrand temperature on the conditions for the determination in solutions of various silver(I) concentrations, was investigated. The error in the determination of 0.5 $\mu g/cm^3$ silver was less than ±2%, and the reproducibility of the method is good.

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ENVIRONMENTAL QUALITY OF THE DANUBE RIVER BETWEEN BAZIASH AND IRON GATE

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The Danube pasts a number of six countries before entering Romania, near Baziash. During this „trip" it collects, more or less cleaned, industry or home originated waste water and other waste materials. Some of these deposit on the river bed, other are transported downstream, by water or fishes.

A measurement and sample collection campaign was organised during august 1997 by the *Centre for Environmental Research and Impact Studies*, from the Bucharest University. Water– and alluvial deposits samples were collected between Baziash and Iron Gate from several sites placed in the middle– and nearby the romanian shore of the Danube river. Some fish samples from the common species living within this area were also collected. Water and air temperature and the water–DO were measured.

This paper presents the result of the analysis, by means of polarography, ICP-AES and chromatography, to which these samples were subjected, concerning the heavy metal– , phenols– and pesticides load.

The results allow to identify the pollution sources and to point out which of them are local. The achieved data also argue for the necessity of a monitoring system along the Danube, which should be integrated to an European monitoring– and data collecting system.

E38

EVALUATION OF TOTAL CONCENTRATION AND SPECIATION OF TRACE METAL IONS IN CERTIFIED AND REAL SEA WATER SAMPLES BY RESIN TITRATION

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The knowledge of the sorption mechanism of metal ions on complexing resins, which has been previously described, [1] allows to quantify the ratio of sorbed to total metal ions on a complexing resin, in a batch experiment in different conditions [1]. The sorbed fraction, f, is given by: $f = c/c_{tot} = 1/(1 + \alpha_{M(I)} V/w K^*)$ (1) where ctot is the total metal ion concentration and c is the concentration sorbed by the resin. The side reaction coefficient of the metal ion M with a ligand HzI present in solution is indicated by (M(I). K* is the ratio of the concentration of sorbed metal ion in the resin to the concentration of free metal ion in solution which is known for each metal, if the sorption equilibria are known. Even using a resin with strong sorbing properties, as Chelex 100, the sorption of the heavy metals as Cu(II), Cd(II), Ni (II) and Mn(II) from seawater samples is not always quantitative. On the basis of eqn. 1 this depends on the ratio $1/(1+(M(I)V/wK^*)$, thus for a given system on the actual value of the side reaction coefficient. In this case the total metal ion concentration can be evaluated by a method previously proposed, called resin titration [2].

When $\alpha_{M(I)}$ has a value comparable with K* V / w it can be calculated from eqn. 1 for each volume treated, once c_{tot} and c are known. When the value of $\alpha_{M(I)}$ is high (>10 K*V/w), the metal will be not sorbed on the resin and when it is too small (<0.1K*V/w) the metal is quantitatively sorbed and $\alpha_{M(I)}$ can not be evaluated. Resins with different sorbing strength allow to determine different complexes. Here the two complexing resins Chelex 100 and Amberlite CG-50 were used for the determination of the total metal ion concentration and of $\alpha_{M(I)}$ in certified seawater samples and in Ligurian Sea samples. With Chelex 100 the certified metal concentration was always obtained, while with Amberlite CG-50 sometimes only a fraction of the total was found demonstrating that a part of the considered metal ion is so strongly complexed that it cannot be sorbed on Amberlite CG-50. Indeed the side reaction coefficients found with Chelex 100 were quite high, for example 109 for Cu and 106 for Ni, higher then those determined in sw with other methods previously used for the evaluation of $\alpha_{M(I)}$.

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E39

DETERMINATION OF LIGAND CONCENTRATION (C_l) AND CONDITIONAL STABILITY CONSTANT (K_l) IN NATURAL WATERS BY METAL TITRATION IN THE PRESENCE OF CHELATING RESIN.

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Metal titration, performed in the presence of a competitive ligand, is one of the approaches currently available for determining the complexation properties of natural waters [1,2]. In these competitive equilibration methods, the metal fraction associated with an added, well-characterized metal-binding ligand (A) is measured. The titration of the sample, included the added competing ligand, with the analyte metal, allows to determine the concentration of the natural ligands and the conditional stability constant, from which the original, unperturbed speciation can be calculated [1,3]. In the present study, a chelating resin is used as competing agent for the titration of ligands in the natural waters. The titration is performed in a way similar to that previously described in the case of the soluble analytical ligands [2], by adding increasing amount of the metal ion to the sample and by measuring the amount of metal ion sorbed on the resin (*c*). If the sorption equilibrium of metal ion on the resin is: $M + n\overline{HL} \leftrightarrow \overline{MH_pL_n} + qH$ with the exchange coefficient $\beta_{1,n,p\,ex} = [\overline{MH_pL_n}] \cdot [H]^q/[M] \cdot [\overline{HL}]^n$, the ratio of the concentration of metal ion sorbed on the resin to the concentration of free metal ion in solution, indicated by K^*, is given by the following relationship: $K^* = c \cdot V/[M] \cdot w = [\overline{MH_pL_n}]/[M] = \beta_{1,n,p\,ex} \cdot [H_iL]^n/[H]^q$ (1) where *c* is the concentration of the sorbed metal ion referred to the solution phase, and *w* and *V* are respectively the grams of water in the resin and those in the solution phase. The species with the overbar are those in the resin phase [4]. Let's considered the simple case of a 1 to 1 complex formation by a ligand H_zI in the considered solution, according to the reaction: $M + H_zI \leftrightarrow MH_yI + xH$ $K_l = [MH_yI] \cdot [H]^x/[M] \cdot [H_zI]$. The total concentration of ligand (c_l) and the conditional stability constant (K_l) are determined by a linearization method derived from the Langmuir isotherm. It has been shown [3] that the ratio of free to complexed metal ion is given by the following equation: $[M]/[MH_yI] = [H]^x/c_l \cdot K_l + [M]/c_l$. When a resin whose K^* is known is used, [M] is obtained by eqn. (1) from the amount of metal ion sorbed on the resin, *c*, and $[MH_yI]$ can be calculated from the total concentration of metal ion. The proposed procedure allows the titration of only those ligands for which the side reaction coefficient $\alpha_{M(I)}$ is in the range $0.1\ K^*\ w/V \div 10\ K^*\ w/V$. In the present study the ligands of aluminium(III) in fresh waters were determined using two different resins: Chelex 100 and AG1X8. They have different sorbing properties towards the considered metal ion, thus natural ligands with different complexing characteristics can be studied by the procedure. The method was previously tested on synthetic solutions containing a known concentration of ligands, as EDTA and F^-, that form complexes with aluminium(III) of known stability and stoichiometry. A good agreement was found in the case of EDTA, which forms a complex with 1 to 1 molar composition, while the concentration of fluoride evaluated by the method was very inaccurate, probably due to the fact that complexes with composition different from 1 to 1 are formed.

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E40

RAPID DETERMINATION OF PAHs IN WATER USING SOLID-PHASE MICROEXTRACTION AND GC/MS

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Solid-phase microextraction (SPME) was investigated as a solvent-free alternative technique for the determination of polycyclic aromatic hydrocarbons (PAHs) in water sample. Analytes were extracted from the water sample into a polymeric phase immobilized onto a fused silica fiber. The fiber was then inserted directly into the injector of a gas chromatograph, and the analytes were thermally desorbed. Using a 7 μm polydimethylsiloxane, gas chromatography and quadrupole filter mass spectrometer, detection limits ranging from 0.63 to 100 ng/L were obtained for fluorene, fenanthrene, anthracene, fluoranthene, pyrene, benzo[a]anthracene, chrysene, benzo[e]pyrene, benzo[a]pyrene, dibenzo[a,h]anthracene, benzo[g,h,i]perylene after a 30 min extraction time. These detection limits exceed the regulatory requirements of U.S. Environmental Protection Agency (U.S. EPA) method 525. Linearity extended from low nanogram per liter to microgram per liter levels for the majority of the analytes studied. The relative standard deviation was in the range of 2-27% and 0.33-0.66% (n =3) for areas and retention times of the chromatographic pikes, respectively. Desorbtion time was 20 min and the initial temperatur of the oven was 45°C.

The developed method allows the determination of PAHs in extremely diluted samples.

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E41

STUDY OF THE METALS DISTRIBUTION IN CONTAMINATED SOILS BY SEQUENTIAL EXTRACTION PROCEDURE

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The mobility, bioavailability and toxicity to plants of heavy metals depend on their chemical and physical forms in which they occur, and their interaction with the different soil phases (clay minerals, organic matter, oxides). Changes in the environmental conditions (pH, redoxpotential) can strongly influence the behaviour of toxic metals. The object of this work was to investigate the distribution of metals in some standard soil type samples (sand, acidic and calcareous). Three samples were unpolluted soil and other three contaminated soil. Content of metals in the soil samples were certified for the acid soluble fraction as the total concentration.

A sequential leaching procedure involving a 4 stages has been developed for the partitioning of metals in the soil samples (Al, Fe, Mn, As, Cd, Cu, Cr, Ni, Pb, Zn) into different fractions: (1) exchangeable and bound to carbonate, (2) Fe/Mn-oxides, (3) organic matter and sulfides, (4) residual (strong acid soluble) [1]. This analytical method was controlled by BCR 601 standard sediment in which the metal content was certified for determination of the trace metals spceiation in the samples. The concentration of the metals in the leaching solution were determined by atomic absorption spectrometry (Perkin-Elmer 5100 PC, GEM software, deuterium background correction, AS-60 autosampler).

On the basis of the results the arsenic, cadmium, and copper ions were found in the exchangeable fractions, and the other elements (Cu, Cr, Ni, Pb, Zn) were bound to acid soluble residue. Comparison of the results of soils and standard sediment sample (BCR 601), it was found that standard soil samples, in which the content of the metals for the sequential leaching procedure was certified, should be produced

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E42

SPECIATION OF INORGANIC SELENIUM IN SOILS

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The knowledge of the different species of selenium present in a contaminated soil can give, more then its total concentration, important indications on the environmental mobility (migration to groundwater, assimilation by vegetables, and so on) and, sometimes, can suggest the causes of the contamination. Selenium is either an essential element for the human life or toxic, the range of concentration between the two opposite effects being very narrow.

The speciation of inorganic selenium is achieved with a sequential extraction, in order, with water, Na_2S and, finally, nitric acid. The three solutions obtained contain respectively selenite and selenates, sulphodiselenide (SSe_2^{2-} from elemental Se) and selenious acid (from seleniures). The direct determination of selenium in these solutions by electrothermal atomic absorption (ETAAS) can be seriously compromised because together with the selenium compounds various constituents of soil are extracted too. It has been possible to eliminate these matrix effects by reducing in the extracting solutions (with KI, H_2SO_4 and ascorbic acid) the selenites to amorphous red selenium which is quantitatively extracted in toluene and easily analysed. The solution containing sulphodiselenide, before the reduction, must be treated with concentrated nitric acid in order to oxidise it to selenious acid.

The proposed procedure has been first verified on mixtures of selenium and its compounds, homogeneously dispersed in calcium carbonate as inert support, and successively on soils and soils spiked with known amounts of the above mentioned mixtures.

Selenates, if present in soils, are extracted together with selenites, but they do not interfere in the determination of Se(IV) in the above mentioned conditions: Se(VI) in fact is not reduced to red amorphous selenium. However a method for the determination in the extracting solution, of both selenites and selenates is being studied: it consists, first in the determination of Se(IV) as previously described, then in a second aliquot of extracting solution it is possible either to reduce Se(VI) to Se(IV) with HCl > 3 M, or to add hydroxylamine which reduces only Se(VI) to amorphous red selenium, while Se(IV) is reduced to elemental black selenium not extractable in toluene.

Both the procedures seem to give fair results, even if it is necessary to standardised better some parameters, such as temperature and working conditions in the reducing step, to improve precision.

E43

INVESTIGATION OF THE CONTAMINATION OF SEDIMENTS FROM TODOS OS SANTOS BAY (BAHIA, BRAZIL) BY EFFLUENTS OF DOMESTIC-URBAN ORIGIN

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The faecal sterols coprostanol, cholesterol and cholestanol were measured in surface sediment samples from the intertidal and submerged areas of the Todos os Santos Bay. Contamination indexes were calculated by the sterols ratios. Todos os Santos Bay is the largest in the Brasilian coast (1000 km ^{2}). The city of .Salvador with about 2.5 million inhabitants is situated at the entrance; in addition there are small tows in the surounding area and two main rivers, which flow through urban areas. A large amount of domestic sewage is discharged into the bay without treatment. Samples from twenty-nine stations were analyzed. The dried samples were soxhlet extracted and after clean up and fractionation of the lipidic extract, the obtained sterols were derivatised and analyzed by High Resolution Gas Chromatography with Flame Ionization detection. Selected samples were positively identified by Gas Chromatography-Mass Spectrometry. In all studied stations coprostanol was identified in 10, cholesterol in all 29 and cholestanol in 20. The contamination indexes indicated that from the twenty-nine statios only four were considered contaminated. The stations were located close to urban areas where domestic effluents are discharged without treatment.

[CNPq]

E44

A USE OF THE ANALYTICAL METHODS COMPLEX FOR THE ENVIRONMENTAL POLLUTION CONTROL

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The modern analytical problems which are linked with the environmental pollution control demand the use of more informational methods which combine high sensitivity as well as the capacity of many compound analysis. Operational efficiency and reliability are of utmost importance. These requirements are stipulated for persistent rise of common pollution level, specific pecularities of control objects themselves and physical-chemical characteristics of studied probes.

The Russian services of state environmental control and monitoring have the basic methods and technical means. It was orientated for the determination of small pollutants group. At present time special attention is payed to the investgation of wider range of organic and inorganic compounds, especially that chemicals which are highly toxidc, accumulate, resistant to physical, chemical and biological degradation and transformation processes.

In the report the authors give common approaches, methodological pecularities and optimal use of complex analytical methods, the means of mobile control for pollutant determination in different environmental objects (air, water, soil). The main methods of this complex are atomic-absorption and atomic-emission spectrometry, ICP/MS, gas chromatography, GC/MS. The results of wide spectrum organic and inorganic compounds are shown in the report. They are heavy metals, PAH, dioxins. The objects for registration these pollutants are energetic, petrochemistry concerns, incinerators, automobile transportation. During study of water, soil and city pollution the main attention was payed to the control of admixtures of heavy metals and petrochemicals.

Using many examples the authors showed practical use that gives much dimensional analytical information which helps to get effective solution for the problem of finding the polluting source, evaluation of its contribution to common environmental pollution. This information helps to choose right criteria for administrative decision.

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E45

IN-SITU DETECTION AND INVESTIGATION OF BIOMOLECULAR INTERACTIONS AT INTEFACES BY FTIR SPECTROSCOPY. A NOVEL SENSOR CONCEPT

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A simple approach to the in situ measurement of infrared spectra of self-assembled molecular layers on gold in aqueous environment is described [1]. A thin gold film (2 - 10 nm) on the surface of an internal reflection element is used as a substrate for the self-assembly of sulfur-bearing molecules. Several materials including germanium, silicon and zinkselenide can be used as substrate. The surface sensitive internal reflection FTIR technique offers an attractive possibility for the functional and structural investigation between ligands and their receptors if the molecules of interest could be functionally active attached to the gold surface in an oriented and controlled manner. We demonstrate a generally applicable method using a synthetic chelator thioalkane which can self-assemble on gold via its thiogroup [2]. It exposes its nitrilotriacetic (NTA) group which serves as a chelator for transition metal ions.

Two systems were investigated (i). The reversible binding of a Fab fragment modified with a C-terminal hexahistidine extension was monitored in situ and the protein structure was investigated in the amide I band region, and compared to that in solution [1]. (ii) As an example of a membrane receptor protein the ligand-gated ion channel 5HT3 receptor was studied on similarly NTA-modified gold surfaces. A receptor protein carrying a hexahistidine tag [3] was immobilized and the subsequent binding of ligands to the receptor was monitored both by ligand-specific and by the protein amide I band.

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E46

ENVIRONMENTAL POLLUTION ASSESSMENT OF A NONFERROUS METALLURGICAL SITE BY DETERMINATION OF MICROELEMENTS IN HUMAN TEETH, HAIR AND NAILS BY ICP-AES METHOD

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The paper presents the ICP-AES method for the determination of heavy metals in human teeth, hair and nails in order to compare toxic elements accumulation amongst people working in nonferrous metallurgy and comparing the said method to the AAS determination method.

Standard solution progressive addidtion method was also studied, discussing the effect of the matrix.

Suggested ICP-AES spectrometer for this material type proves to be more adequate than the often cited Flame-AAS spectrophotometer, due to the possibility of multielement determination, with a high sensitivity provided by the matrix, and due to the low detection limits.

E47

ELIMINATION OF SULFUR INTERFERENCES IN THE ORGANOTIN ANALYSIS OF SEDIMENTS WITH GC/FPD

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Most methods for the speciation for OTs in sediments described in the literature are based on a multistep procedure consisting of acid leaching of the sediment, derivatization (by $NaBEt_4$ or Grignard reagents) of the extracted OTs, clean-up of the sediment extract and GC separation coupled with different detectors (FPD, AAS, AES, MS). In this work, a flame photometric detector was used since it is a very sensitive and cheap detector and selective for tin when fitted with a band pass filter (610 nm).

During the derivatization of sediment extracts (toluene/acetic acid) containing high sulfur amounts with Grignard reagent (PeMgBr), alkylation of the sulfur species occurs. These organosulfur compounds can affect the organotin speciation analysis due to interferences when using the FPD as detector. Therefore, different clean-up and desulfurization procedures were compared in order to check their efficiency in eliminating elemental sulfur and organosulfur compounds from sediment extracts, and recoveries of butyl- and phenyltin compounds were determined. Conventional clean-up procedures in the organotin analysis of sediments such as adsorption column chromatography cannot remove high amounts of elemental sulfur and have no capability of eliminating the interfering organosulfur compounds. Treatment with activated copper powder only removes elemental sulfur, but organosulfur compounds remain in the extract, and additionally to that also phenyltins are partially lost (up to 50 %). It is shown that ligand exchange chromatography with $AgNO_3$ coated silica gel as adsorbent removes effectively elemental sulfur and interfering organosulfur compounds from the sediment extract allowing the quantitation of butyltins with recoveries > 80 %. If Ag NO_3 coated silica gel is added directly to the concentrated sediment extract in the vial, elemental sulfur and all interfering organosulfur compounds are removed nearly quantitatively yielding recoveries of the butyltins > 85 %, and no time consuming column chromatography is necessary. Since the phenyltin compounds are strongly affected by the desulfurization step, they should be measured in the untreated extract.

E48

SIMPLE IMMUNOASSAY TESTS FOR DETECTION OF PESTICIDES BASED ON BIOTIN-STREPTAVIDIN SYSTEM AND COLORED COLLOIDAL DYES

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The analytical control of drinking water, food and soil for pesticides contamination is of great importance for healthy environment. However conventional methods such as gas or liquid chromatography widely used for pesticide detection are time-consuming and require expensive equipment and specially trained personnel. Alternative immunoanalytical approach is of special interest for environmental monitoring due to the simplicity, rapidity and high sensitivity of immunoassay techniques.

To improve the detection limit of pesticides simple method for preparation of highly active streptavidin-peroxidase conjugate (STR-HRP) has been developed. The activity of STR-HRP conjugate increases due to oligomerization of HRP before conjugation. The sensitivity of bioanalytical methods based on the developed highly active STR-HRP conjugate could be improved approximately 4 times. To simplify the assay procedure simple method for preparation of non-enzymatic streptavidin-colloidal dye conjugate (STR-DYE) has been developed. The activity of different color (black, blue, red and yellow) STR-DYE conjugates and STR-HRP conjugate was compared. The sensitivity and specificity with STR-DYE conjugates was approximately the same as with the conventional HRP conjugates with known insoluble substrates. The most active conjugate (STR - Cubic Black) was used for development of immunofiltration and comb dot-assay for pesticide detection.

Competitive ELISAs and simple competitive immunofiltration and comb dot-assay for simultaneous detection of simazine and 2,4-dichlorophenoxyacetic acid (2,4-D) based on the obtained highly active (HA) STR-HRP or STR-DYE conjugates have been developed. The assay duration of developed tests was approximately 5 (immunofiltration), 15 (comb dot-assay) or 90 (ELISA) min. The detection limit of both pesticides for immunofiltration, comb dot-assay and ELISA was compared (Table 1). The developed tests are simple to perform, economical, rapid, stable and can be used in the areas with few laboratory facilities and by personnel with little laboratory experience.

Table 1. Detection of pesticides by developed methods

Pesticide	Detection limit, ng/ml			
	Comb Assay	Immunofiltration		ELISA
	STR-DYE	STR-DYE	STR-HRP (HA)	STR-HRP (HA)
Simazine	2	4	2	3
2,4-D	2	4	2	4

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SPECIATION OF Se IN SOILS WITH HIGH CONTENT OF ORGANIC MATTERS

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Selenium is a trace element present in environment at levels which may be anywhere between essential and toxic to living organism. The behaviour (toxicity, biovailability, mobility, reactivity, distribution) of Se depends on many factors. In environmental matrices, among the possible oxidation states, selenium is mainly present as Se^{+4} and Se^{+6}, even if several organoselenium compouds may be present. There is increasing interest for the determination of the chemical forms of Se compounds due to their different toxicity and the next important properties influenced the environment. Hydride generation atomic absorption spectrometry (HG AAS) is preferred method for the determination of selenium, particularly at low concentrations. The measurement requires destruction of the sample matrix and the residue taken up in solution. Therefore decomposition of the sample is one of the most important steps in trace metal determination using atomic absorption method. The solubility of Se-containing minerals ranges from the very soluble (Se^{+4} and Se^{+6} minerals) to the extremly insoluble ones (Se^{+2} and Se^{0}). In addition, the high content of organic matters which associated or occluded the multioxidation states of Se can complicated not only decomposition process but the determination by HG-AAS method as well.

The aim of this work is to evaluate the different decomposition procedures and sequential extraction in different type of soils with extremely high content of organic matters. The verification of accuracy was performed by model samples which were prepared with CRM soil materials and different amounts of plants materials of known composition. The results were statistically evaluated and recommended procedure was applicated on the determination of Se in natural soil samples.The total content of Se does not indicate the mobility, biovailability, and toxicity of Se.

E50

SPECIATION OF ARSENIC IN SURFACE WATERS

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The content of arsenic in the environment is of great concern because, it is recognized as a cumulative poison to animals and people. Arsenic is also a potential human carcinogen [1]. The wide use of inorganic and organic arsenic compounds in agriculture and industry results in releasing this element into the enivronment. The measurement of individual species of arsenic in the aquatic environment is particularly important because of the variations in toxicity and carcinogenicity of the different compounds of this element. Arsenic (III) is not only more toxic, but also may represent a greater carcinogenic hazard than the other compounds such as As(V) or organic species of arsenic.[2]
In the present study, samples were taken from the river Zayandehrood, which receives the agricultural and some industrial waste-waters. The sample PH was adjusted to 2 with hydrochloric acid. The extraction of As was performed using methyl thioglycolate (MTG) and cyclohexane. Speciation of total inorganic and organic species was performed by a Philips (Model PU 4400) gas chromatograph, equipped with a FID detector and fused-silica capillary column RSL-150 (polydimethylsiloxane, 10m x 0.53 mm, i.d.). Speciation of inorganic arsenic was carried-out by hydride-generation atomic absorption spectrometry. Table 1 shows the average concentrations of the different species of arsenic in the samples.

Table 1 Concentrations of arsenic species in the river Zayandehrood ($ng\ l^{-1}$)

Sampling station	As^{3+}	As^{5+}	Organic arsenic (MMA + DMA)
1	310	3154	35
2	276	2457	32
3	195	2910	28

MMA = monomethylarsenate , DMA = dimethylarsinate

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[2] J. J. Yu and C. M. Wai, ***Anal. Chem.***, 1991, 63, 842-845.

E51

INDIRECT DETERMINATION OF IODIDE BY COLD-VAPOR ATOMIC ABSORPTION SPECTROMETRY

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Different methods for indirect determination of iodide by atomic absorption spectrometry have been reported by several researchers.[1,2] Iodide is a serious interferent in the determination of mercury by cold-vapor atomic absorption spectrometry (CVAAS). The indirect determination of iodide by CVAAS is based on the determination of decrease in the mercury absorption signal in the presence of iodide. With respect to the low concentrations of iodide in environmental samples especially in drinking waters, the CVAAS technique still requires development.
In this study, we have used an absorption tube containing gold coated sand for pre-concentration of mercury by amalgamation process. Then, mercury was released from the gold surface by thermal desorption and transferred into a quartz ended windows cell located in the pass way of hollow cathode lamp in the atomic absorption spectrometer. This technique has raised the sensitivity of CVAAS method and is able to determine trace concentrations of iodide precisely. In the present study, the concentrations of iodide in drinking water resources of the city of Isfahan have been determined. Table 1 summarizes the concentrations of iodide in the underground drinking water resources.

Table 1: Average concentrations of iodide in the drinking waters as $ng\ ml^{-1}$

Sampling location	Concentration of iodide
1	18
2	14
3	16
4	16

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E52

SIMULTANEOUS DETERMINATION OF MERCURY(II) AND CADMIUM(II) USING SEQUENTIAL INJECTION EXTRACTION.

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Cadmium is toxic to every system in the human body, whether ingested, injected or inhaled. Exposure to mercury can cause brain damage to a developing foetus and the exposure is considered more dangerous for small children because their nervous system are still developing and thus are more sensitive to these compounds. The determination of cadmium and mercury at these low concentrations which may be of toxicological significance requires highly sensitive methods, such as photometrical determination with dithizone. Depending on the reaction conditions, mercury(II) ions form an orange-yellow dithizonate [$Hg(HDZ)_2$] with dithizone in the acid range and violet secondary dithizonate in the neutral to alkaline range. Cd-dithizonate is pink and is very stable in the strong alkaline range. The huge difference in pH makes it possible to separate Cd and Hg. The intensely coloured products make photometrical detection possible.

A flow-based extraction method is described where an aqueous sample and organic solvent are injected sequentially into an extraction coil, then mixed and separated due to the differential flow velocities of the aqueous and organic phases. A 200$\mu\ell$ aqueous samples is propelled through a 25 $\mu\ell$ segment of organic solvent whose flow is impeded due to hydrophobic interactions with the walls of the Teflon extraction coil. This wall drag allows the faster moving aqueous sample to penetrate through and ultimately separate from the slower organic solvent. Carbon tetrachloride is used as solvent due to its hydrophobic properties. The Hg and Cd complexes are measured at 500 nm.

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E53

DETERMINATION OF IRON IN WATER : RESULTS OF INTERLABORATORY STUDIES IN YUGOSLAVIA

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During the last few years there were extensive activities in Yugoslavia regarding the introduction of quality system based on ISO 9000 standards. The system for accreditation of laboratories was also established and participation in interlaboratory studies is one of the requirements. Therefore several interlaboratory studies were initiated at the Faculty of Chemistry of Belgrade University. In some of them the spectrophotometric determination of iron was a compulsory part of the program. The methods proposed by Yugoslav standards (JUS) were used for analyses. In addition, determination of iron by AAS was offered as an option.

Nine to eighteen laboratories from water supply organizations, medical and public health institutions, pharmaceutical, chemical and allied industries, research institutes, universities, etc, were included in these interlaboratory studies.

Samples for laboratory intercomparison in 1996 were prepared by addition of corresponding components to tap water. For the interlaboratory study in 1997 river water (river Danube near Belgrade, just after its receiving of the Sava river), was used as sample matrix.

Among laboratories similar variations were found for both applied methods. Somewhat better agreement was obtained by the spectrophotometric method. Corresponding standard deviations were 0.07-0.46 (SP) and 0.08-0.67 mg / L (AAS), respectively. Although good results were obtained in most laboratories, additional efforts were required in some of them in order to improve their analytical work.

E54

HETEROCYCLIC COMPOUNDS IN ANALYTICAL CHEMISTRY OF ANIONS

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In the message the informations on determination of some anions in objects of an environment with application of heterocyclic compounds are resulted. Objects of the analysis - natural waters (river, lakes, springs). Difiniendums anions - NO_3^- and NO_2^-. A trial reactant - 1-phenyl-2,3-dimethylpyrasolon-5 (antipyrin). A medium - strong solution H_2SO_4. Time of interaction - practically instantly at the expense of development of high temperature of an analyzable mixture (H_2SO_4 :H_2O=1,5:1 $\Rightarrow$ ~383 K). The structure of formed products of interaction - nitrate and nitrite antipyrins is established.

The method of the relation of densenesses in variant Trzeszczynski [1] is applied for joint determination of components. Is shown, that the optical denseness of analyzable solutions for want of selected lengths of waves measured on a photoelectric colorimeter is higher, than on a spectrophotometer. It is stipulated by availability of two extremums on electronic spectra of products of a response. The limit of detection NO_2^- and NO_3^- in recalculation on nitrogen makes 0,016 and 0,015 ppm accordingly. The determination is not hindered by fair quantities of many ions. In conditions of realization of the analysis the oxidizing properties of iron (Ш) are exhibited. The method it of neutralizing for want of determination of total nitrogen is resulted. The determination of nitrites both nitrates in the painted and muddy solutions is possible. The relative standard deviation (S_r) does not exceed: NO_2^--0,13; NO_3^- - 0,031.

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E55

DATA BASE OF ENVIRONMENTAL ORGANIC CONTAMINANTS FOR THE REGIONAL CHEMICAL MONITORING

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A data base (DB) has been created for chemical monitoring and to predict environmental changes in West Siberia regions and to assess pollution of Arctic Ocean by Ob river waters.

DB is operated and managed by MS Exel and MS Access software. It includes name, formula, molecular weight, concentration and time variaton for more than 500 contaminants identified and quantified in surface and ground waters and soils based on ten year observations by GC/MS technique (Method 625 EPA USA). The compounds observed include aliphatic and aromatic hydrocarbons (C6 and larger), PAH, chlorinated hydrocarbons, phenols, organic phosphates, carboxylic acids, esters, amines, alcoholes, aldehydes, azaaromatics, chlorinated pesticides and carbamates.

The DB allows to estimate protection degree of underground aquifers from surface influence and to observe the migration and transformation processes of different ecotoxicants under the effect of climatological and geophysical factors. Using specially developed algorithms, the DB enables us to trace priority pollutants for particular regions and to develop target analytical techniques for solution of special problems of enviromental monitoring.

The DB is used for inventory of industrial wastes and location of sourses of accidental pollutions, for environmental monitoring as well as for technological and social managment. Thus, under the study of consequences of a great accident happened in 1993 at a radiochemical plant in the Tomsk Region, DB of organic contaminants and GC/MC technique for analysis water and soil allowed us to locate borders of the territory polluted by the products of the damaged reactor. Higher sensitivity and selectivity were achieved in comparison with radiation monitoring.

E56

COMPLEX OF ANALYTICAL METHODS FOR DETERMINATION OF IMPURITIES IN PRODUCTION OF "SOLAR" QUALITY SILICON

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The complex of methods is used for the determination of 50 elements with in range of contents from n% in the initial raw material to 10^{-4} –10^{-10}% in intermediate and the final products. It includes the direct analytical methods and those assuming a preliminary solution of solid samples and a concentration of impurities.

In direct express multielement methods (Direct-Current Atomic Emission Analysis, X-ray Spectrometry and/or Energe Dispersive X-Ray Fluorensces Analysis) there should be complete similarity of the composition of analysed assays and calibration samples to minimize of matrix influence on the accuracy. Because the choice of standard reference materials of quartz and metal silicon is limitted, the role of intermethod control increases. The difference of analytical weighed charges was used in these methods (0.050 g and 2.00 g, accordingly) allows to hold the quality control of sampling and to calculate a representative weight for instrumental methods with preliminary chemical preparation.

The determination of impurity contents below the detection limit of direct analytical methods is fulfilled by the methods with a preliminary sample solution: DC-AEA with concentration of admixtures on the graphite powder, variants of ICP-Mass Spectrometry. The difficulties arise in determining boron and phosphorus. For these reasons the intermethod control using one-elemental methods of analysis, such as Atomic Absorbtion Spectrometry and Spectrofotometry and the creating of the reference standard samples of an enterprise are necessary for obtaining of credible analytical results.

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E57

OPTIMIZATION OF ON-LINE HPLC-MICROWAVE OXIDATION-HG-AAS FOR ARSENOBETAINE AND ARSENOCHOLINE DETERMINATION

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Arsenic compounds are widely distributed in the enviroment, depending their toxicity on their molecular forms present in foods. Although arsenobetaine and arsenocholine are arsenic species which exhibit low toxicity, their detection and quantification is very important because they are the main arsenic species present in marine organisms.

HPLC coupled with a microwave oxidation was used for these cationic organoarsenic species separation. The detection was performed by on-line HG-AAS.

As a first step the anionic arsenic species (As (III), As (V), MMA, DMA) were separated from the arsenobetaine and arsenocholine on a sep-pack, making use of the different ionic charge.

In order to separate arsenobetaine and arsenocholine an ion-exchange column was used with phosphate buffer as mobile phase. Due to those species do not generate asenies without a predecomposition, a previous oxidation with persulphate in a microwave oven was employed. The parameters that affect the separation, oxidation and hydride generation were optimized.

The detection limits, reproducibility and recovery were calculated.

E58

A COMPARISON OF ANALYTICAL METHODOLOGIES FOR DETERMINATION OF As IN SOILS BY ETAAS

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Pollutants have certain intrinsic properties which determine the likely effect that they will present after emission or discharge into the environment. These properties include short and long term toxicity, dispersion properties, chemical reactions that the compounds undergo, including their decomposition, tendency to be bioaccumulated in food chains and ease of control. Due to these effects nowadays the availability of an analytical technique is desirable, which should be free from interferences over the concentration range of the concomitant species and should be capable of measuring 10% of the maximum allowable contaminant in several environmental samples for public health protection.

Because of the advantages shown by the ElectroThermal Atomic Absorption Spectrometry (low detection limits, minimum sample preparation allowing "in situ" injection and minimization of the background signals close to the analytical line of the analyte) this technique is at present one of the most widely used.

The aim of this work is to evaluate the performance of an analytical methodology for the determination of As in soils, by comparison of modifiers (Pd and Ru) reducing agents (hidroxylamine hydrochloride and argon-hydrogen stream gas) together with the effect of background correction devices (continuum source and Zeeman-effect). Once the analytical conditions were optimized for the comparative method studied, the analytical quality assurance was evaluated with standard soil reference materials and the developed methodology was applied to the analysis of soil samples from northern Mexico.

E59

DETERMINATION OF FIPRONIL RESIDUES IN DIFFERENT MATRICES

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Regent is a permitted pesticide in the Slovak Republic into cereals against Lema spp., into potatoes to control Leptinotarsa decemlineata, as well as into rapeseed and in forestry as insecticide into pines and pine tree nurseries.

Residues of Fipronil, the active ingredient, were determined in order to get a decomposition curve in rapeseed plants and bodies of honey bees after application of Regent insecticide.

There have been developed a new analytical method for determination of Fipronil residues: the ethyleneacetate extraction step performed in a horizontal shaker is followed by an ultrasonic reextraction. The unwanted coextracts were elimined by column chromatography. The final determination of Fipronil residues was preformed by gas chromatographic method - using NPD and GC- MS systems.

E60

APPLICATION OF THE IDA MICROELECTRODES IN Se TRACE ANALYSIS IN ENVIRONMENTAL WATER

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The lowering the size of the working electrode under 10 μm brings significant advantages which designate microelectrodes for application in ultra-trace analysis. Nevertheless, the currents are low which causes some problems with their measurement. One possibility of signal increasing is their arrangement to arrays. Especially effective are the interdigitated array (IDA) microelectrodes capable of independent polarization of both its segments.
The stripping voltammetry is the only electroanalytical method which can fulfill the high sensitivity requirements of ultra-trace analysis. Analysis can, however, be disabled by multiple peaks formation during dissolution of the deposit.
In this work the procedure solving this problem is proposed. It is a modification of the "enriched solution" method. IDA microelectrode with the vertical arrangement was applied. It consists of two segments with 26 fingers each. Segments are vertically separated by 0.3 μm wide insulation layer. One segment of the array is polarized by the potential at which selenium is deposited for accumulation. Next the potential is stepped to positive and Se is stripped. Se(IV) sticks to the "rastered" surface of the microelectrode in the laminar part of the diffusion layer and is at disposal for the following reduction done at the second segment at high recovery. The reduction current was used for evaluation because it is almost free of the capacity component since its potential is constant.
In comparison with "enriched solution" our method has some advantages. The recovery of Se(IV) is near 100 % in our method because of very low insulator width (0.3 μm). In the method of "enriched solution" it is much lower because of diffusion losses during the stripping process preceding cathodic scan. Our method was tested using synthetic samples and results were compared with the methods applying Hg hanging and Au disk working electrodes. Our method provided more reliable results. It can be recommended as an advantageous alternative for Se monitoring at the trace level in environmental water.

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E61

AN ALTERNATIVE METHOD FOR THE MEASUREMENT OF DISSOLVED TOTAL NITROGEN IN WASTEWATER

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The characterization of wastewater has become necessary to supervise the treatment process efficiency and to control the quality of treated water. Wastewater quality is usually characterized by global parameters like Biological Oxygen Demand (BOD), Chemical Oxygen Demand (COD), Total Organic Carbon (TOC) and Total Suspended Solids (TSS) and by the measurement of nitrogen and phosphorus compounds. Nitrogen compounds occur in wastewater in inorganic as well as organic forms. The standardized determination of nitrogen [1] consists of an acid digestion followed by an indirect dosage of the ammonium thus formed. This method (called Kjeldahl method) requires strong conditions and needs a long reaction time.

However, it is possible to oxidize by UV radiations the inorganic and organic nitrogen forms into nitrates and nitrites that are directly measured by UV spectrophotometry. The use of far direct UV (185 nm) show an improvement of the experimental procedure compared with the Kjeldahl method especially for reaction times (5 h to 10 h for Kjeldahl method ; 2 h to 3 h for direct UV). A more effective method consists of using the far UV radiations with a strong oxidant (10 min to 30 min reaction time). Thus, we propose an alternative method based on UV radiations in order to oxidize the different nitrogen forms and also to determine wastewater nitrogen concentrations.

The procedure is based on the conversion of ammonia nitrogen and organic nitrogen into nitrates by potassium persulfate promoted by UV radiations (emitting at 185 nm and 254 nm). The oxidization reaction is automatically followed by an on-line UV spectrophotometer. The nitrates are measured by an UV spectrophotometry deconvolution method of which the principe is to consider the UV absorption spectrum as a linear combination of a few numbers of reference spectra [2]. The effects of several parameters (pH, oxidant concentration, etc.) were studied in order to determine the optimum conditions for a quantitative conversion. A pH 9 buffer and a 4 $g.l^{-1}$ potassium persulfate solution were founded as the best conditions.

The procedure was first applied on model compounds : ammonium chloride and urea, respectively an inorganic and an organic nitrogen form. The mixture of the two nitrogen forms was studied too. In the three cases, the percentage of conversion was around 90% with the mentioned conditions. More complex molecules (glycin, glutamic acid, acetyl glucosamine, nitrophenol, aminophenol, atrazine) were also tested and conversion yields were dependent to the structure molecules (aromatic molecules are weak oxidized). Then, the procedure was extended to the measurement of dissolved total nitrogen in samples from several sewage treatment plants and from a distillery. The results were compared with those obtained by the Kjeldahl method. A high correlation coefficient (0.98) between these two methods was established.

[1] Kjeldahl J., Z. Analyt. Chem., 1883, 22, p 366.
[2] Thomas O., Métrologie des eaux résiduaires, Cebedoc/Tec et Doc, Liège, 95

E62

CHARACTERISTICS OF NATURAL ORGANIC MATTER: SIZE, DIFFUSION COEFFICIENTS AND ELECTROPHORETIC MOBILITY

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When characterizing NOM, it is essential to (1) *use several techniques in parallel* both to derive as much structural information as possible and to act as a cross-check on the possible production of artifacts by the sample preparation and analysis and (2) *employ preparative methods which minimally perturb the system*, since structural determination of NOM can be substantially biased by processes such as sorption, coagulation and sedimentation. The techniques of Atomic Force Microscopy (AFM), Transmission Electron Microscopy (TEM), Fluorescence Correlation Spectroscopy (FCS) and Capillary Electrophoresis (CE) were used to derive complementary information about the size, diffusion coefficients and electrophoretic mobility of the NOM samples. The TEM and AFM gave complementary, but not identical, information regarding the conformation of the natural organic matter. A large majority of the material in all samples appeared as points with AFM heights of approximately 1 nm. Larger aggregates (up to several microns) were also apparent with both techniques, particularly with TEM. FCS gave values for diffusion coefficients which were in the range 2.1-3.0 * 10^{-10} m^2 s^{-1}. Assuming a sphere, this corresponds to molecular weights of 2000-4000 and molecular diameters of between 1.6 and 2.0 nm, in reasonable agreement with both the TEM and AFM. The large aggregates visible by TEM and, to a lesser extent, AFM were not apparent by FCS, most likely because of the low fluorescence of the aggregates. CE was carried out using both fluorescence (excitation at 325, 457 and 488nm) and UV-absorbance (200, 210, 254 and 288 nm) detection on several samples. The different modes of detection gave qualitatively similar electropherograms. Although enhanced fluorescence was observed when exciting at 325 nm compared to 488nm, qualitatively similar electropherograms were also observed at different fluorescence excitation wavelengths. Electrophoretic mobilities were calculated and found to be in the range -3 to -7.5 x 10^8 m^2 s^{-1} V^{-1}.

E63

A VERSATILE NOVEL TOOL FOR TRACE METAL ANALYSIS BASED ON HOLLOW FIBER SUPPORTED LIQUID MEMBRANE

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Metal ions are present in various chemical forms in environmental samples, in particular in natural water. To understand the role of a specific species in terms of bioavailability, bioaccumulation, mobility and persistence in environment, development of analytical techniques that are sensitive and specific to a given element or compounds is of utmost importance. The analysis of trace metals in natural waters i.e. in the concentration range 10^{-12} to 10^{-8} mol/l is still a challenging task. Methods allowing reliable and real time analysis as well as automation need to be developed for water quality control especially to meet the water quality requirements incorporated in the legislation For this purpose a versatile tool for speciation of trace metals particularly Cu, Pb and Cd based on flat or hollow fiber supported liquid membrane (HFSLM) consisting of 1,10 didecyl diaza crown ether (R), fatty acid (FA) and a mixture of toluene and phenylhexane(1+1) is well suited. The supported liquid membrane method allows simultaneous separation and preconcentration of target metal ions. In this poster hollow fiber supported liquid membrane for trace metal speciation in particular Cu and Pb in drinking water, fresh water and sea water will be presented. Metal analysis were done off line using AAS and on line using voltametry. The applicability of SLM for on field measurements of Cu and Pb in fresh water will be demonstrated. Detection limits > 10^{-11} mol/l can be achieved by combining HFSLM with very sensitive analytical detectors. The major limitation of this method is long term stability. In order to improve this, detailed investigations of mechanism of the transport of metals across such system, with flat sheet supported liquid membrane, and ways of improving the stability of the supported liquid membrane will be presented.

E64

ANALYTICAL ASPECTS OF STUDY OF ENVIRONMENTAL ANTIMONY SPECIATION

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There is a number of antropogenic sources of antimony pollution in the environment connected with fossil fuel power stations, mining and industrial applications of antimony in electronics, glasses, fire retardants and others. The speciation analysis is mainly connected with differentiation of the oxidation states of antimony (III) and (V), however there are also information about the occurence of methyl derivatives of antimony. Generally it is known that these methyl derivatives are less toxic than the inorganic forms, in particular Sb (III), being more toxic than Sb (V). The reliable information on antimony speciation requires the preliminary study of stability of antimony compounds in conditions used frequently for mineralisation of environmental samples.

The low levels of antimony in the environment require sensitive procedures of its determination. The most common one is based on the atomic absorption spectrometry combined with the hydride generation. Because of the interest in low concentrations such procedure usually should be combined with some enrichment step. This may be based on preconcentration of antimony directly in the graphite furnace, or on its specific sorption on a solid sorbent. Such procedures have been applied in the analysis of a number of environmental samples.

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G1

MULTICOMPONENT GAS ANALYSIS OF A MIXTURE OF CHLOROFORM , OCTANE AND TOLUENE USING A QUARTEZ MICROBALANCE SENSOR ARRAY

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Piezoelectric devices with gold electrodes and quartz crystal (AT-cut) coated with polydimethyl siloxane (PDMS), polyether urethane (PEU),polyethyl cellulose (PEC), and polycyanopropyl methylsiloxan (PCPMS) were used in an array of quartz microbalance sensors. The quartz crystals were mounted in a thermostated chamber equipped with an inlet and outlet for gas permeation. The data acquisition and gas flow was PC controlled. The calibration of organic vapors was carried out by isothermal exposure at room temperature with concentrations ranging from 100-1000 ppm for toluene and chloroform, and from 250-2000 ppm for octane. In binary mixtures of toluene and chloroform the prediction values as deduced from a multicomponent analysis after appropriate calibration showed statistical errors below 12% . In toluene and octane mixtures the errors were slightly higher. For ternary mixtures of the vapors of the following three volatile organic compounds (VOC's) tested, statistical errors amounted 6%for octane, 8% for chloroform and up to 25 % for toluene. The results are finally discussed based on partition coefficients to describe individual interaction mechanisms between the organic volatiles and the polymers.

G2

DEVELOPMENT OF AN AMPEROMETRIC PEROXIDASE ELECTRODE IN REVERSED MICELLES

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The possibilities and advantages of using reversed micelles as appropriate working media for the development of amperometric enzyme biosensors with analytical purposes are discussed. Horseradish peroxidase (HRP) biosensors in reversed micelles offer an alternative and relatively faster and more sensitive method for the quantitative analysis of peroxides such as H_2O_2, organic and inorganic peroxides. The possible pollution and toxic effects arising from wide application of this class of compounds requires that they are closely monitored.

The nature of the organic solvent (ethyl acetate and chloroform) and the surfactant (Triton X-100 and dioctyl sulfossuccinate) used to form reversed micelles, as well as the concentration of the aqueous dispersed phase have been investigated. All these experiences allowed us to conclude that the most suitable solvent for a good performance of the proposed biosensor with analytical purposes was ethyl acetate. Moreover, the optimum hydratation of the enzyme is an essential aspect of the performance of the biosensor in these media. The enzyme electrode showed a rapid response to the changes in the 2-butanone peroxide concentration, the steady-state current being reached in 25 s.

In conclusion, it can be said that the most important advantages of the use of reversed micelles for enzymatic reactions are: these systems can be employed for solubilization of both hydrophilic and hydrophobic substances, the amount of water necessary for obtaining the optimal degree of the enzyme hydration, and, consequently, of the enzyme activity in water-immiscible solvents, is very easy to control and finally the enzyme electrodes in reversed micelles can be prepared by direct adsorption of the enzyme on the electrode surface (graphite electrode with rough surface).

G3

APPLICATION OF FIBER OPTIC CHEMICAL SENSORS IN WATER TREATMENT

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Fiber optic chemical sensors (FOCS) and systems are finding increasing number of applications in industry, environmental monitoring, medicine and chemical analysis. Advantages of FOCS result from the properties of fiber optics and physical or chemical phenomena utilised in their construction. There are several reviews on FOCS published over the last decade [1,2].

The principle of the operation of fiber optic chemical sensor is a chemically sensitive receptor part which can be called a chemooptical interface. This interface converts information on measured analyte into changes of optical signal and it governs the performances of the whole sensor. Often such an interface is made of a polymeric membrane containing an appropriate indicator. Some methods of design and optimization of the chemooptical interface will be presented and the typical application of the sensors will be given. Recent experimental results concerning the design of a multiparameter fiber optic probe suitable for on-line monitoring of drinking water will be described. The multiparameter fiber optic probe, which consists of pH, temperature and calcium ions sensors was tested in laboratory conditions with the use of artificial samples [3]. Each of the sensors is based on the absorbance changes of an appropriate reagent. Light emitting diodes (LEDs) are used as light sources and they are matched to maximum absorbance of the reagent immobilized in the chemooptical interface.

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2. G. Boisde, A. Harmer, Chemical and biochemical sensing with optical fibers and waveguides, Artech House, Boston - London, 1996.
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G4

TITRATIONS WITH ELECTROGENERATED HYPOBROMITE IN THE DIFFUSION LAYER OF IDA MICROELECTRODE

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Interdigitated array system composed of generator and collector microelectrodes was used to study the transfer of hypobromite between the two segments. Influence of ammonium and iodide on the transfer has been evaluated and applied for their determination. The technique has been named diffusion layer titration. It utilizes chemical reaction proceeding quantitatively only in a close vicinity of the electrode. One segment of an interdigitated array serves for galvanostatic anodic generation of hypobromite ($Br^- + 2\ OH^- \rightarrow BrO^- + H_2O + 2e^-$) and the second set immersed in the diffusion layer of the generator, detects its unreacted flux. The detector (collector) is potentiostated to the potential of the limiting diffusion current of hypobromite reduction. Because of short distance between generator and collector the collection efficiency is very high (about 85%). The diffusion layer titration curves (collector current versus generator current plots) measured 'point by point' or by slowly scanning the generator current, show very good reproducibility. Since no bulk phase chemical reaction actually proceeds, the experiment can be repeated extensively in the same solution.

The sensitvity of this method is 2383 $\mu A\ M^{-1}$ and the determination limit is 2.4×10^{-6} M for ammonium determination (based on the chemical reaction $3\ BrO^- + 2\ NH_4^+ \rightarrow N_2 + 3\ Br^- + 2\ H^+ + 3\ H_2O$). For the determination of iodide the sensitivity was 4810 $\mu A\ M^{-1}$ and determination limit 5×10^{-7} M (overall reaction $I^- + 3\ BrO^- \rightarrow IO_3^- + 3\ Br^-$).

The method was applied to the trace determination of ammonium in the river water as well as to the analysis of iodide content in the eaten salt.

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G5

BASICAL STUDY TO DEVELOP SENSORS AND BIOSNSORS FOR FREE RADICALS

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The determination of free radicals is mainly performed y ESR or by some colorimetric semiquantitative tests. Comparatively, despite of the importance of free radicals, particularly oxygen free radicals due to their involvement in serious diseases, there are few methods based upon electrochemical measurements, particularly on electrochemical sensors and biosensors, even if these devices are generally inexpensive, easy to be built and to be used.

Recently, we have approached the problem starting from the determination of oxygen free radicals, in particular the superoxide radical, assembling several new kinds of electrochemical sensors and biosensors suitable for this purpose. To this aim, we based our research on a superoxide dismutase enzyme biosensor, somewhat similar to that recently described by *Min Ik Song et al.*

Studied biosensors are based on superoxide dismutase with two different types of amperometric transducers, one for the determination of oxygen and the other for the determination of hydrogen peroxide; the latter one gave the best results. Both were studied in aqueous solutions and applied to check the ability of several substances to act as radical scavengers.

We also tried to develop an organic phase solvent enzyme electrode (OPEE), using the superoxide dismutase enzyme sensor but we obtained poor results with the classical model. A new way of assembling the biosensor using a sandwich of the SOD enzyme between two gas-permeable membranes coupled to the oxygen amperometric transducer, was studied. The results show its ability to work in demethylsulphoxide solutions.

A second approach consists of an electrochemical system able to detect superoxide radicals produced by an enzymatic reaction: the system is based on the reduction of cytochrome *c* by the superoxide radical produced in the oxidation reaction of xanthine catalysed by the xanthine oxidase; then the reduced form of the cytochrome is electrochemically detected. Measurements are performed firstly by cyclic voltammetry, then we developed a true carbon electrode having cytochrome *c* as mediator and Fe(III)-protoporphyrin as promotor for continuous superoxide radical determination working at constant applied potential.

A third approach consists in the assembly of two new electrochemical sensors (one a classical selective membrane potentiometric sensor and the other one a solid state glassy carbon or CHEMFET) suitable for the determination not only of superoxide radicals, but also of other free radicals (like the hydroxide radical). Both these devices are based on a selective membrane containing benzylidenphenylnitrone able by a *spin trapping* reaction to generate adducts when reacts with radicals.

Even if the last approach needs further investigations, the results obtained can be considered as a starting point for further researches in this field.

G6

SUBMICROMOLAR DETECTION LIMIT OF SOLVENT POLYMERIC ION-SELECTIVE ELECTRODES: INFLUENCE OF SAMPLE AND INNER ELECTROLYTE COMPOSITIONS

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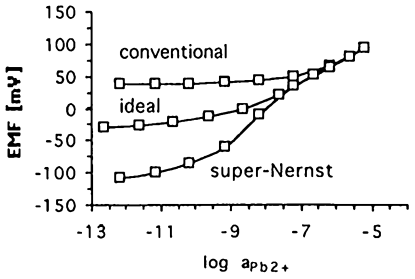
The lower detection limit of ion-selective membrane electrodes (ISEs) is improved by generating ionic gradients in the membrane. It is shown that both the lower detection limit and the shape of the ISE response function depend on the compositions of the inner electrolyte and the sample. The results are interpreted in terms of a model describing the influence of concentration gradients generated through ion-exchange processes at both sides of the membrane. Gradients that induce a flux of primary ions towards the sample cause the lower detection limits to be too high. On the other hand, when this flux is directed towards the inner reference electrolyte, the detection limit is improved. However, if it is too strong, the membrane surface is depleted of primary ions and the ISE response is super-Nernstian (see Figure for three ISEs based on the same Pb^{2+}-selective membrane). Such ISEs show an ideal response to most of the discriminated ions in the concentration range of 10^{-1} to 10^{-4} M thus allowing the determination of unbiased Nicolskii selectivity coefficients. It has also been found that much lower concentrations of interfering sample ions than expected from the Nicolskii equation already influence the detection limit.



G7

USE OF ION EXCHANGER ON THE BASIS ION ASSOCIATE TETRAETHYL-AMMONIA DIBENZYL-DITHIOPHOSPHATE IN ION-SELECTIVE ELECTRODE

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The possibility of creation and use of a liquid - membrane ion - selective electrode sensitive to dibenzyldithiophosphate -one of the frequently found sulfurcontaining organic reagents - widening application on inorganic analysis was studied by us. The ability of tetraethylammonia salts to form an ion associated complex. With potassium dibenzyldithiophosphate was used for the creation of an electrode sensitive to dibenzyldithiophosphate - ion. The resulting complex acts as electrode active substance in the membrane.

Basic analytical parameters of the created dibenzyldithiophosphate ion - selective electrode are given: concentration range, detection limit, response time of the electrode, sub - Nernstian behavior.

Slopes Ion -selective dibenzyldithiophosphate electrode's behaviour nas studied in potassium dibenzyldithiophosphate and other inorganic ions solutions on the reagent concentration range $10^{-7}...10^{-1}$M. Influence of ion exchanger concentration and internal standart solution concentration on a work of dibenzyldithiophosphate was studied. Dependence of ion-selective electrode potential on pH was investigated by adding hydrochloric acid and sodium hydroxide to the solution of potassium dibenzyldithiophosphate (concentration 10 mol/l). The electrode potential is stable over the pH range 2-10. It was found that dibenzyldithiophosphate ion-selective electrode is characterised by rather good analytical parameters;response time is 50 sec, detection limit is 6.10-6mol/l, sub-Nernstian slopes 60 mB/decade.It has made possible the use of this electrode for dibenzyldithiophosphate-ion determination. The tapping of dibenzyldithiophosphate ion-selective electrode on potentiomentric titration of potassium dibenzyldithiophosphate by Ag, Hg(I,II), Cu(II), ion is possible.

G8

DEVELOPMENT OF FLUORIMETRIC OPTODE MEMBRANE COATED ON OVERHEAD TRANSPARENCY FOR SULPHIDE DETERMINATION

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Sulphide-selective optode membranes have been developed by immobilizing tetraoctylammonium fluorescein mercuric acetate (TOAFMA), tetraoctylammonium hydroxide and tributyl phosphate into ethyl cellulose. These membranes were coated on overhead transparency films as solid support and employed as sensing devices for fluorimetric determination of sulphide.

The sensing scheme is based on the fluorescence quenching of TOAFMA by hydrosulphide ions, which can be related to the concentration of the sulphide present in solution. The response behaviour of the membrane is slightly pH dependent at pH value higher than 10.0. At pH 12.5, the useful detection range is 0.066 to 4.4 μM of sulphide. The detection limit is found to be 66 nM.

The concentrations of sulphide in spiked water samples determined by the sulphide-selective optode membranes at pH 12.5 were found to fairly agree with the added concentrations.

The optode membrane has a fast response time of less than 1 min. The fluorescence signal of the optode membrane can easily be recovered by rinsing with a solution of 0.42 mM of sodium hypochlorite and 0.10 mM of sodium acetate.

Anions including bromide, nitrate, perchlorate and dichromate interfere seriously to the detection but other anions such as sulphite, oxalate, thiosulphate, iodide, sulphate, nitrite, acetate, fluoride, chloride and carbonate either do not interfere or interfere slightly.

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G9

ABOUT UNCERTAINTY OF MEASUREMENT AND LEGISLATIVE LIMITS

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Uncertainty of measurement (UOM) is an essential parameter for comparing analytical results. A major problem still under debate is how to take into account UOM in evaluating compliance to legislative limits. As a matter of fact, the inadequacy of existing norms mainly stems from inattention to or rejection of UOM by legislators and policy-makers and from some misunderstanding of the involved matter.

To evaluate compliance to a legislative limit, the analyte concentration in the suspect matrix, C_X, has to be compared with the the allowed value, *i.e.* with the maximum acceptable concentration, C_M. This implies the comparison of the relevant signals, (S_X and S_M, respectively). However, in order to take into account both α and β errors [1], the *minimum detectable inadmissible signal*, S_I, which is higher than S_M, must be considered. The higher is the desired confidence level, the higher is S_I. Moreover, S_X is affected by UOM, being obtained by repeated measurements of the suspect matrix, while S_I, by its very definition, is not. The comparison can be made by proper statistical techniques.

However, some technical decisions have to be *a priori* taken and some practical problems have to be solved to properly evaluate compliance as above specified. The matter is critically discussed in the light of literature information [2,3] to show how analysts can compensate legislative inconsistencies by proper data analysis.

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G10

Prussian Blue based amperometric biosensor for the detection of glutamate.

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We reported earlier that the high sensitive first generation amperometric biosensors could be developed on the basis of Prussian Blue modified electrodes [1,2]. Optimizing the method of Prussian Blue deposition we synthesized the completely selective electrocatalyst of hydrogen peroxide reduction insensitive to oxygen in a wide potential range. Since such selectivity was the property of biocatalysis we called the Prussian Blue as 'artificial peroxidase'. The problem found with application of artificial peroxidase in electroanalysis was the stability of Prussian Blue layer at negative potentials as compared with (Prussian Blue)/(Prussian White) redox potential. The stabilization of the electrocatalyst was achieved by deposition of Prussian Blue from solution of 0.1 M KCl and 0.1 M HCl where all ferrous ions were not expected to contain any hydroxide ions in their coordination spheres. The resulting Prussian Blue modified electrodes were stable at negative potentials in neutral supporting electrolyte solutions.

To develop Prussian Blue based biosensors suitable for analytical applications we used flow-injection technique. Glutamate oxidase (GMO) was immobilized on the surface of modified electrode in Nafion layer. Enzyme containing Nafion membranes were made from water-ethanol mixture with high ethanol content. The response of GMO biosensor to glutamate was based on amperometric detection of enzymically generated hydrogen peroxide at -50 mV vs SCE. The calibration range for glutamate was 1.10^{-7}-3.10^{-4} M and the detection limit was 1.10^{-7} M.

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G11

SnO_X THIN FILM GAS SENSOR WITH STABILISED ELECTRICAL CHARACTERISTICS

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Solid-state gas sensors based on the metal oxide are world-widely utilised for many years as gas analysers or as a part of multisensor systems to recognise the range of specific gases and odours. Thin-film structures are more attractive ones to develop the sensors compared with sintered powders and thick layers mainly because of ability to apply novel microelectronic techniques under their production.

Among the variety of available techniques, the magnetron sputtering has been usefully employed to grow uniform metal oxide thin films in a very accurate way with a high gas sensitivity. There are two approaches to obtain films with the desired stoichiometry in frames of the technique: 1) the film deposition in the Ar atmosphere with the following annealing and, 2) the film deposition in the Ar/O2 mixture. Both ways suggest the creation of a number of oxygen vacancies which are responsible for the film gas-sensitive properties. The undoped SnOx sensors prepared by both methods were found in this study to have a high sensitivity to reducing gases. However, the long-term instability of the film conductance caused by an oxygen diffusion at advanced operating temperatures has terminated the film application in gas sensors. The film doping by copper atoms under the sputtering has allowed to stabilise the sensor electrical characteristics. The effect is discussed assuming a decrease of oxygen vacancy mobility in the presence of Cu atoms in the film.

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G12

ANALYTICAL ABILITY OF CHOLINESTERASE AMPEROMETRIC BIOSENSOR IN THE PRESENCE OF VARIOUS ACTIVATORS

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The activation of catalytic activity of some particular enzymes by the compounds of various nature has been less studied than inhibition. This is also the fact for cholinesterase (ChE). However, the use of activators opens up new analytical possibility for biochemical sensors. Several ways of such compounds application can be considered

In the presence of alkaline and alkaline-earth metals in the solution observed increases in 1,5-2 times of analytical signal produced with ChE amperometric biosensor (ChEBS). This effect depends on the nature of substrate and activator and their concentrations, pH and enzyme activity in the biosensitive part of the sensor. We observed a decrease in activating behaviour from Ca(II) to Ba (II) among alkaline-earth metals.The activation constants are $(3.8\pm0.3)\times10^{-6}$ mol/l for Ca(II) and $(8.4\pm0.3)\times10^{-6}$ mol/l for Ba(II). The lower limit of determination (C_{lim}) of ChE inhibitors is decreased by 1,5-2 orders due to the influence of above mentioned ions. The increase of ChEBS signal was also observed in the presence of metal-ions (Pb (II), Cd (II), Tl (I), Hg (II)) known as environmental pollutants. These ions act as activators if the concentration is lower than 1×10^{-7} mol/l.

Immunoenzyme sensors for pathogenic fungi such as Candida albicans (CA), Phytophthora infestans (PhI), Trichophyton rubrum (TR) were developed by modification of biosensitive part of ChEBS with antibodies against corresponding fungi. When antibodies vs. CA are 1:20 diluted then C_{lim}= 1.6×10^{-16}mol/l. For PhI C_{lim} is 6×10^{-14} mg/ml for 1:50 dilution. The activation constants for CA are $2.1(\pm0.2)\times10^{-7}$-$5.6(\pm0.4)\times10^{-10}$ l/mol depending on experimental conditions.

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G13

Discrimination Between Contaminated Milk Samples Using an Array of Coated Piezoelectric Quartz Crystals

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Headspace analysis of milk samples and contaminated milk samples was performed by means of an array of polymer coated piezoelectric quartz crystal and a fuzzy logic pattern recognition scheme.

The discrimination between uncontaminated milk, milk contaminated with *Bacillus cereus* and milk contaminated with *Pseudamonas fragi* has a potential role, as indicators to pre- or post pasteurisation contamination.

A membership function for a class is developed using the mean sensor array response, standard deviation of array response and a height parameter. A grade of similarity of each test sample with reference knowledge base is calculated according to the following equation

$$\mu_{ref \bullet test} = \frac{\sum_{i=1}^{n} \min\left[R_i, T_i\right]}{\sum_{i=1}^{n} \max\left[R_i, T_i\right]} \qquad i = 1, 2, 3, \ldots$$

$$= \frac{\left[R_1 \cap T_1\right] + \left[R_2 \cap T_2\right] + \ldots}{\left[R_1 \cup T_1\right] + \left[R_2 \cup T_2\right] + \ldots}$$

The grade of similarity was used to successfully classify the unknown samples.

G14

NEW DATA SUPPORTING THE INTERPRETATION OF K^+ POTENTIOMETRIC MEASUREMENTS IN ALBUMIN CONTAINING SOLUTIONS

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Ion selective electrodes are useful electroanalytical tools whose characteristics offer well known advantages in terms of both functionality and quality of results.

Nevertheless, matrix effects from complex media have been reported in situations such as physiological conditions [1,2].

Results concerning potentiometric analysis of K^+ with valynomicin based ion selective electrodes in albumin containing solutions have been interpreted as effects at the membrane surface and at the liquid-liquid interface with the reference half-cell [3,4].

In this work, the data of recent spectroscopic (FTIR) [5] and potentiometric (Batch and Flow) studies are presented and discussed aiming at a better understanding of both contributions and, therefore, improvements of the analytical methodology.

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G15

ANALYTICAL APPLICATION OF SOLID-CONTACT POTENTIOMETRIC ANIONIC SURFACTANT SENSORS

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Control for the content of anionic surfactants (AS) in the presence of organic and inorganic substances is a complicated analytical problem. Potentiometry with ion-selective electrodes (sensors) is a perspective method for the determination of these toxicants in industrial and environmental objects.

The potential stabilization of sensors with graphite current taps is related to the graphite surface features. In the present work, plasticizer (dibutylphthalate) penetration into a graphite current tap with formation of carbon compounds has been experimentally proved and its quantitative determination has been carried out by means of spectrophotometry and IR-spectroscopy.

The studied AS-sensors can't determine individual anionic surfactants in complex AS mixtures. Their membranes were modified by chitin (pore sizes 10 nm, 100 nm) and nylon (pore sizes 45 nm) molecular sieves as well as synthetic ones with fixed pore sizes for increasing the selectivity of AS-sensors. Two techniques of the molecular sieve covering on the membrane surface were proposed. The modified solid-contact AS-sensors allow one to detect separately anionic surfactants, different from each other by one CH_2-group, in complex environmental objects at the limit acceptable levels.

All the developed anionic surfactant sensors are applicable for the determination of individual surfactants (modified sensors), the overall content of AS by direct potentiometry method (conventional sensors), for the rapid control over the various surfactants content in small sample volumes (10-20 µl). Solid-contact sensors based on a ionic associate cetylpyridinium–dodecylbenzenesulphonate were employed for the determination of the content of sodium alkylbenzenesulphonates and intermediate compounds of technical sulphonol production in industrial sewages.

G16

LIQIUD MEMBRANE ION-SELECTIVE ELECTRODES FOR POTENTIOMETRIC DOSAGE OF SOME METAL IONS

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Four electrodes with liquid membrane, Cu^{2+}-selective and Ni^{2+} -selective, respectively, not described previously in the literature, were prepared and characterised. From these electrodes, 1 and 2 are based on simple complexes of Cu(II) and Ni(II) with 2,3-dithio-6-nitro-benzoquinoxaline-5,10-dione, as ligand belonging to the dithiols class. Electrodes 3 and 4 are based on the corresponding mixed complexes in which the ammonia molecule acts as the second ligand along with 2,3-dithio-6-nitro-benzoquinoxaline-5,10-dione as the first ligand.

Both Cu^{2+}-selective electrode and Ni^{2+}-selective electrode respectively have been used to determine the concentration of Cu^{2+} and Ni^{2+} ions in aqueous solution both by direct potentiometry and by potentiometric titration with EDTA. There were determined the selectivity constants for their practical use to potentiometrically determine the content of copper and nickel.

By comparison with the electrodes based on the simple complexes (1 and 2), the electrodes based on mixed complexes (3 and 4) present a better selectivity regarding the interfering ions and also, they have greater potential rises of the titration curves.

For that reason, the electrodes based on mixed complexes are better suited for titrations from dilute solutions, down to 10^{-5} M. All these electrodes present a Nernstian answer that is 29 mV at 25° C, in a concentration range comprised between 10^{-1}-10^{-5} M for the electrodes 1 and 2, respectively 10^{-1}–10^{-6} M for the last two electrodes. Direct potentiometric methods for the determination of Cu^{2+} and Ni^{2+} ions in aqueous solutions and in industrial waters were also studied.

The experimental analytical results were checked by using the method of standard additions and also by comparison with atomic absorption spectrometric determinations.

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G17

EQUIVALENCE POINT IN NEUTRALIZATION REACTIONS WITH USE OF PRETREATED GOLD ELECTRODES

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Experimental data that have been obtained through the zero-current bipotentiometric method in the acid-basic titration based on the use of two differently pretreated gold electrodes: anodisation in 1N H_2SO_4 at 1,5 V vs. S.C.E. (oxidized) and cathodization in 1 N H_2SO_4 at 0,6 V vs. S.C.E. (reduced) are presented. To obtain differentiated response to the pH variations two identical rectangular gold fold electrodes were used, each having an apparent geometrical surface of 1 cm^2. During the investigation, the hydrogen peroxide was found to have an important part in the stabilization of the function of gold as a pH indicator.
Small quantities were found to be sufficient for the stabilization, about 0,08 M (~0,2%) H_2O_2 , indifferently of the pretreatment. In these cases, the electrode functions are linear on a large pH range (1,68 - 13,00), their slopes being similar to the Nernst slope. The stability of the oxid film on the gold surface in alkaline medium is greater than in acid medium. These data prove that using such electrode in the acid-basic titration, common titration curves can be expected, with inflexion points round the equivalence point. Analysis of the electrode potentials reveals that these form appear since the potential variations of one of the electrodes during the titration are generally small. This electrode is used as referrence electrode. According to the electrode polarization,the resulted bipotentiometric titration curves have normal or revesed S-shape. The procedure of the equivalence point indication in the acid-basic titrations is better concerning the accuracy and precision comparatively with the classic potentiometry. The advantages of the measurements without reference electrodes lie in the simplicity. The procedure suits to continuous determinations and can become automatic by the use of the classic recording devices.

G18

OPTICAL SENSOR BASED ON THIN FILMS OF POLYANILINE

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Abstract
Polyaniline (PANI) films have been used for optical measurement of pH, various neutral sugars and ascorbic acid in a wavelength range suitable for diode lasers.
We show that PANI films are suitable materials for optical sensing of pH. Thin films of PANI were polymerized chemically in hydrochloric acid solution on supports such as polystyrene cuvettes. The films undergo pH-dependent changes in the visible/near infrared range and give titration curves covering a wide pH range. The pK_a values range from 5.3 to 10.5 and depend on the aniline used. Copolymers of aniline and anthranilic acid are useful supports for immobilization of enzymes such as urea. Such films can be used for detection of urea. PANI films are redox-active and also respond to reductants such as ascorbic acid.
Copolymerization of aniline and 3-aminophenyl boronic acid (1:1) yields a sugar binding polymer which also shows pH-dependent absorption changes. The copolymers were used to determine glucose, fructose, sorbitol, mannitol and ascorbic acid at pH 7.2. Concentration-dependent bathochromic shifts and changes of the absorption maxima can be observed. Sorbitol, fructose and mannitol showed higher effects compared to that of glucose. Importantly polyaniline shows no effects on addition of sugars.
Such films represent an interesting alternative to enzyme-based glucose sensors because of the low cost of preparation, the compatibility with LED light sources and the ease of preparation.

G19

CONCENTRATION AND SEPARATION OF METAL IONS Zn(II)-Cd(II) AND Zn(II)-Pb(II) WITH CHELATING REAGENTS BY ZONE MELTING TECHNIQUE

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The concentration and separation of Zn(II), Cd(II) and Pb(II) traces after their extraction with an thionalide (HA) excess, have been studied.
It was analysed the concentration and separation capacity function of: the type of phase diagrams temperature - composition for binary systems HA-MA_2; the value of the effective coefficient distribution for MA_2; the chelate compounds solubility in a chelating agent; the speed of passing the melting zone; the elements concentration [1,2].
In order to increase the separation factor, the ligand excess has been substituted with a "solid solvent", diphenyl.
Regarding to the concentration of chelate compounds from the HA-MA_2 and diphenyl-MA_2, systems, it can be concluded that: the separation factors increases with the increasing of the chelate compounds solubility in a chelating agent or in the solid solvent used; the effective coefficient distribution decreases with the increasing of chelate compounds solubility in the studied system and the limit repartition needs a small number of zonal passings; higher values of the concentration factor have been obtained for values lower than unity of the effective coefficient distribution and at higher speed of passing the melting zone.
Referring to the chelate compounds separation, this process is determined by the same parameters like for the concentration process.

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G20

PREPARATION AND APPLICATION OF SOLID STATE SELENITE ION SELECTIVE ELECTRODES

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Selenite ion selective electrodes using solid salts of Cu_2S, Ag_2S, Ag_2Se and Ag_2SeO_3 in various compositions were prepared. Among them two were found to be highly sensitive to selenite ion. One electrode had a composition of 90% Ag_2Se 10% Cu_2S and the second one 80% Ag_2Se, 10% Ag_2SeO_3, 10% Ag_2S. Their optimum working conditions for selenite determination is investigated. The change of potential was linear in 10^{-5}-10^{-1} M concentration range of selenite. The slope of the linear portion was 28 mV / 10 fold change in selenite concentration for the electrode of 80% Ag_2Se, 10% Ag_2SeO_3, 10% Ag_2S, for the second electrode on the other hand the slope was 21.5 mV. It was therefore decided to work with the electrode which had higher slope throughout the work. This electrode was also very sensitive to OH^- ions, there was a linear response for OH^- ion in 10^{-7}-10^{-2} M concentration range with a slope of 53 mV. Thus this electrode can be used for the determination of high pH values, where alkaline error takes place with glass electrodes. Because of the sensitivity to OH^- ions, the pH has to be hold fixed during selenite ion determination. The expected interferences of SO_4^{2-}, SO_3^{2-},S^{2-},Cl^-,Br^- and I^- ions were also examined. The amount of selenium in anodic slime was determined using this electrode and consistency with different methods was obtained.

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NEW AMPEROMETRIC IMMUNOSENSORS FOR DRUGS ASSAY

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Novel amperometric immunosensors based on graphite paste (graphite powder and paraffin oil) have been constructed. The graphite paste is impregnated with antibody.
The proposed amperometric immunosensor construction provides the immunosensors with excellent features to develop immunoassay. The construction is simple; the immunosensors can be made fast and reproducible. The reliability of the analytical information is assured by the low RSD values obtained for the recovery tests and by the fast response of the amperometric immunosensors.
The sensitivity of the immunosensors as well as the low limit of detection made them suitable for a lot of drug assay, like thyroid hormones (T3 and T4) at lower concentration levels: ppb-ppt.

G22

CHARACTERISATION OF THE 5HT$_3$ SEROTONIN RECEPTOR USING A FLUORSCENT LIGAND

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At present the knowledge on the structure and function of ligand-gated ion channels is limited. Our final aim is to correlate ligand binding with structural changes and channel opening to obtain a dynamic view of the receptor's architecture. All serotonin receptors are G-protein coupled, except the 5HT$_3$ receptor that acts as a ligand-gated cation channel.

The 5HT$_3$ serotonin receptor was purified from mammalian cells in an active form and the ligand binding site was investigated by fluorescence spectroscopy. In this respect, an antagonist ligand has been labelled with fluorescein, exploiting the environmental sensitive fluorescence of this probe. The fluorescent ligand, called GR-fluorescein, showed fluorescence properties similar to fluorescein.

The binding of the GR-fluorescein to the 5HT$_3$ receptor was observed in real time by measuring the concomittant fluorescence intensity change. The dissociation constant Kd fo the binding of GR-fluorescein to the 5HT$_3$ receptor was determined from the final (equilibrium) fluorescence intensities, or from the time course of fluorescence decreased (kinetics). The two different determination yielded a Kd of 0.24 nM and 0.26 nM respectively, similar to the Kd of 0.32 nM obtained from a competition assay with the radioactive ligand [^{3}H]-GR 65630.

The pharmacology of various ligand non-fluorescent was investigated by competiton with the receptor binding of GR-fluorescein. The Kd values determined were similar as those obtained from a radioactive competition assay.

Exploiting the environemental sensitivity of the fluorescent ligand, the ligand binding site was assigned to have an acidic character involving predominantly electrostatic interactions rather than hydrophobic.

Finally, accessibility of the binding site was investigated by fluorescence quenching of the GR-fluorescein bound to the receptor. The quencher used was the antigen binding fragment (Fab) of the anti-fluorescein antibody, as charged molecules are known to modulate the receptor activity. Radioligand-binding assay, electrophysiology and confocal fluorescence measurement suggested that the ligand binding site of the 5HT$_3$ receptor is located on the surface of the protein.

G23

REACTIVE SPUTTERING OF IRIDIUM OXIDE ON POLYMER FILMS FOR THE DEVELOPMENT OF A STABLE PH-SENSOR - AN ELECTROCHEMICAL INVESTIGATION

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Several metal oxides especially in the platinum group have been used as pH-sensitive materials. These electrodes are stable to high temperatures and pressures as well as to aggressive chemicals. Therefore they are very suitable as pH-sensors in a wide range of applications [1]. Iridium oxide electrodes can be prepared by anodic oxidation of iridium or thermal decomposition of iridium chloride. In the last years the preparation by reactive sputtering from an iridium target became more important [2]. Different materials like aluminia, titanium or stainless steel as substrates are described. In the presented work different polymer films like PET (polyethyleneterephthalate), PC (polycarbonate) and PS (polystyren) were investigated as substrates. Iridium oxide is sputtered in an oxygen/argon plasma under different conditions and various materials are used as an adhesive layer, especially for the decrease of the electrical resistance. The pH-sensitive properties of these electrodes were investigated in different solutions in a range from pH 0 to pH 14. The potential varied linearly with the pH range and the slope was near Nernstian sensitivity with 57 to 59 mV/pH. Electrochemical properties in different solutions are investigated by ac impedance spectroscopy and cyclic voltammetry. Additionally, the surface conditions and morphology of sputtered iridium oxide films (SIROF) are examined by AFM, SEM and XPS.

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G24

POTENTIOMETRIC BIOSENSORS BASED ON INTERNAL IRIDIUM OXIDE pH SENSOR

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Species of acidic and basic properties are products of numerous enzymatic reactions. Hence, chemical pH sensors are often utilised as internal sensors for the design of biosensors sensitive to substrates of these reactions. Most frequently potentiometric detectors are used, although increasing interest is observed recently in the use of optosensing. In enzymatic potentiometric biosensors membrane electrodes with glass or polymeric membranes and pH ISFET's are most often used. In such applications pH sensitive oxide electrodes offer several advantages.

In this study the iridium wire electrodes covered thermally with iridium oxide are shown as satisfactory internal sensor for enzymatic electrodes sensitive to urea and butyrylcholine.

For both biosensors cellulose triacetate (CTA) and poly(vinyl chloride)(PVC) were examined as matrices for the entrapment of enzymes at the electrode surface. In both cases the suspension of enzymes in solution of CTA or PVC in appropriate solvents were evaporated on the surface of Ir/IrO_2 electrode. Better long-term stability, reproducibility and sensitivity of the urea biosensor were obtained for urease entrapped in a PVC layer. Biosensor with linear response in semilogarithmic co-ordinates from 0.2 to 4.0 mM urea can be used for indirect detection of Hg(I), Hg(II) or Ag(I) with a detection limit of about 50 nM, based on measurements of the initial rate of potential change after addition of substrate with inhibited enzyme in biosensor.

For the butyrylcholine biosensor better results were obtained when immobilizing butyryl cholinesterase in a CTA layer. Such a sensor can be used for the indirect determination of fluoride in the milimolar concentration range based on reversible inhibition, as well as for determination of pesticide paraoxon in sub-ppm range based on irreversible inhibition of enzyme activity.

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G25

TIME EFFECT ON INHIBITION OF Na^+,K^+-ATPase AND Mg^{2+}-ATPase ACTIVITIES BY SIMULTANEOUS EXPOSURE TO $Pb(NO_3)_2$ AND $Cd(NO_3)_2$

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Time effect on the inhibition of Na^+, K^+-ATPase and Mg^{2+} -ATPase activities by *in vitro* exposure to $Pb(NO_3)_2$ and $Cd(NO_3)_2$ was investigated in the rat brain synaptic plasma membranes (SPMs). The simple optical test for the determination of the ATPase activity based on the colored reaction of liberated inorganic phosphate (PO_4^{3-}) by hydrolysis of adenosine triphosphate (ATP) catalyzed by these enzymes was developed. Investigations were carried out with the aim to develop a (bio)sensor for the simultaneous detection of these metals in waste waters.

The effect of $Pb(NO_3)_2$ and $Cd(NO_3)_2$ on the Na^+, K^+-ATPase and Mg^{2+} -ATPase activity was investigated varying the concentration of the corresponding salt from 10^{-9} to 10^{-3} M. The results showed the concentration and time dependent inhibition. The IC_{50} values (salt concentration that produced 50% inhibition) obtained after ten-minute exposures of enzymes to the salts were 5.3×10^{-4} M ($Pb(NO_3)_2$) and 1.3×10^{-5} M ($Cd(NO_3)_2$) for Na^+, K^+-ATPase and 7.2×10^{-4} M ($Pb(NO_3)_2$) and 3.7×10^{-4} M ($Cd(NO_3)_2$) for Mg^{2+}-ATPase. The 40-minute exposure of the enzymes to the salts did not influenced IC_{50} values for $Cd(NO_3)_2$, but significantly decreased IC_{50} values for $Pb(NO_3)_2$. The value 1.5×10^{-5} M for Na^+, K^+-ATPase was obtained. Simultaneous exposure of the enzymes to $Pb(NO_3)_2$/ $Cd(NO_3)_2$ showed that $Pb(NO_3)_2$ did not influence $Cd(NO_3)_2$ induced inhibition after 10 min, but 40 min exposure of both enzymes to the mixture of the investigated salts induced an additive effect.

G26

THE NEW Pb-SELECTIVE ELECTROD

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Recently [1] it was noted that hexagonal ferrites with the structure of magnetoplumbite can find use for creation of Pb-selective electrodes.

The paper studies some characteristics of new Pb-selective electrode based upon a solid solution the system $SrFe_{12}O_{19}$ - $PbFe_{12}O_{19}$. All synthesised samples were prepared by ceramic technique and were single phase ($Co_{K\alpha}$–radiation, 2θ= 20–60°, V=1°/minute). The electrodes of two kinds were studied: with ceramic membrane and with polymer (polystyrene) membrane which was filled by oxide materials. Both electrodes have solid contacts.

The best characteristics have electrodes based upon a solid solution $Sr_{0,95}Pb_{0,05}Fe_{12}O_{19}$. The linear concentration dependency for interval $1\cdot10^{-6}$ – $1\cdot10^{-1}$mole/l and interval pH 2,5 - 5,0 with slope 29±4 mV/pC has been established. The multiple excess of ions K^+, Ni^{2+}, Co^{2+}(1000), Cu^{2+}(100), Ag^+(50), Sr^{2+}(10), Ba^{2+}(4) non disturbed the determination of concentration Pb^{2+} ions. The lead was determined by the method of precipitating titration with potentiometric indication of a titration endpoint.

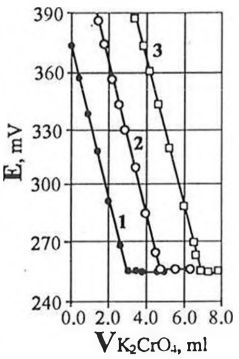

Fig. Titration curves Pb(II) by C_{K2CrO4} = 0.1000 mole/l: 1 - 0,3; 2- 0,5; 3 - 0,7 mmole Pb^{2+}.

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G27

SUBMICROMOLAR DETECTION LIMIT OF SOLVENT POLYMERIC ION-SELECTIVE ELECTRODES: SIMULATION OF THE RESPONSE

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Ion fluxes through the membrane of ion-selective electrodes (ISEs) in contact with highly diluted sample solutions influence the local ion activities at the membrane surface. So, concentrations in the aqueous surface layer of conventional electrode membranes are found to be in the order of 10^{-6} M even when the bulk of the sample virtually does not contain any analyte.

Ion concentration gradients, and thus fluxes, can be influenced by the choice of the inner electrolyte. The quantitative model presented here considers ion exchange equilibria at the membrane surfaces as well as transport kinetics in both the organic and the two contacting aqueous solutions. It is shown that the composition of the inner electrolyte has an influence on the lower detection limit and response function of the ISE. On the one hand, the lower detection limit is improved by orders of magnitude when small decreasing concentration gradients of the primary ion towards the inner electrolyte are induced. However, large gradients are predicted to lead to a significant depletion of primary ions at the aqueous membrane surface and thus to super-Nernstian response.

Simulations (cf. Figure) based on this transport-dependent model agree with the experiment.

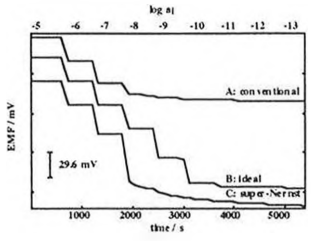

Figure: Simulated calibrations of different ISE types conditioned to steady state in 10^{-3} M sample solution. The stepwise tenfold dilution calibration simulation was started at 10^{-5} M.

G28

A COULOMETRIC CARBON DIOXIDE SENSOR FOR A MARINE APPLICATION

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The ocean plays an important role in moderating the atmospheric concentration of carbon dioxide. Therefore the dissolved carbon dioxide-concentration has to be known. A common method for the determination of carbon dioxide uses water samples from Niskin bottles analysed by gas chromatography or NDIR-analysers [1]. In order to allow continuous measurements we have transferred the coulometric measuring principle described previously [2] to a marine application.

Carbon dioxide diffuses through a hydrophobic membrane and reacts with an alkaline electrolyte (e.g. pH 10.5) causing a pH value shift which is detected by an iridium oxide pH electrode. When the decrease of the pH value reaches a fixed value (e.g. pH 10.3) the electrolyte is titrated with coulometrically generated hydroxide ions until the starting pH value is reached again. The duration of the pH value change is an indicator for the carbon dioxide partial pressure. At the moment the dissolved carbon dioxide can be measured in concentrations between 20 ppm and 400 ppm. Using other membrane types for example this linear measuring range can be extended. The coulometric measuring principle allows long-term online carbon dioxide measurements in sea water. The design of the sensor is prepared for high pressure resistance to enable deep sea measurements of dissolved carbon dioxide-concentrations.

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I1

NEAR IR SPECTROSCOPY: APPLICATION IN THE IDENTIFICATION AND QUALIFICATION OF THE PHARMACEUTICAL OINTMENT

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The paper deals with the identification and qualification of some formulations of propolis extract based - ointment by NIR spectroscopy coupled with pattern recognition algorithms.

The second derivatives spectra (1100 - 2200 nm) were used to build the data basis. Library validation and test set are presented and the advantages and disadvantages of the methods are discussed.

I2

ESTIMATION OF UNCERTAINTY IN METHODS SUPPORTED BY LOW EFFICIENCY STEPS - Determination of PAH/s in waters -

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The estimation of the analytical measurements uncertainties through random error propagation laws can be affected by several problems. There are some important sources of uncertainty of difficult estimation, due to insufficient information (ex: calibration certificates without specified confidence level) or to the impossibility of distinction, through replicate analysis of major steps uncertainties (ex: recoveries).

The ISO and Eurachem guides overcome those problems correcting incomplete information through the assignment of assumptions or by simple judgement Type B estimations. They also make clear that the estimations based on more complete information (ex: obtained from experimental data), Type A, are to be preferred.

In this work we present a procedure for the study of low recoveries common on sample pre-treatment used in separative techniques, through a more like Type A estimation. The detailed knowledge of the instrumental interpolation uncertainty is possible after a careful choice of the mathematical model describing the calibration curve. The volumetric or gravimetric steps can easily be studied making use of the Eurachem's guide suggestions. Considering that all sources, but one (mass transference-concentration and/or extraction) are known, the unknown source can be calculated through the comparison of the information available in the experimental uncertainty. The equivalence of the combined standard deviation with the experimental dispersion allows the estimation of the recovery. Its absolute value can be estimated through the correction of the obtained values against the expected ones, assuming the recovery as the only source of systematic errors during the process.

This treatment was applied to the determination of 10 PAH/s by HPLC-UV/Vis after extraction and concentration steps.

I3

A MINERAL STUDY OF RAW MATERIALS USED IN BREWING

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The metal role in brewing showed that metal concentration in a commercial beer depended on 1) the amounts of metal in raw materials carried by the brewing plant uptake, 2) processing effects such as boiling with hops, fermentation, filtration, etc and 3) possible contamination after completion of processing. Not much has been said about extracting metals from the malt. The amounts vary according to mashing conditions and malt composition.

The mineral sustances present in raw materials contribute to ionic content of the wort and are not directly controllable by the brewer. As certain metallic ions have significant effects on the fermentative performance of brewer's yeast, it is important to control their concentrations in the liquor so as to optimize wort fermentability.

In this paper we have presented a systematic study of metals contained in raw materials used in brewing processes. Mineral elements (major, minor and trace elements) were determined by atomic absorption spectrometry or inductively coupled plasma spectrometry in raw materials (corn grits, brewest yeast, hops, etc.), products for the brewing process.

A sealed, pressure bomb of stainless steel with safety device and internal teflon reaction flask has been used to digest samples in concentrated acid without loss of trace metal.

Analytical survey of the prevalence of heavy metals and other metallic and semimetallic elements regarded as toxic in the brewing process is discussed.

I4

ANALYTICAL STUDIES CONDUCTED TO DEVELOP PHYSICAL-CHEMICAL METHODS FOR IDENTIFICATION OF ACTIVE INGREDIENTS IN MODERN COSMETIC PRODUCTS

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As well known, nowadays, modern cosmetic industry uses a large range of derivatives of fatty acids and sugars, amino acids, proteins and of other bioactive ingredients mainly natural.

The paper describes the analytical studies carried out to render evident several bioactive ingredients in various types of cosmetic bases (emulsions, gels, creams).

The identified active ingredients found in low and very low concentrations in the cosmetic products and analysed in this paper are: allantoin, cholesterol, elastosol, vitamin E, vitamin F, salicylic acid, urea, menthol, carotenoids, 1,8 cineole.

For which of the hereinabove active ingredient, specific methods of extraction from the cosmetic product base were developed. They were identified using Gas Chromatography, Thin Layer Chromatography, UV-VIS Spectrum.

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15

APPLICATION OF THE MODIFIED DILUTION-ADDITION METHOD TO THE QUANTITATIVE ANALYSIS OF COMPLEX INDUSTRIALS MATERIALS USING XRF

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The analysis of certain complex synthetic materials used in the ceramic and cement industries and especially in the case of frit and ceramic glazes is difficult due to the wide variety of components/elements involved and their different concentrations. For accuracy, the use of any instrumental technique requires standards of a similar matrix to the material to be analysed. The great diversity and complexity of composition of the materials in this study make it difficult to obtain reliable standards for each case.

The instrumental techniques available to analyse these materials are AAS, ICP/MS and XRF. As is well known XRF is the most widely used for several reasons. Traditional XRF determination uses different precisely calibrated standards from a wide number of different standard samples (bead and pressed power) to obtain different calibration curves. Given the possible wide variety of composition, a very large number of standards would be needed and would be difficult to obtain. Application of th Hyperbolic Model from the Modified Dilution-Addition Method would simplify this problem enormously, since only one standard of a similar composition to that of the unknown would be needed.

In this study, the above method has been applied to the analysis of cements and different glazes, both transparent and opaque, with satisfactory results.

16

EXAMINATION OF THE MORPHOLOGICAL HOMOGENEITY OF A DRUG SUBSTANCE

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The polimorphism of drug substances has become an important question in the last few decades. In some cases different modifications of the drug exhibited significantly different biological activities. In other cases dramatic morphology-dependent differences were observed in the pharmaco-technological features. Usually both effects are present to a smaller degree.

Nowadays the accepted modifications of the drugs are defined by their standard infrared spectra in the Pharmacopoeias. However, the uniformity of the respective infrared spectra does not *per se* guarantee morphological identity. The manufacturing of drug substances requires an in-depth knowledge of *a)* those parameters which may influence the morphological composition of the product, *b)* the sensitivity and detection limits of those measurement techniques which are applicable in contolling the morphological characteristics.

Here we report the examination, with different instrumental analytical methods, of the homogeneity of an antiulcer drug having two modifications A and B. Our main aim was to determine the limits of detection for A as a contaminant of B, and vice versa. FT-IR, FT-Raman, DSC and powder X-ray examinations were performed. The FT-Raman spectra of this drug will be presented here for the first time.

Our results showed that the different instrumental methods gave very different values of sensitivity. In our examinations X-ray powder diffraction proved to be the least sensitive in respect of both modifications. The detection limit was ≈5% by this method. However, we obtained interesting results with FT-IR and DSC. While traces of form A was easily detectable in modification B by DSC, this method was much less sensitive when modification B was investigated in form A. Conversely, the determination of modification B in modification A by FT-IR proved to be similarly sensitive.

Generally a few % of morphological impurity does not degrade the applicability of the material, but its examination and continuous control can be a key point in the quality assurance of the whole manufacturing procedure.

17

APPLICATION OF INTERNAL STANDARD FOR DERIVATIVE-SPECTROPHOTOMETRIC DETERMINATION OF COENZYME Q_{10} IN COMMERCIAL FORMULATIONS

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The internal standard (IS) method is commonly applied in various chromatographic techniques. This approach allows to avoid bias errors of sample preparation and to eliminate the influence of variable physical conditions on analysis process.

In this work the use of IS for derivative-spectrophotometric determination of Q_{10} in commercial formulations is proposed. The HPLC method is generally used for analysis of Q_{10}. The contents of coenzyme in pharmaceuticals is relatively high (10 or 30 mg per capsule) and HPLC analysis requires many-fold dilution. It could be a serious source of analytical error. To avoid such inconvenience the internal standard method has been applied. Tocoferol acetate has been chosen as internal standard for analysis of Q_{10} in pharmaceuticals. The analysis has been performed by zero-crossing technique. The first derivative of spectra allowed to read value of derivative spectrum of coenzyme at 284 nm while the signal of IS was negligible. Also, at 274 nm occurred the peak of IS and the differential signal of analyte has zero value. The proposed method allowed to determine Q_{10} in range 0.1-5 ppm (^1D=0.7939x+0.0214, r^2=0.9997, detection limit = 0.058 μg/ml). The analyte has been determined in Vita Care capsules (10 mgQ_{10}/capsule). The results (9.96±0.60%) were in good agreement with declared content of coenzyme Q_{10} in preparation.

18

ACCEPTANCE CRITERIA FOR VALIDATION PARAMETERS OF ANALYTICAL METHODS

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The basic aim of the validation process is the estimation of the fitness for purpose of the analytical method (i.e. for needs of the application for which the method was developed). Both the validation parameters and design of experiment should be chosen according to this aim. After treatment of the experimental data and calculation of the validation parameter values the answer on the question "Are they satisfactory or not?" is important because this answer defines the result of the validation. Obviously, the answer is dependent not only on the values of the validation parameters but on the acceptance criteria also. Namely acceptance criteria expresses the requirements to the method, to its fitness for purpose.

The acceptance criteria are based usually on an previous experience. For example, criteria formulated in AOAC "Peer-Verified Methods Program" lean on the data averaged for more than hundred methods on dependence of repeatability, reproducibility and other parameters on concentration of an analyte. These criteria are not specific and therefore in some cases they can lead to an erroneous assessment of the validation parameters and, correspondingly, to a false conclusion about the fitness for purpose of the method. Alternative criteria should be formulated on base of comparison of relevant methods or another principle.

The problem is illustrated on the results of validation of an new pH-metric method for acid value determination in oilseeds without titration.

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I10

COPPER STANDARDS OF SPIN CONCENTRATIONS FOR EPR; PREPARATION AND EVALUATION OF HOMOGENEITY

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The quantitative determinations of paramagnetic centers in solid samples by EPR need suitable standards. The main problem in the preparation of the solid standards is to get homogeneous distribution of the paramagnetic substance in a diamagnetic diluent.
The present work is a continuation of our studies on the preparation and evaluation of the quality of powder standards containing paramagnetic ions of copper. In the present stage of work a special attention was paid to obtaining as good homogeneity of the standards as possible.
Five standards (based on $CuSO_4.5H_2O$ diluted with K_2SO_4), each of mass of ca. 5 g, were prepared using the procedure described elsewhere [1], with some modifications. The concentration of Cu in each preparation was the same, i.e. 5×10^{19} atoms/gram.
From these preparations four series standard samples, according to the three-way orthogonal hierarchical experimental plan, were obtained. Each series contained 20 samples with masses of ca. 0.05 g.
The samples of two series were sealed in quartz tubes for EPR measurements. In the samples of two next series the copper contents was determined by AAS method.
All the results were interpreted by statistical methods considering factors such as: a) irreproducibility of average composition between preparations, b) macro- and micro-inhomogeneity of chemical composition within preparations, c) accidental error of EPR and AAS measurements.

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I11

TECHNOLOGIC PARAMETER AS A CRITERIA FOR ANALYTICAL METHOD'S ACCURACY EVALUATION?

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Accuracy of an analytical method is undoubtedly one of the most important parameters which obviously should be appropriately checked for each analytical procedure. Many different possibilities for evaluating accuracy are already well known to analytical chemists world-wide. The main insufficiency of the most preferred way i.e. analysing certified reference material is that it is quite often that there is no suitable CRM on the market. In such a case, interlaboratory study could be of great help, specially if different analytical methods are used for determining analytical parameters, but usually it is hard to find at least three laboratories familiar with the same or similar matrices. Moreover, if the research analytical laboratory works for industrial purposes it is often undesirable to exchange the results with laboratories of the concurrent factory.
As a producer of titanium(IV) oxide white pigment we found ourselves in the above described situation many times. But when some problems in managing technological process in pilot reactors occured last year, we systematically approached the problem.
All technological parameters of the process were under control and determined in advance. The dissolution process in reactor was repeated six times with the homogenised raw material formerly analysed. While the tehnologists deal with technological characteristics of the studied problem, analysts have had a lot of work to do with the analytic of the suspensions obtained after raw material dissolution process. Many problems i.e. separation of filtrate from the sludge, ensuring the homogenity of the suspension, determination of the temperature of ignition etc. are now solved and the accuracy of obtained results for the concentration of titanium in suspension is evaluated by calculating the mass bilance of the reaction.
Undoubtedly this could not be the absolute criteria for analytical method's accuracy evaluation, but we found out to be a valuable tool in situations where no other possibility of accuracy evaluation is available.

I12

TRACEABLE HIGH-PRECISION pH MEASUREMENTS BY MEANS OF A MULTI-POINT CALIBRATION PROCEDURE

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The knowledge of the quantity pH is relevant in many fields, environmental protection, biotechnology and human health care being among the most important.
pH measurements are carried out using glass electrode cells. These cells must be calibrated since they suffer from several kinds of deficiencies:

- Glass electrodes generally exhibit imperfect, so-called sub-Nernstian slope factors (mV/pH).
- Different liquid junction devices cause different and above all unknown diffusion potentials. They result in an inconsistency of the calibration function and other deficiencies, summarised under the heading residual liquid junction potential error.

The two-point calibration commonly in use is not designed to quantify the uncertainties, caused the above mentioned deficiencies. Therefore the multi - point calibration with linear regression has been used [1] employing several pH reference materials including biological buffers. The multi-point calibration allows for a quantitative evaluation of the uncertainty of the calibration function and hence of the measurement uncertainty of the pH of an unknown solution pH(X) [2]. pH(X) values thus obtained can be traced back to primary pH reference materials and ultimately to the definition of pH.

The multi - point calibration is also designed to characterise the residual liquid junction potential error of a particular liquid junction device. Capillary, ceramic, platinum and double junction devices have been tested. Some of them have been shown to cause uncertainties in the unknown pH value pH(X) of up to U(pH(X) = 0.08.

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I13

USE OF THE TOTAL YOUDEN BLANK IN THE MICROCOULOMETRIC DETERMINATION OF AOX IN BLEACHED KRAFT MILL EFFLUENTS

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The determination of adsorbible organic halogen (AOX) in bleached kraft mill effluents (BKME's) is of special interest since may of the sequences used for bleaching paper pulp involve using Cl_2 and/or ClO_2, which can produce a variety of chlorinated organic compounds. This has led to the widespread recognition of chlorinated organics in BKME as an environmental issue [1]. Despite controversy over the use of AOX as an effluent quality parameter, the regulatory agencies are setting discharge limits for AOX. Moreover, the presence of abundant AOX in BKME has fostered research aimed at developing effective means for reducing their proportions.
Also, the significance of this analytical parameter has aroused the interest in establishing various standards for the determination of AOX including DIN 38 409 H 14, SCAN-W 9:89, CPPA H.6P, ISO 9562. Notwithstanding the substantial energy expended in attempts at decreasing the amount of chlorinated compounds in BKME and the standards issued for their determination, inadequate attention has been paid to the significance of using a correct blank test in this determination. The use of a correct blank test is crucial if the results obtained must be free of the constant error component [2,3].
This paper demonstrates the significance of using a correct blank test fot the determination of AOX in order to eliminate any constant error in the laboratory sample, the Total Youden Blank, by considering four types of blank tests, *viz.* the method blank (MB), placebo blank (PB), system blank (SB) and Total Youden Blank (TYB). All this is demonstrated in the microcoulometric determination of AOX, according to standard SCAN-W 9:89, in two types of BKME's.

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I14

QUALITY, RELIABILITY AND FLEXIBILITY IN ANALYTICAL CHEMISTRY

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Three main concepts of greatest importance for the development of Analytical Chemistry are discussed. Quality represents the first step concerning the sample characterization. Reliability means maintaining the quality in time. Flexibility means the reliability of the quality.
All these factors influence the final results of the analytical characterization of samples and contribute to the improvement of the quality control of various materials.

I15

APPLICATIONS OF AUTOMATIC WATER SORPTION ANALYSIS BETWEEN 0 AND 100% RELATIVE HUMIDITY

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New equipment for the automatic water sorption analysis of solid and liquid samples is now available. Replacing labour-intensive traditional methods, this innovative approach has research and quality assurance applications in fields as diverse as biomimetics, pharmaceuticals, food and additives, gas filtration, archaeology, building materials, textiles and packaging.

Investigations have been carried out at relative humidities between 0 and 100% and temperatures between 10 and 60°C. To date the following features have been studied:

- the extent of reversibility of water sorption of a variety of samples;
- crystal (trans-)formations mediated by water sorption;
- a comparison of the kinetic and thereby mechanistic properties of the water sorption of tablets and powders;
- thermodynamic parameters of water sorption;
- drying behaviour of archaeological wood;
- water sorption characteristics of natural compared with manmade materials;
- a comparison of the water sorption characteristics of closely related samples;
- moisture leakage of packaging materials.

The findings have resulted in a better understanding and improved processes in research and production.

I16

INTERCOMPARISON MEASUREMENTS OF GAS MIXTURES BETWEEN SMÚ AND NMi

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The Slovak Institute of Metrology and the Netherland Meetinstitut (NMi) have made regular intercomparisons of the gas mixtures. The four mixtures (CO_2 in nitrogen, CO in nitrogen, propane in nitrogen and synthetic natural gas (CO_2, N_2, CH_4, C_2H_6, C_3H_8, n-C_4H_{10}, i-C_4H_{10})) have been compared. The intercomparisons were founded by project PSO96/SK/2/2.

The gas mixtures have been prepared by NMi according to ISO standard 6142 (Gas analysis - Preparation of calibraton gas mixtures - Weighing methods). They were afterwards analysed by SMU. The primary reference materials (PRMs) for calibrations curves were supplied by NMi. The CO_2 in nitrogen, CO in nitrogen, propane in nitrogen were analysed by ND-IR monitor and the natural gas by gas chromatography. The results were evaluated according to ISO 6143 (Gas analysis - Determination and checking of calibration gas mixtures - Comparison method).

The results are presented in the following table:

No. of mix.	Compound	x grav. NMi (mol/mol)	U (mol/mol)	x anal. SMÚ (mol/mol)	U (mol/mol)	Rel. differences (%)
1	CO_2 in N_2	0,15001	0,00010	0,15009	0,00018	0,05
2	CO in N_2	0,04570	0,00004	0,045730	0,000104	-0,06
3	C_3H_8 in N_2	0,0008966	0,0000008	0,000897	0,000004	-0,04
4	natural gas CO_2	0,042474	0,00013	0,04242	0,00045	-0,12
	N_2	0,041248	0,00012	0,04116	0,00065	-0,22
	CH_4	0,85045	0,0009	0,84809	0,0108	-0,28
	C_2H_6	0,038125	0,00009	0,03810	0,00021	-0,08
	C_3H_8	0,021936	0,00008	0,02191	0,00096	-0,14
	n-C_4H_{10}	0,0028826	0,000012	0,00289	0,00013	+0,24
	i-C_4H_{10}	0,0028802	0,000012	0,00289	0,00012	+0,35

The relative differences between gravimetric values and measured values were below 0,1% (two component mixtures) and below 0,5% (natural gas components). The intercomparisons have confirmed good measuring capabilitis of "Laboratory of gas mixtures - SMU" for these four types of gas mixtures.

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K1

DETERMINATION OF AMINO ACIDS BY ONE AND TWO-DIMENSIONAL HPTLC AND MASS SPECTROSCOPY

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Two-dimensional TLC is a powerful separation technique with the potential to separate mixture containing more than 150 components. Unfortunately, it is much more difficult to optimize two-dimensional than one-dimensional TLC. Aditionally, disadvantages of 2-D method include difficult interpretation of results, reduced reproducibility compared to 1-D TLC, poorer detection sensitivity because of greater diffusion during two developments. Additionally, it is difficult to make the reliable in situ quantification for compounds having a wide range of response characteristics due to the fact that standards cannot be developed together in both directions.

This paper will present the state of the art in solving such problems by using one and two-dimensional HPTLC for determination of 18 amino acids from food samples. Since TLC/MS has already been shown to be technically feasible and applicable to wide variety of problems in both qualitative and quantitative analysis, we used these techniques for the identification of the amino acids in a mixture. The amino acids of interest is eluted from the chromatographic plate, collected and than introduced by atmospheric pressure chemical ionisation as a discrete sample to the mass spectrometer. The obtained results were compared to those obtained by slit-scanning densitometer and Camag Video Documentation System.

K2

OCCURENCE OF RESIDUES FROM EPOXY PHENOLIC COATINGS IN CANNED FISH IN OIL.

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The levels of Bisphenol-A-diglycidyl-ether (BADGE) and Bisphenol-F-diglycidyl-ether (BFDGE) were quantified as part of a European survey on the migration of residues of epoxy resins into oil from canned fish. BADGE and BFDGE are monomers which are used for the production of epoxy based polymers for canned foods. These coatings provide chemical and corrosion resistance to cans both during the heat process and the long shelf life of the food product. There has been concerns about the potential toxicity of such residues upon migration into the food. In order to assess the exposure to BADGE and BFDGE from canned foods in fatty medium, the contents of 379 samples of fish cans from all 15 Member States and Switzerland were analysed. The samples were dissolved in hexane, extracted with actonitrile, and analysed by reverse phase HPLC with fluorescence detection after a rapid membrane filtration. The analysis of the fish showed that about 3% and 6% of the samples contained BADGE and BFDGE, respectively, at a level superior to 1 mg/kg. The samples exhibiting higher concentrations were mostly anchovy cans. This might be due in part to the fact that the cans tended to be of smaller dimensions and the area to fish weight ratio was thus larger. No correlation could be found between high BADGE or BFDGE concentrations and country of production, since additional information on the can coding system would be necessary to trace the origin of cans and lids. The samples with higher concentration were mostly from cans manufactured in 1991-1995, hence prior to the appearance of concerns.The correlation with an intake study will provide a more realistic assessment of the actual consumer exposure.

K3

Migration from Adhesives used in Food packaging

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Consumer safety demands the close analysis of all materials used in food packaging and their potential to migrate into foodstuffs. Polyurethane laminated films are extensively used for food packaging. This paper details a study of the migration of diisocyanate and polyol components.

The European Union has introduced a number of Directives which include guidelines for testing migration, global and specific migration limits and a positive list of plastics, monomers and additives used.

DMU, funded by MAFF, are investigating adhesives used in food packaging. Previous work has included the analysis of coldseals utilised in confectionery bars etc, and currently polyurethanes.

Packaging is becoming more complex to meet the demands of:

a) better food storage, longer shelf life
b) convenience food which can be "cooked in the bag"

Many of these requirements are met by laminated films.

Polyurethanes are complex polymers formed by the addition of a polyol and diisocyanate with the addition of additives designed to enhance the properties of the polymer without significantly altering its chemical structure. A number of techniques have been used for the analysis of possible migrants from such adhesive systems, these include HPLC, LC-MS, GC-MS, MALDI-MS and a colorimetric method with SPE. Results to date have shown a number of migrants including residual monomers, oligomers, and additives.

K4

AN IMPROVED DIGESTION PROCEDURE FOR THE INSTRUMENTAL ANALYSIS OF INORGANIC BROMIDE RESIDUES IN FUMIGATED MUSHROOMS

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Methyl bromide is used extensively for the fumigation of mushrooms in that it does not remain long into foodstuffs after fumigation, owing to its volatility and reactivity. It acts in fact as a methylating agent, leaving bromide ions as residue. Of course, these last ions are indistinguishable from natural bromide ions, so that a total bromide determination is unable to give a correct quantitation of the fumigant employed. This notwithstanding, the concentration of total bromide ions in foodstuffs is used as an indicator of the degree of their treatment and some jurisdictions have set legal limits for their maximum content in many foodstuffs. This is the reason why most methods have been directed to this determination. A fast conversion of mushrooms into solutions suitable for instrumental analysis can be easily achieved by microwave digestion. However, complete and reproducible conversions are only achieved by acid oxidizing digestions which can cause bromide loss, as HBr or Br_2 during digestion or in the vessel opening at the end of the process, as well as some bromide convertion into ionic oxygenated bromine species. To overcome this drawback, we propose that the acid oxidizing digestion is performed in the presence of silver ions. The digestion performance has been tested successfully on both bromide synthetic samples and a series of boletus edulis samples. With this purpose, bromide determinations on the solutions obtained have been conducted by different instrumental approaches (ICP-MS, cathodic stripping voltammetry, vis-spectrophotometry and high performance ion cromatography). The problems arising for each approach from the sample composition are discussed together with the methods adopted to overcome these problems. Advantages and disadvantages offered by these instrumental approaches are also underlined.

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K5

ALCOHOL-SENSITIVE MEMBRANE COATED ON OVERHEAD TRANSPARENCY FILM WITH AN OXYGEN OPTODE AS THE TRANSDUCER

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Alcohol sensing membranes coated on overhead transparency films for the continuous monitoring of ethanol, propanol and butanol have been successfully fabricated. Alcohol oxidase was covalently immobilized on a plasticized carboxylated poly(vinyl chloride) membrane and the oxygen-sensitive dye ion-pair was entrapped in the same membrane.

The sensing scheme is based on the enzymatic oxidation of alcohol by alcohol oxidase with subsequent depletion of the oxygen level. In conjunction with an oxygen-sensitive dye ion-pair, tris(4,7-diphenyl-1,10-phenanthroline) ruthenium(II) didedocylsulphate, the sensing membrane relates oxygen consumption, as a result of enzymatic oxidation, to alcohol concentration.

Measurements have been performed in air-saturated alcohol standard solutions of pH 7.0. Analytical ranges, storage stability, reproducibility and the effect of pH on sensing membrane performances have been studied in detail.

The alcohol sensing membrane proposed here is simple to prepare and has a fairly rapid response time of less than 1 min. It has been successfully applied to the determination of the ethanol contents in various wine samples.

K6

SEQUENTIAL INJECTION ANALYSIS OF CATIONIC SPECIES IN WINES BY FLAME ATOMIC ABSORPTION SPECTROMETRY

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Sequential injection analysis (SIA) is one of the most recent continuous flow techniques well suited to accomplish distinct sample pretreatments without any physical change of the analytical setup[1]. The aim of this work was to demonstrate the versatility of SIA when combined with flame atomic absorption spectrophotometry in the analysis of different cationic species in wines. Zinc, Mn and Fe contents evaluation in white, red and Port wines were selected to attain this purpose. To sample volumes between 25 and 1000 µL corresponded a decrease in the respective characteristic concentrations by an order of magnitude, allowing evaluations with different degrees of precision. By selecting sample volumes of 340 µL, Zn and Mn determinations could be performed in the analytical ranges of 0.05-1.3 mg/L and 0.4-2.8 mg/L, respectively. A sample volume of 85 µL enabled the determination of total iron content between 0.1 to 20 mg/L. The obtained results were compared with those furnished by the conventional methodologies [2] showing relative deviations lower than 5%, in all cases. The sample throughput was about 120 samples per hour with reproducibility better than 3%.

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K7

COMPARISON OF VARIOUS DETERMINATION METHODS FOR THE NITROGEN CONTENT OF BABY FOOD

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It is very important to know the protein content of milk and milk products. For this propose various protein determination methods were developed. Direct spectrophotometric protein determination method is based on the measurement of absorbance at 280 nm wavelength [1]. The another spectrophotometric method is based on the measurement of absorbance of the coloured complex obtained by the reaction of protein with copper salts [2] or with phenol and copper salts in basic medium[3]. These methods are not sufficiently selective especially in the presence of lipid and sucrose. Proteins can also be determined directly by the infrared light absorbance at 6.465 mm wavelength by the N-H bonds within the protein. Well known protein analysis methods are based on the determination of nitrogen and the estimation of protein content from the nitrogen content of sample. Nitrogen determination by Kjeldahl method involves conversion of nitrogen to the ammonium salt by digestion of the sample with sulfuric acid, in the presence of salts and a metal catalyst, followed by basification of digest and distillation of ammonia produced into a standard acid solution[5]. In the modified Kjeldahl method, after digestion ammonium is determined by spectrophotometric method[6].The Kjeldahl method is time-consuming and is not reliable for low-level nitrogen analysis.

Nitrogen is determined by elemental analysis technique. But this method requires the expensive apparatus. The colorimetric nitrogen-determination method used in this study based on modified Lassaigne method[7]. Protein-nitrogen in baby food was determined by colorimetric nitrogen determination method and the results were compared with those obtained by Kjeldahl and Elemental analysis methods. These three methods were used for the analyse of sixteen commercial formulation baby food samples, and each sample was analysed three times to reduce the human error. In addition, the reproducibility of these three methods was tested by analzing ten replicates of Nutrima samples. According to the statistical evaluations, there was no significant difference at 95% confidence level.

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K8

DETERMINATION OF SELENIUM IN BLOOD-SERUM BY ETAAS

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The essentiality of selenium in human nutrition is well established. Selenium as a cofactor of the enzyme glutathione peroxidase plays an important role in intracellular defence against oxidative stress caused by free radicals. It is known that free radicals play a key role in various degenerative processes such as cardiovascular diceases, cancer, arthridis and neuro-degenerative diseases.

The aim of this work was to obtain reference values for Se serum concentration levels in the healthy Slovak children population. In this study 68 children from Bratislava region aged 2 weeks - 16 years were un-vestigated for selenium levels.

In this work a relible procedure for determination of Se serum concentrations directly after dilution in the presence of Pd and Mg nitrates as modifiers using atomization from the pyrocoated graphite tubes and L'vov platform is presented. The accuracy of Se determination was checked by analysing the standard reference material of serum. The mean result obtained for Se serum (Seronorm™ Batch No. 010017, Oslo, Norway) for 10 determinations was 94,95 ± 2,35 µg/l, while the certified selenium concentration is 97,0 µg/l (confidence interval: 92,0 - 102,0 µg/l).

The results from this work indicate that reference Se serum values (mean ± SD) for the Slovak children population were 49,42 ± 4,68 µg/l. In our study 44 % (32 children) of all subjects had a Se serum concentration lower than 45 µg/l. The method - being reliable and relatively simple and rapid is suitable for use in epidemiological screening.

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K9

Determination of ethylenethiourea (ETU) and propylenethiourea (PTU) in foodstuffs by off-line SPE-HPLC

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Dithiocarbamates are the class of fungicides most commonly applied worldwide. Reports on concentrations of these compounds in fruits and vegetables exceeding the legal limits are becoming increasingly frequent.

A method is proposed for analyzing ethylenethiourea (ETU) and propylenethiourea (PTU), decomposition products of several dithiocarbamates. ETU is classified as a possible human carcinogen. In the EU, the maximum permitted residue level of ETU in foods is 0.05 mg/kg. In Switzerland, no legal limit has been set so far.

A 20 ml aqueous extract is reduced to 1 ml on a rotary evaporator. It is then absorbed on an Extrelute/aluminium oxide solid phase cartridge (SPE). After desorption with dichloromethane and solvent exchange, samples are injected into a RP-18 LC column and eluted isocratically with ethanol/water. UV absorption is determined at 240 nm. The column is then backflushed and reconditioned.

Recoveries are between 85 and 95 %, detection limits at 2 µg/kg. The method has been applied to baby foods, salads, fruits and vegetables or their juices, as well as to alcoholic and non-alcoholic beverages.

The proposed method miniaturizes previous procedures, reducing the aliquot of sample being worked up by a factor of ten. In this way, time and solvent is saved.

K10

INDIRECT DETERMINATION OF SULPHATES IN ALCOHOLIC BEVERAGES

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The ion sulfate forms not many coloured systems. This explains the lack of spectrophotometric methods for its direct determination. A good alternative is the indirect determination by precipitating ion sulfate with barium, that is, adding a known quantity, and further spectrophotometric determination of barium in excess [1]. In this work a method for the indirect determination of sulphates in thirty-five alcoholic beverages (anise, gin, vodka, rum, *etc.*)

The proposed spectrophotometric method uses the dimethylsulphonazo III as a reagent and presents an absorption maximum at 672 nm to pH between 5-6. *Beer*'s law is fulfilled in the interval of 4-19 mg of sulfate/l and presents a degree of variations less than 2.5%.

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K11

DETERMINATION OF GLUCOSE IN REFRESHMENT AND SUGAR CANNE JUICE EMPLOYING MULTICOMMUTATION AND ENZIMATIC REACTION IN FLOW SYSTEM

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Keywords: Glucose determination; Multicommutation; Flow analysis

A flow system employing multicommutation approach for glucose determination involving enzymatic reactions was proposed. The procedure was based on oxidation of glucose catalyzed by glucose oxidase. Afterwards, the generated H_2O_2 reacted with 4-aminefenazone plus phenol to form 4-(p-benzoquinone mono imine) fenazone. This reaction was catalyzed by peroxidase enzyme and monitored spectrophotometrically at 510 nm. The flow network comprised a set of three-way solenoid valves controlled by means of a microcomputer furnished with electronic interface. A software wrote in QuickBASIC 4.5 was designed to implement the multicommutation approach. The system provided facilities to handle sample and reagent solutions, performing sample dilution on line without modifications in the flow network.

The procedure was applied to refreshment and sugar canne juices. Accuracy was assessed by comparison with results obtained by usual procedures. The proposed system presented a linear response ranging from 0.05 to 0.20 % (w/v) glucose with a correlation coefficient of 0.9999 and slope of 0.019. Others profitable features such as, a r.s.d of 0.12 % (n=7) and an analytical throughput of 30 samples per hour were also observed.

CAPES, FAPESP, CNPq, JNICT, PRONEX

K13

STUDY OF THE OXIDATION PRODUCTS IN EDIBLE OILS AND FATS BY ^{1}H-RMN

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The degradation of edible oils and lard exposed to episodes of heating associated with normal usage (80-300°C, 20-40 min) has been studied by ^{1}H-RMN spectroscopy. The thermal oxidation of polyunsaturated fatty acids (PUFAs) is a free radical chain reaction, in which hydroperoxides are generally recognized as the primary major products. Hydroperoxides of PUFAs are easily decomposed into a very complex mixture of secondary products such as alcohols, aldehydes, free fatty acids and ketones leading to oxidative rancidity. Oils frequently used in food frying such as Olive oil, Sunflower oil, Corn oil and Seeds oil (sunflower, safflower and *canola seed*) and lard were studied. These samples were subjected to 80, 150, 200, 250 and 300°C for 20 and 40 minute time periods at each temperature.

The RMN-^{1}H spectra show the two stages in the thermal oxidation of edible oils and fats. In the first stage, to heating of 150°C, the fat takes the oxygen to form hydroperoxides, they produce their corresponding spectral signal at δ=8-8.5ppm. When the hydroperoxide concentration reaches a certain level they undergo a second oxidation with the formation of new carbonilic compounds, mainly aldehydes. The alkanals originate signals at δ=9.7, 2.5ppm, trans-alkenals at δ=9.42, 6.7ppm, alka-2,4-dienals at δ=9.49, 7ppm and hydroxialkenals at δ=9.55ppm. Also a decrease in unsaturation percentage during the heating is observed in the RMN-^{1}H spectra, the signals corresponding to unsaturated components (2, 2.7, and 5.3 ppm) are less intense than the same signals in the sample without heat treatment. This variation in unsaturation grade provides evidence of the transformation of essential polyunsaturated fatty acids and the subsequent decrease in the oils' nutritional value.

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K14

QUANTITATIVE METHODOLOGIES TO EVALUATE THE OXIDATIVE DETERIORATION OF EDIBLE OILS AND FATS BY FTIR

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Oils and fats are very important in the human diet because they have a high energetic content and they contain essential fatty acids necessary for the correct development of human tissues. Oils and fats start decomposing from the moment they are isolated from their natural environment. The heat accelerates the oxidative rancidity and the strong frying at high temperatures produces a thermal degradation with the formation of decomposition products, such as aldehydes, ketones, free acids and hydroxilic compounds that in high levels can be harmful for human health.

The decomposition products formed up to a heating to 300°C were evaluated by means of FTIR spectroscopy. The IR spectra show that thermic oxidation produces a decrease in unsaturation grade, generation of carbonilic and hydroxilic compounds and an increase in trans-isomers.

Quantitative methodologies to quantify the variation in lipids' composition during strong heating were developed. They were based on the addition of a standard (Valeronitrile) to the samples and the measurement of the absorbances ratio to employ a sample preparation without the need to know the film thickness. A new procedure to quantify the carbonilic compounds generated was proposed: *"Areas Ratio Method"*. A methodology to correct absorbance measurements of overlapped peaks was developed, this method was applied to quantify trans-isomers and evaluate hydroxilic compounds. Also the unsaturation percentage was obtained.

This investigation proves the worth of FTIR spectroscopy in quantitative analysis and shows there is an important transformation in all studied oils and lard when they are submitted to heating. This information is the basic requirement for studies on the toxicological effects associated with the regular consumption of these compounds.

K15

COMPLETELY-CONTINUOUS ON-LINE PROCESS MONITORING

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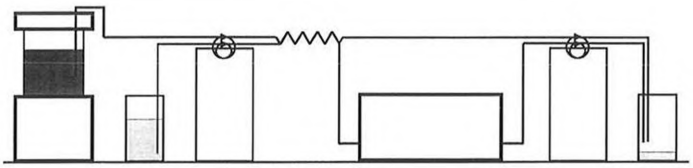
Although numerous glucose biosensor papers are published monthly, there is hardly any continuous monitoring sensor system available for industrial applications.

Therefore, a recently developed sensor system was applied to monitor grape-juice fermentation completely continuously (see figure). The only requirement was the dilution of the sample to meet the linear range from 1 to 200 mM glucose. Since the flow rate can be reduced to less than 1 ml/h, the sensor may be operated with minimum consumption of specimen in long-term measurements. The modular design of the sensor system enables to operate several working electrodes in series or in parallel and, therefore, to quantify various analytes simultaneously.



The third-generation biosensor incorporates an electrode mediated with an organic conducting salt (TTF-TCNQ), that was certified as non-toxic. Because of the direct electron transfer, no H_2O_2 was produced and the applied potential could be reduced to -25 mV vs.SCE. Hence, no diffusion-restricting outer membrane was necessary to prevent the sensor from interfering compounds.

K16

A LC/MS METHOD FOR DETERMINATION OF UNDERIVATIZED AMINO ACIDS IN FOOD SAMPLES

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The biological importance of amino acids affects on large interest in methods for their determination. Mostly chromatographic separations of derivatized and underivatized amino acids followed by different detection methods, e.g. UV, fluorescence, ELS, MS are used.

A method for rapid quantitative and sensitive determination of amino acids has been developed. The separation of 19 amino acids, found in food hydrolizates, was obtained on a NH_2 column with an acetonitrile / ammonium acetate buffer gradient. Detection of the underivatized amino acids was accomplished on LCQ ion trap mass spectrometer by atmospheric pressure chemical ionization (APCI). The APCI - soft ionization technique provides molecular weight information to confirm the presence of an expected compound in samples. The quantitative evaluation was achieved using mass peak detection. This technique excels in the selectivity and sensitivity of quantitation of amino acids in different food samples. It is useful for the determination of free amino acids and amino acids in hydrolizates.

The developed LC-MS method was validated and then applied to the analysis of amino acids in wine and must.

K17

DETERMINATION OF Pb AND Cd IN WINES BY ETAAS AND DPSV

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Cadmium and lead are commonly determinated in food and beverages due to their toxicological effects. Their permitted concentrations are very low, so the methods for their determination should be very sensitive. In this paper the direct detrmination of Cd and Pb in six white and red wines from different Serbian wine-growing regions was performed comparatively by two different micro methods.

In order to investigate the possible matrix effect, the standard addition method was applied too. The alcoholic calibration solutions were used.

In the case of application of electrothermal atomic absorption spectrophotometry (ETAAS), the temperature program and gas flow rates were optimized. In the course of direct Pb determination the obtained results were not reproductive, therefore the matrix modifier was applied.

The same samples were analysed parallelly by applying the differential puls stripping voltametry (DPSV). The determination potentials were :-0.65V for Pb and -0.82V for Cd. The other experimental conditions were optimized too. The influence of matrix was very significant in these determinations, so only standard addition method was applied.

Analysing the obtained results it can be concluded that ETAAS enables the direct Cd determination in all samples while in the case of Pb the standard addition method and matrix modifier have to be applied. In the case of DPSV, the matrix effect is more pronounced especially for red wines. In order to explain this effect, the detailed IR study of the wine's dry residue was performed.

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K18

STUDY OF TOXIC ELEMENTS REMOVAL FROM ROMANIAN WINES

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Separation conditions were studied for the removal of undesirable elements as: Cu, Zn, Pb, Fe, P, Mg, Ca, Sn, Na, K from various Romanian wine varieties.

As adsorbents of toxic elements diatomite, bentonite and active carbon were used. Quantitative determination was carried out by double beam AAS for Ca, Na, K, and by ICP-AES spectrometry for Cu, Zn, Pb, Fe, Mg, Sn.

K19

DETERMINATION OF SELENIUM AND LEAD IN COW MILK BY DIFFERENTIAL PULSE STRIPPING VOLTAMMETRY

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The selenium and lead contents in the milk samples from Turkey were determined on hanging mercury drop electrode (HMDE) using differential pulse cathodic stripping voltammetry (DPCSV) and differential pulse anodic stripping voltammetry (DPASV), respectively. In this method, the milk samples were digested in HNO_3 : $HClO_4$ (1: 1) acid mixture by wet digestion procedure. The DPCSV of milk sample in 0.1 M HCl solution showed a peak for selenium at -0.56 V , and DPASV for lead showed a peak at -0.35 V. The effect of deposition potential, deposition time and scan rate on these peaks were used to determine the optimum experimental conditions. A deposition potential of -0.2 V for selenium, and -0.5 V for lead were suitable. The standard addition method was used to determine selenium and lead in the sample. The linear domain range of Se(IV) was $9.5x10^{-7}$ M - $1.5x10^{-8}$ M with a correlation coefficient of 0.9981, for lead $9.0x10^{-7}$ - $4.2x10^{-8}$ M with a correlation coefficient of 0.9945. The proposed method provides a simple and suitable procedure for the determination of trace amounts of selenium and lead. In this method, there is no need for sophisticated instruments and tedious separation procedure. Selenium and lead contents of milk samples from three distinct regions of Turkey were obtained between 21.5 - 69.4 µg/l and 22.1 - 59.2 µg/l (n= 4 -5), with the relative standard deviations of 10.3 - 10.7 % and 6.8 - 7.9 % , respectively.

K20

FURTHER STUDIES ON THE OPTIMIZATION OF LIQUID CHROMATOGRAPHIC TECHNIQUES FOR THE ANALYSIS OF SEAFOOD TOXINS

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Along the last years, several algal toxins have been associated with contaminations in the marine environment. Paralytic and Amnesic shellfish poisoning (PSP and ASP) toxins are some of the main toxic compounds responsible for bivalve contaminations in several places worlwide causing serious risks for human health, due to their specific and severe toxicologic consequences.

There is a real need to develop sensitive analytical techniques for the control of these toxic compounds in seafoods, in order to find a serious alternative to the mouse bioassay which has been used rutinary as official method of analysis in most of the countries, being not sensitive and selective enough for such analysis. Several methods have been developped in the last decade to overcome the lacks of the biological assay. Chemical methods, such as liquid cromatography with fluorescence detection and postcolumn derivatization with peryodate, has been proved to be a reliable method for the analysis of PSP toxins; for ASP analysis liquid chromatography with UV detection has resulted a sensitive technique as well.

This work was focussed on the search of the optimized conditions for both PSP and ASP analysis by liquid chromatography. Different steps involved in sample preparation, such as extraction and clean-up of the extracts were also optimized, by mean of recovery experiments. The efficiency of these steps was taken into account in order to evaluate the efficiency of the chromatographic analysis and consequently to achieve the most reliable quantitative information about the PSP and ASP toxins present in the studied samples.

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L1

DETERMINATION OF TRACES OF NITRITE AND NITRATE IN WATER BY SOLID PHASE SPECTROPHOTOMETRY

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A simple and sensitive method for the determination of nitrite and nitrate in water, using solid phase spectrophotometry is described. The method utilizes the quantitative and rapid sorption of the colorful dye formed from nitrite, using Griess reaction, into a thin-layer of polyurethane foam (PUF)where a preconcenration factor of >140 has been achieved. Nitrate is pre-reduced using a cadmium reductor befor applying the Griess reaction.The direct spectrophotometric measurement of the dye enriched in the solid foam phase has allowed the detection of as low as 5 and 40 ppb for nitrite and nitrate, respectively. Optimisation of the parameters affecting the quantitative formation and sorption of the dye into PUF has been considered. Analysis of natural water samples has been also performed.

L2

PREDICTION OF AVIATION JET-FUEL PROPERTIES USING LIQUID AND VAPOUR-PHASE FT-mir MEASUREMENTS

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Several parameters measured to define the aviation jet-fuel quality are quite slow, tedious and prone to rather subjective assessments. Therefore, the aim was to develop alternative methods able to predict several properties: gravity, freezing point, flash point, initial boiling point, final boiling point, viscosity and percentage of olefins and parafins. Fourier transform-medium infrared spectroscopy (FT-mir) measurements were made considering the 4000-600cm^{-1} on aviation jet-fuel samples (kerosene, JP1, etc.), both at the liquid and vapour phases.

A Perkin-Elmer 16PC FT-mir spectrophotometer and NaCl fixed pathlenght cells (0.01 mm) and SiO_2 cells (10.0 mm pathlenght, 3000-2500 cm^{-1} range) were used to register one spectrum for each sample (average of six scans, resolution=4cm^{-1}). The NaCl cells were employed to register spectra from kerosene liquid samples and a SiO_2 cell was used to register the vapour-phase spectra.

Multivariate models (PLS, polynomial-PLS, Local Regression Models) were, used to get models which accurately take account of the eight studied properties of kerosenes. Repeatability (r) and reproducibility (R) values are both well bellow the ASTM reproducibility figures for each parameter, and even the FT-mir-chemometric reproducibility values are bellow the ASTM repeatability figures. Regarding accuracy, it was found that all the standard errors of prediction (SEP) are bellow the ASTM-reproducibility values and, thus, the multivariate models seem to be adequated for use in the routinary quality control of the kerosene.

L3

STUDIES OF INTERFACIAL REACTIONS - CORRELATION BETWEEN MACROSCOPIC WETTING PHENOMENA OF A POLYMER MELT AND CHEMICAL REACTIONS AT THE INTERFACE BETWEEN THE POLYMER AND MODIFIED SILICON SURFACES

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Macroscopic wetting and adhesion phenomena have their origin in intermolecular forces acting between the solid and the liquid or between two solids. Dependent on the chemical composition of the interacting partners in addition to van der Waals interactions, acid-base interactions and hydrogen-bonding or even chemical bonding can occur at the interface. The latter should improve adhesion. However, systematic experimental investigations quantifying the effect of these interactions on the macroscopic wetting and adhesion behavior are still lacking.

The advancement of the FT-IR ATR spectroscopy and wetting measurement techniques open new opportunities for the characterization of surface phenomena at higher temperatures and under defined ambient conditions.

We used amino functionalized (γ-Aminopropyltriethoxysilane) ATR silicon elements and wafer. A maleic acid anhydride copolymer with C_{14}-C_{16}-α-olefin sidechains were used for the overlayer as a model for a reactive thermoplastic polymer matrix. It is known that the anhydride groups react in the stirred melt quickly and quantitatively with amines to imide groups [1]. The monitoring of the chemical interfacial reaction was realized with FT-IR ATR technique; the macroscopic spreading behavior of the copolymer melt was investigated by a new contact angle technique using Axissymmetric Drop Shape Analysis - Profile (ADSA-P). We could demonstrate that the chemical reaction at the interface is correlated with the macroscopic wetting kinetics of the polymer melt.

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L4

ARGON MICROWAVE INDUCED PLASMA WITH AQUA-ORGANIC AND ORGANIC SOLVENT INTRODUCTION - SPECTROSCOPIC AND ANALYTICAL CHARACTERISTICS

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Two areas of an analytical application of microwave induced plasma atomic emission spectrometry (MIP-AES) have been developed. The MIP is a promising analytical excitation source for emission spectrometry being an alternative to dominating ICP and is popular detector in chromatography. A considerable and growing attention into discharges operating with organic and aqua-organic solvents has been observed. It is mainly due to the large interest to speciation analysis. The present study of spectroscopic and analytical characteristics of the argon MIP with aqua-organic and organic solvents has been undertaken to know solvent aerosol and solvent vapour interaction with plasma. It should allow extension and improvement in analytical performance by the MIP-AES. Plasma was produced by the 2.45 GHz microwave generator (Plazmatronika Ltd.) with continuously variable output power up to 600 W and coupled to a TE_{010} rectangular cavity. The MIP flame was observed in a conventional „end-on" mode. Aqua-organic and organic solvents (methanol, ethanol, carbon tetrachloride, chloroform and MIBK) were employed. Elements such as Zn, Cu, Mg, Cr and Fe were selected for analytical measurements. Studies were performed at various experimental conditions (microwave power, argon flow rates and solution uptake). Spectra of atoms (Ar I, Zn I, Zn II, Cu I, Mg I, Mg II , Cr I , Fe I and Fe II) and molecular species (OH, CN, CH, CO, NH, C_2) were excited and analysed. Excitation and rotational temperatures were determined under a variety of experimental conditions. Signal-to-noise and signal-to-background ratios were investigated. A comparison between organic and aqueous solvent introduction in terms of emission spectra, ion to atom line intensity ratio and excitation and rotational temperatures has been demonstrated and discussed both from physical and analytical point of view.

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L5

COMPUTER-ASSISTED OPTIMISATION OF AN ON-LINE PRECONCENTRATION SYSTEM FOR DETERMINATION OF NICKEL IN SEA-WATER BY ELECTROTHERMAL ATOMIC ABSORPTION SPECTROMETRY

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Although electrothermal atomic absorption spectrometry (ETAAS) has very low detection limits for trace metals in aqueous solution, the direct determination of trace metals in sea-water by ETAAS is difficult even with sophisticated background correction and chemical modification. This is due to the low concentrations and strong interference from the sample matrix. ETAAS with on-line sorbent and preconcentration can solve the two problems mentioned above and lead to easy determination[1].
Sample introduction into the graphite tube is usually performed manually, using a microlitre pipette, or automatically by a special autosampler. In this work an on-line preconcentration system for determination of nickel is achieved by replacing the sample tip of the autosampler arm by a microcolumn packed with a silicagel chelating resin functionalised with 1-(di-2-pyridyl)methylene thiocarbonohydrazide (DPTH-gel). A modification of the AS-70 autosampler in the tubing line and circuit allowed either the flow of the sample through the column or the operation of the autosampler in the normal mode, where microlitres of HNO_3 2N, which acts as elution agent, pass through the microcolumn eluting Ni(II) which is directly deposited in the graphite tube as a simple drop of a precisely defined volume.
Optimum operating conditions were sough by a software which integrates the Simplex optimisation method and quality requirements as sensitivity, precision and sample throughput, parameters that they define the overall analytical quality[2]. Seven variables were considered.

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L6

ANALYTICAL CONTROL OF ADSORPTION PROCESSES IN $3CaO.SiO_2$ - PLASTICIZER - WATER SYSTEMS BY UV SPECTROMETRY

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The data presented deals with the monitoring of the hydration-hydrolyse processes in the $3CaO.SiO_2$ - H_2O system in the presence of some variable proportions of new fluidizer from lignosulphonates class (LSC and LSC+Na_2CO_3) by means UV spectrometry.
Quantitative determination of the above mentioned plasticizer admixtures concentration in the aqueous phase of $3CaO.SiO_2$-H_2O system performed at λ=221nm with an Camspec UV-VIS M-330 spectrometer
The influence of the additives upon the hydration-hydrolysis processes appears at different stages of their development and it depends on the nature of the additives and the time of the reactions [1,2].
The additives influence the kinetics of the hydration-hydrolyse process, by delaying or intensifying it, as the main phenomenon is the adsorption of additives on the anhydrous or partially hydrated surface of the particles in to system (fig.1).

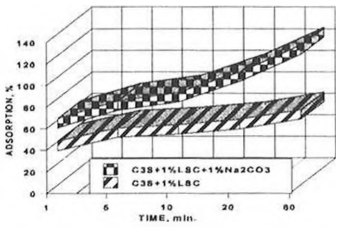

Figure 1 Evolution of adsorbed plasticizer proportion versus time

The influence of the additives from the structural and compositional point of wiew also appears to the process of evolution of the hydrocompounds which are formed.

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L7

FLUORIMETRIC DETERMINATION OF FERRIC ION BY SALICYLIC ACID

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The spectrofluorimetric determination of Fe(III) using salicylic acid as an emission reagent has been investigated by measuring the decrease of fluorescence intensity of salicylic acid due to the complexation of Fe(III)-salicylic acid. An emission peak of salicylic acid, which is decreased linearly by addition of Fe(III), occurs at 409 nm in aqueous solution with excitation at 299 nm, and allows selective and sensitive determination of the Fe(III) ion in the range of 0.0558-0.558 μg/ml. The quenching effect of Fe(III) ion on the fluorescence intensity of salicylic acid may be considered on the basis of complexation between salicylic acid and Fe(III) ion. The effects of foreign ions were investigated.

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L8

ELUCIDATION OF THE PRODUCTS FORMATION SEQUENCE BY THE ANALYSIS OF ELECTRONIC AND ATR IR SPECTRA OF THE AUTOXIDIZING FILMS OF CAROTENOIDS

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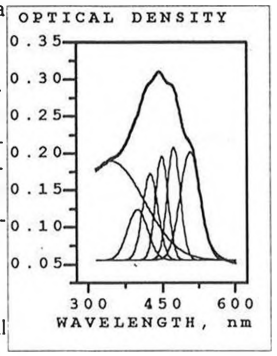
The investigation of autoxidation of thin solid films of polyenes on solid supports was previously shown to be a powerful method for the study of the autoxidation of the compounds by molecular oxygen [1]. In the given communication we present the results of the analysis of the electronic and IR-spectra of the oxidizing films of some carotenoids. The films were prepared and handled as described previously and the electronic and multiple ATR FTIR spectra were recorded. The fitting of complex absorption bands by the composing ones was performed using multiple Gaussian and Lorentzian fits of the electronic and infrared spectra correspondingly. The Figure shows the Gaussian analysis of of an absorption band of a partly oxidized β-carotene film. According to the data obtained the sequence of the formation of some autoxidation products was suggested. Initially formed compounds are polymeric peroxides of the original polyenes. The peroxides transform into epoxy and carbonyl compounds. A gradual autoxidation of polyenic parts of so formed carbonyl compounds was demonstrated by the shift to the shorter wavelengths and progressive disappearence of the bands corresponding to the ν(C=O) vibrations of conjugated carbonyls. It appeared that the final products contain no more than three conjugated C=C bonds.



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L9

Automatic Internal Standardization and Overrange Dilution for Flame Atomic Absorption

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Automation of the method of internal standardization in flame AAS using the SIPS technique [1] is described.

Solution viscosity and surface tension affect solution uptake rate and nebulization efficiency. If these are different between standards and samples, erroneous results are obtained. Internal standardization compensates for varying viscosity and surface tension eliminating the need for matrix matching of standards. Also samples with different matrices can be determined sequentially against the same calibration standards.

A two pump SIPS system is used to deliver standard or sample from one pump and internal standard from the other. The nebulizer is free running (neither force fed or starved) ensuring that there is no affect on the analyte signal.

SIPS will automatically calibrate from one bulk standard solution and dilute overrange samples without operator intervention.

Use of DDE, transfers data immediately to an Excel™ spreadsheet, a macro performing the internal standardization calculations.
Data will be presented showing the accuracy of results and time saved.

The system described drastically reduces solution preparation and therefore operator errors.

L10

STUDY BY UV-VIS SPECTROPHOTOMETRY AND FT-IR SPECTROSCOPY OF AGEING OF ADHESIVES USED IN RESTORATION OF ARCHAEOLOGICAL GLASS OBJECTS

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This contribution shows the results obtained in a study which aimed to compare the stability of five adhesives commonly used in the restoration of archaeological glass objects when subjected to several ageing agents. The adhesives studied were: Araldit XW396/XW397, Vitralit 7256 and Loctite 350, Desmodur N 75 Viacryl SM 564/65 , Krafft silicone resine.

The experimental procedure involved the preparation of two series of test specimens. Both series were subjected to three different accelerated ageing tests: 1) Thermal ageing. 2) Cyclic ageing in SO pollutant chamber. 3) UV light ageing which consisted in irradiating the samples with an OSRAM L36/73 fluorescent lamp which emits UV light with a maximum between 350 and 400 nm, at a distance of 12 cm for 4 weeks.

The absortion spectra obtained between 200 to 800 nm. from test specimens before and after ageing were compared with the L*, a* and b* coordinates defined from the tristimulus values X,Y and Z (Colour measurement system CIELAB 1976, DIN 6174) as well as measured by spectrophotometer. IR spectra were also obtained. The analysis carried out, showed that the cyclic ageing is more effective, in general in all the adhesives. It is also significant the action of UV light over silicone resin, Vitralit and Desmodur because it is clearly visible the cromatic changes produced. The thermal ageing was significantly visible in the acrylic adhesives as it is shown in the increasement of the bands at 835 and 704 cm^{-1} and in the decreasement of the C=O stretching band at 1732 cm^{-1}.

L11

ARE UV-VIS SPECTROSCOPY AND SPECTROPHOTOMETRY OBSOLETE METHODS ?

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As a consequence of the development and spreading of more advanced spectroscopic methods (mainly NMR and MS) the importance of UV-VIS spectroscopy as a tool for the structure elucidation of organic compounds of synthetic or biological origin has greatly decreased. At the same time, however, in the last fifteen years the introduction and rapid spreading of diode-array spectrophotometers attached to high-performance liquid chromatographs and capillary electrophoretic instruments as well as thin-layer densitometers suitable for scanning reflection spectra have created excellent possibilities for the rapid identification of small components: impurities and degradation products in bulk drugs and their formulations as well as drug metabolites in biological samples. It will be demonstrated on several examples including steroids, heterocycles, etc. that it is very useful from the point of view of rapidness and economy of the analytical work to draw as many conclusions from the UV spectra thus obtained as possible.

The tendencies of the use of UV-VIS spectrophotometric methods for the quantitative analysis of bulk drugs and drug formulations in the leading pharmacopoeias will be discussed and some thoughts presented on the criteria of up-to-dateness of newly developed spectrophotometric methods [1].

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L12

IMPROVEMENT OF SELECTIVITY IN FLAME ATOMIC ABSORPTION SPECTROMETRY BY MEANS OF FOURIER TRANSFORMS.

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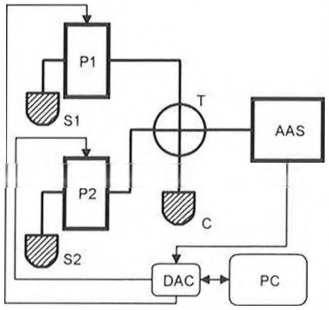
The usual way of introducing the sample solution in flame atomic absorption spectrometry (FAAS) is direct aspiration by the suction effect produced in a pneumatic nebulizer. If the sample solution, instead of being aspirated, is supplied to the nebulizer by means of a peristaltic pump, the readout of the spectrometer fluctuates, due to the pulse caused by the action of the peristaltic pump rollers. It has been proved elsewhere [1] that this drawback can be converted into an advantage, since the time-variable absorbance profile can be translated to a frequency spectrum by means of Fourier transform (FT). In this way, a new analytical signal is obtained with advantage over the conventional analytical signal (absorbance).

This communication reports new advances founded in the same basic idea: if two solutions containing the same analyte are simultaneously supplied to the nebulizer by means of two peristaltic pumps turning at different speed, once the FT of the absorbance-time profile is made, it is possible to discriminate between the signals arising from each one of the two solutions being used. To prove such a possibility, which increases FAAS "selectivity" in an unusual way, the manifold on the left, where P1 and P2 are computer-controlled peristaltic pumps, was used. A detailed study on the optimal experimental conditions is reported.



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L13

VERTICALLY POSITIONED AEROSOL COOLED PLASMA -A NEW DESIGN APPROACH FOR MIP-AES WITH SOLUTION NEBULIZATION

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Steadily growing attention has been concentrated on overcoming the major technical limitations of microwave induced plasma (MIP) technique, i.e. a low tolerance to the solvent loading and the short lifetime of the torch due to corrosion [1-3]. In this work a new design approach for MIP-AES, supported by a vertically positioned aerosol cooled torch, is presented.

As observed for ICP, axial viewing of the plasma improves the analytical performance of the analyte emission measurements in terms of sensitivity and detection limits. However, for the „end-on" viewing configuration, often used in the MIP technique, the distortions of the plasma symmetry and operation may occur especially when wet aerosol is introduced to the plasma with a low gas flow. Then the „top-down" viewing mode with vertically positioned torch is suggested.

It is known from practice that a microwave induced plasma operating at higher power levels usually causes severe degradation of the discharge tube. Different technical solutions have already been proposed to reduce melting or etching of the tube. Water, which can serve as a very efficient cooling agent seems to be simply too efficient for this specific application. Such over-efficient cooling leads to an over-cooled torch and this results in excessive energy loss in a MIP system. In the system proposed distilled water aerosol has been used as cooling agent. Measurements of the spectroscopic temperatures and electron density made to support this design concept are described.

L14

STUDY OF ORGANIC SOLVENT ADDITION ON TRACE DETERMINATIONS BY FAAS

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It is known from literature that addition of organic solvents to water solutions causes changes in signal intensity of trace analyte determined by FAAS. However, these results are rather controversial. Therefore, the aim of this paper is to investigate the possible sources of this effect.

The investigations involved elements (Cu, Cd, Fe and Ca) of different physical parameters, in the presence of various quantities of ethanol and acetone. The ratio of signal intensity in the presence of organic solvent and without it, (F), was measured.

The influence of solution's physical parameters (ρ, σ, η), flame conditions and aerosol formation and transportation to the plasma on F was followed.

It was found that the effect depends not only on the solution's physical parameters but also on the analyte type. Therefore the flame temperature, as important plasma parameter, was measured. No significant effect was found. In order to investigate the role of solvent vaporisation and analyte transport to the plasma, the measurements were performed with different nebulization systems. The obtained results confirm that the aerosol formation and transport, together with solvent evaporation and analyte atomisation have the main effect in organic solvent enhancement.

L15

RADIATION EFFECTS ON THE BINDER OF BRIQUETTED SAMPLES IN X-RAY EMISSION SPECTROMETRY

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Preparation of reference and standard samples for control analysis by X-ray emission spectrometry in iron and steel production is a complex and time--consuming job. Therefore, the wish to prolong as much as possible the time of use of prepared samples is very often present. However, it has been observed that standard samples, such as iron ores, sinters, mixtures for sinters and blast furnace slags, formed into briquettes with organic binders, diminished their wear resistance (cracking and edge sprinkling appear) after irradiation with X-ray. The effect of X-ray radiation on binders such as starch, cellulose and graphite, having also as a consequence lower results of measurement of K_α lines intensities, was confirmed during previuos investigations [1,2]

In this paper the behaviour of boric acid as binder was investigated. On the basis of debyegrams and secondary electron micrographs radiolytic changes of boric acid were proved. Debyegrams of a sample of boric acid showed that spottiness and prefered orientation were enhanced after exposure of sample to X-rays. In secondary electron micrographs interruption of regularity of initial lamellar structure after irradiation of a boric acid sample could be seen as broken lamellas and appearance of round-shaped crystals with adhering particles. These radiolytic changes have as a result an increased briquette porosity and are considered to constitute a limiting factor for longer use of samples prepared with boric acid as binder.

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L16

Direct Solids Elemental Analysis by Radio Frequency Glow Discharge Atomic Emission Spectroscopy (rf-GD-AES)

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One of the greatest challenges posed to analytical methods employed for solid materials analysis is the wide range of sample matrices which is encountered. Traditionally, direct solids elemental analysis referred to the determination of transition metals in bulk metals and alloys. Thus, arc and spark emission spectroscopy have, and still do, enjoyed a great deal of success. The scope of elemental analysis has changed to include glasses, ceramics, polymers, and composite materials. The vast differences in chemical composition and physical attributes make the use of a single solids technique a great challenge. For example, the direct analysis of glasses and ceramics by arc and spark sources is not possible due to the lack of electrical conductivity of theses materials. On the other hand, these materials often contain low atomic number non-metals, which are difficult to determine by x-ray fluorescence (XRF) spectroscopy. Operation of a low pressure, glow discharge source with radio frequency (rf) powering at 13.56 MHz permits the direct sampling of these nonconductive (as well as conductive) materials through sputter atomization followed by analyte excitation and ionization [1,2]. Thus, direct solids elemental analysis can be performed by atomic emission (AES) or mass spectrometry (MS). We describe here the basic methodology and analytical characteristics of rf-GD-AES for the analysis of precious metals, glasses and bulk polymers.

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L17

THE APPLICATION OF THERMAL ANALYSIS TO THE HYDRATION PRODUCTS OF A REFRACTORY CALCIUM ALUMINATE CEMENT.

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Abstracts: The differential scanning calorimeter (DSC) and X-ray diffraction are becoming increasingly recognized as an important instruments for the study of calcium aluminate cement hydration products.

The hydration of Secar 71 has been studied at several temperatures, in the range from 12 to 60°C up to 50 days at a water ; cement ratio of 0.5.

At 12°C the only hydrates observed were CAH10and gibbsite with increaing amount by the ageing of hydration; where as at 20°C C3AH6 started to form after 4 days of hydration as a result of conversion. This conversion reaction is accompanied by an increase in porosity, which can lead to a loos in strength and vulnerability to chemical attack. Various methods of thermal analysis have been applied as a roution test to determine the degree of conuersion. Thermal analysis is a useful technique for identification of the various hydrates that can form in these systems, especially at early stages of hydration when poorly crytalline phases are present.

L18

RUTHENIUM DETERMINATION BY AAS AND DSP-EAS TECHNICS

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In the present work are presented comparatively two new methods for the ruthenium determination using AAS and DSP-EAS techniques in a matrix also containing other precious metals which are more sensible and accurate than other reported methods and interferences are practically eliminated. The proposed methods were verified both on synthetic mixtures and real samples and the results were statistically evaluated.

Samples were decomposed using a microwave digestion under pressure Milestone MLS-1200 Mega processor or by a chemical procedures. The sample digestion with the microwave processor is faster, with less reactives consumption and superior digest efficiency.

The instruments used were: - a AA Varian Techtron Type AA5 atomic absorption spectrophotometer;- Spectra Span V Beckman atomic-emission spectrometrum.

For the AAS determination the spectral buffers $CuSO_4$ + $CdSO_4$(0.5%) were used for enhancing the analysed signal and removing the platinum metals interferences.

For the DSP-EAS determination was used the background correction with the dynamic background compensator (DBS).

The calibration graphs were registered. The elements concentration from the synthetic and real samples were determined both with the direct method and the standard addition method. The results are presented comparatively . We can see that the DSP-EAS method is more sensible than the AAS method: the detection limits are 0.002µg/ml and 0.42 µg/ml, respectively, the calibration graphs were linear for 0.002-100 µg/ml and 0.62-75µg/ml.

In the case of ruthenium determination the recoveries were 98.87% and 99.40% for the AAS method and 100% for the DSP-EAS method.

The DSP-EAS technique is more effective, however we recommend the AAS- technique -the standard addition method- and in the presence of spectral buffers for ruthenium determination.

L19

APPLICATION OF INTERNAL STANDARDISATION IN DETERMINATION OF HIGHER CONCENTRATIONS OF PALLADIUM AND RHODIUM IN THEIR ALLOYS WITH PLATINUM USING INDUCTIVELY COUPLED PLASMA ATOMIC EMISSION SPECTROMETER

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This procedure utilizes Sr as an internal standard for the determination of higher concentration levels of Pd and Rh in their Pt based alloys. [1] The Pd and Rh concentration range varies from 1 to 15%.

The previous analytical procedure without internal standardization, included considerable dilution that might consequently induce the dilution error.

The advantages of this method compared to those without internal standardization are the following: direct measurement without additional dilution thus, errors arising from dilutions are avoided so, method is simpler; satisfactory compensation for various matrix effects and sample compositions that allows various sample weights. [2]

However, despite the possible dilution error, the results obtained by this approach are in fair correlation with those obtained without internal standardization. F-test proved that between the two mentioned methods there was no significant precision difference at 95% confidence level.

The spectrometer used in this method was ARL 3410+ ICP.

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L20

DETERMINATION OF GOLD IN GEOLOGICAL SAMPLES BY GRAPHITE FURNACE ATOMIC ABSORPTION SPECTROMETRY

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All samples of copper ore, mined daily in RTB - Bor, are accompanied with specific content of noble metals. Because of that, it is necessary to know and follow concentration of these metals, particularly gold as rare and precious metal.

Fire assay is used for gold and silver determination in geological samples. This method is known for a long time, and it allows us a determination of low concentrations with good accuracy and precision. Its basic disadvantage is long time for carrying out. This paper represents an attempt for finding out the suitable method for the determination of low concentrations of gold in short time.

Sample is dissolved in mixture of acids (HF:HNO3 : HCl = 3 : 3 : 1) in teflon beaker with teflon plate on it for 4 hours and 30 minutes. Saturated solutions of H3BO3 is added after dissolving, and warming up is continued for 15min. After that, the solution is transferred into graduated polyethylene jag and completed to 20ml.

Gold content is determined by use of analytical curve technique. Concentrations of reference solutions are 10 - 40ng/ml. Calibration is performed under the addition of matrix modifier solutions. The obtained results are compared with fire assay result.

Content of gold in analyzed sample using fire assay method is 5.5g/t. Average result from eight determinations using our method is 5.4g/t. Thus, we should conclude that determination of gold in geological samples by graphite furnace atomic absorption spectrometry can be equally used with fire assay.

The investigation has shown that detection limit for gold determination, using this method, is 1g/t.

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L21

DESIGN OF A ROWLAND-POLYCHROMATOR FOR LASER-INDUCED PLASMA SPECTROSCOPY (LIPS)

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For Laser-induced Plasma Spectroscopy (LIPS), most of the current commercially available spectrometer/detector-systems are based on Czerny-Turner designs in combination with an intensified CCD-camera. Besides the high cost of the image intensifier needed for time-resolved, these systems do not provide the spectral coverage urgently needed for multielement analysis and high spectral resolution at the same time. Therefore, such systems do not qualify easily for multielement analysis in unknown and complex matrices. For overcoming these limitations we realized a Rowland-Polychromator in combination with a set of photo-multipliers (PMT). Especially for applications, where a fixed range of elements (e.g. heavy metals) have to be observed and a low cost system is required, the use of a Rowland-Polychromator system is the method of choice. The system should be modular in design with a fiberoptical interface and suitable for 19"-rack systems. Besides briefly documenting the merits of LIPS analysis, the poster will mainly address the concept and realization of both the spectrometer and the detection modules consisting of a gated PMT and a low-cost boxcar-integrator with µs time resolution. The spectrometer was set up in the Paschen-Runge configuration with the fiberoptical interface connected to the entrance slit, the grating, and the exit slits placed on the Rowland circle. Using a concave grating with a focal length of 498.1 mm and 2400 l mm^{-1} (blazed at 210 nm), emission lines from 200-420 nm can be detected with high spectral resolution (bandpass 50 pm using 50 µm slits). To demonstrate the ruggedized set-up of the spectrometer measurements were taken under various environmental conditions in a mobile LIPS systems. Preliminary measurements on glasses and heavy metal aerosol loaded filters revealed that the current spectrometer/detection-system can easily compete with commercially available Czerny-Turner systems in terms of detection limits. Taking into account the multielement detection capability due to the large spectral coverage and the high spectral resolution, the Rowland-Polychromator is a good choice for low-cost LIPS systems.

L22

ANALYSIS OF CLAY MINERALS USING TG-DTG, FTIR AND ICP-AES TECHNIQUES

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The characterization of clay minerals was performed by thermal analysis (TG-DTG), simultaneous infrared spectroscopy (TG-FTIR) and inductively coupled plasma atomic emission spectrometry (ICP-AES). The clay samples were taken from the various sites in the South-Estonia, near Tartu. The analysis are important for the restoration of historical terra-cotta figures (13^{th}- 14^{th} centuries) in the St.John Church (Tartu, Estonia) [1].
The temperature at which ancient ceramics, terra-cotta and pottery were fired varies in a wide range 500-1300 °C and depends on the type of clay. The clay minerals are the main materials for the production of terra-cotta figures. TG-DTG analysis and FTIR methods can be used for the study of characteristic reactions such as dehydration, dehydroxylation and decomposition associated in the course of the heating.
The TG-DTG curves were obtained using a Perkin-Elmer PC series TGA-7 Thermogravimetric Analyser in the temperature range 25-900 °C and the dynamic experiment were carried out in the air and nitrogen atmosphere. The infrared evolved gas analysis was performed using a Fourier Transformed Infrared Spectrometer (FTIR) Perkin-Elmer System 2000 TG-IR in the dynamic nitrogen atmosphere.
For the determination of chemical composition of clay minerals: SiO_2, Al_2O_3, Fe_2O_3, CaO, MgO, PbO, ZnO, TiO_2, K_2O, Na_2O (%) a sequential PU 7000 Philips ICP-AES was used. The samples were decomposed by fusion and the method was tested by analysing the US Geological Survey reference materials GXR-3 and GXR-4.

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L23

OPTIMAL CONDITIONS FOR EUROPIUM DETERMINATION IN CaS:Eu LUMINOPHORS BY INDUCTIVELY COUPLED PLASMA ATOMIC EMISSION SPECTROMETRY

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CaS:Eu phosphors are the red-emitting cathodoluminophors. For the synthesis of CaS:Eu, CaS:Eu, Cl phosphors the required amount of dopants (Eu_2O_3 for Eu and anhydrous $CaCl_2$ for Cl) was added to high purity grade CaS. The samples were heated with 2-10 % sulphur in the dynamic argon atmosphere at 1370-1420 K.
For the determination of europium in the luminophors a sequential PU 7000 (Philips) inductively coupled plasma atomic emission spectrometer (ICP-AES) was used. ICP-AES was found to be a versatile technique for the europium determination. The europium emission lines Eu II at 381.967 nm and Eu II at 412.970 nm were compared. The effect of changes of forward radio frequency power coupled into plasma on emission intensity of various Eu spectral lines was studied. The plasma power was changed from 0.8 to 1.2 kW in step of 0.1 kW and the change in the net intensities (%) of the europium lines were calculated. The matrix effects due to calcium were studied by measuring analyte intensities (1.0 mg l^{-1} of europium) in solutions containing various concentrations of calcium. The relative intensities of the analytes in a Ca matrix of 0-2000 mg l^{-1} were calculated. The influence of the Ca matrix on the europium emission signal Eu II at 381.967 nm and Eu II at 412.970 nm was < 1.5 %. The scans of different emission lines are presented.
The samples of CaS:Eu (0.05-01±0.0002 g) were dissolved in 6 M HNO_3 (Suprapure, Merck) and transferred into a 25 ml volumetric flask. Five calibration standards of europium were used in the following range: 0.05-10.0 mg l^{-1}. The different samples of luminophors CaS: Eu (0.002-0.16 at % Eu) were analysed and the precision of the determinations (RSD) ranged from 0.3-1.6 %.

L24

Characterization of Hydrocolloids by Laser-induced Plasma Spectroscopy (LIPS) with an ICCD-Echelle Detector

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The versatility of laser-induced plasma spectroscopy, LIPS, has been demonstrated for a wide range of matrices as different as soil, industrial materials (metals, glasses), gases, and aerosol particles. The almost complete lack of sample preparation and the resulting low temporal and financial efforts for a single measurement predestine LIPS as an ideal tool for the fast screening of environmental samples. A main drawback of a LIPS-analysis is the actual identification of emission lines in a complex multicomponent spectrum of an unknown sample. Due to the lack of spectral resolution of the usually employed detection systems or unsatisfying free spectral range a definite identification of a set of emission lines is only feasible with a priori knowledge about the sample. However, Echelle spectrometer combine a spectral resolution $\Delta\lambda/\lambda$ better than 10000 with a spectral range of several hundred nanometers. The application of an Echelle spectrometer for a sensitive LIPS analysis requires, like every LIPS analysis, a time resolving detection system, that means an intensified CCD-camera (ICCD). The presentation will illustrate the adaptation of a Echelle spectrometer to an ICCD system for analysis of hydrocolloids by LIPS [1]. Hydrocolloids became a field of increasing interest due to the suspected influence on the migration of pollutants like heavy metals in the aquifer. Since most conventional analytical methods are comparable time-consuming, the aim of this study was to develop a sensor system for quantitative characterization of colloids, which does not require much sample preparation and allows fast measurements with high sample throughput for field studies. To avoid artefact formation a sub-surface sampling device based on ultrafiltration (polycarbonate filter, cut-off 100 nm) was designed and utilized for characterization of ground- and surface-water [2]. The elemental composition of the particles concentrated on the filter surface is then detected quantitatively by LIPS. Besides an overview of the experimental set-up and sampling procedures for colloids, we will provide a characterization of the Echelle detection system and the conventional system based on an intensified diode array and a Czerny-Turner spectrograph in terms of feasibility for field applications, sensitivity, and detection limits for relevant heavy metals. Due to the unsurpassed combination of spectral resolution and free spectral the Echelle system allowed also the characterization of totally unknown hydrocolloid samples with absolute detection limits in the lower ng-range.

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[2] C. Haisch, J. Liermann, U. Panne, R. Niessner, Anal. Chim. Acta, 1997. 346, 23

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L25

LUMINESCENT ANALYTICAL SPECTROSCOPY OF POLYCYCLIC AROMATIC HYDROCARBONS BASED ON TRIPLET-TRIPLET EXCITATION ENERGY TRANSFER IN MICELLES OF ANIONIC SURFACTANTS

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Polycyclic aromatic hydrocarbons (PAH) are among the widespread dominant pollutants owing to their both mutagenic and carcinogenic action. The method of luminescent analysis used for the determination is sensitive, but current procedures require either low temperature (77 K) or prior separation of mixture components.

Methodology developed in present work assumes increasing the selectivity of PAH determination by using triplet-triplet (T-T) excitation transfer from donor to acceptor. It has been found that the process is far more effective in microheterogeneous anionic micellar media than in homogeneous aqua, mixed organo-aqueous or nonaqueous solutions. Two variations of luminescent analysis can be realized.

The first is T-T annihilation activated delayed fluorescence. The donor and acceptor can be the same or different (mixed annihilation) molecules. For example, the systems consisting of triphaflavin (donor) and pyrene (acceptor) or anthracene (donor) and rhodamine 6G (acceptor) solubilized on micelles of sodium dodecylsulphate (SDS) satisfy the required conditions.

The second is observed for the first time room temperature phosphorescence (RTP) sensibilized by T-T energy transfer on micelles of SDS in the presence of heavy atom. This process is lacking in the homogeneous solutions. The pair triphaflavin-pyrene was investigated and phosphorescence signal was observed. In the proposed two variations of luminescent analysis, the deoxygenation of solutions was carried out by chemical way. The approaches developed will be used for selctive determination of PAH in different environmental objects.

The work was supported by Russian Foundation for Basic Research, grant N 97-03-33393a.

L26

QUANTITATIVE DETERMINATION OF DOPANT CONCENTRATION BY X-RAY FLUORESCENCE IN CERIUM-ACTIVATED STRONTIUM SULFIDE FILMS

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SrS:Ce thin film is used as blue-green emitting phosphor in electroluminescent (EL) flat panel displays. Cerium concentration is one of the most important factors influencing the EL emission intensity and the colour purity of SrS:Ce films [1, 2]. X-ray fluorescence offers a fast, non-destructive method for the determination of the average Ce content in the SrS thin film matrix. SrS:Ce thin films were deposited at 380 °C by the Atomic Layer Epitaxy (ALE) method on soda lime glass substrates with or without an Al_2O_3 ion barrier layer. Some samples had also an upper Al_2O_3 layer which can be used in a test EL device as an upper insulator. The source materials for the deposition were $Sr(thd)_2$, $Ce(thd)_4$, and H_2S.

Filter papers, impregnated with solutions of ammonium cerium nitrate or cerium nitrate and strontium chloride, were used as calibration standards. The intensity ratio of Ce Lα and Sr Kα lines was measured using a Philips PW1480 XRF spectrometer equipped with a Cr X-ray tube and calibrated against the known wt-% (Ce/Sr) concentrations. Two series of thin film samples were analysed by different instruments (ICP-AES, ICP-MS), and the results were compared to the XRF analyses. The determined ratio of (Ce/Sr) ranged from 0 to 2 wt-%. For the first series, approximately 40 % higher Ce concentrations were determined by XRF, compared to ICP. For the second series, 5 % difference was observed. Absorption and chromatographic effects present in the filter paper standards have an influence on the XRF calibration curves. On the other hand, dissolution of the thin film samples is a source of error in ICP analysis, where also instrumental calibration may play a role.

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L27

OPTIMIZATION OF THE APPLICABILITY INTERVAL OF THE DILUTION-ADDITION METHOD IN QUANTITATIVE XRF ANALYSIS

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This work is a detailed study of the behaviour of X-Ray fluorescence intensity for a wide interval of dilution-addition factor values.

The chemical system formed by the unknown and standard of identical matrixes(cement-cement, clay-clay) and different matrixes (cement-clay) was used. Different materials were worked with in the form of both tablets and beads.

The procedure was to use a constant concentration of diluent (manitol in the case of the tablets and lithium tetraborate for the beads) and then the diluent concentration in the different samples was varied.

The optimum dilution-addition factor intervals for both forms of sample preparation for the quantitative analysis of the different materials used has been deduced; the results obtained with both procedures have been compared.

L28

DETERMINATION OF GOLD IN LEAD CONCENTRATES BY FLAME ATOMIC ABSORPTION SPECTROMETRY

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Gold is usually present in ores or concentrates together with a number of other elements and in relatively small concentrations. In order to be able to carry out an assay for the gold content, prior separation of the gold from the other components is necessary. This is usually done with the so-called fire assay and. Another possibility, as described in this paper, is to separate the gold content of ores or concentrates by wet extraction processes, followed by other purification procedures.

Prior separation is also required in most cases when gold solutions are to be analyzed in order to eliminate the numerous components present in these solutions and simultaneously to concentrate the amount of gold present to a determinable concentration level.

Gold requires a very strong oxidizing medium for dissolution and that is why gold and the other elements in the sample are brought into the solution by wet acidic digestion.

The major element in the studied sample is lead (50-60%), compared with gold content of about 0.005 - 0.01 %. Lead must be removed from the sample in order to avoid interference during the following steps of the method, and it is separated by precipitation as $PbSO_4$.

Separation of gold from other elements in the solution is achieved by liquid-liquid extraction using isobutyl methyl ketone; the organic phase is than destroyed and gold is brought in a hydrochloric acid solution, from which is determined by flame atomic absorption spectrometry (FAAS).

Studies concerning the most appropriate acidity of the final solution containing gold and submitted to FAAS determination were carried out. Tables and graphs illustrate the results.

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L29

X-RAY FLUORESCENT ELECTROCHEMICAL TECHNIQUE - A NEW APPROACH TO THE ANALYSIS OF MULTI-LAYER METALLIC STRUCTURES AND THEIR WEAR-RESISTANCE

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New analytical method of simultaneous determination of the element composition and wear-resistance of multi-layer metallic coatings is offered, which is based on the direct X-ray fluorescent - electrochemical determination of metals in the products of wear.

The original sampling apparatus with measured load upon the abraded surface, allowing completely to standardize the conditions of selection of samples for analysis, has been created. At the beginning the X-ray fluorescent determination of metals is done on the surface of the abrasive based on the intensities of the corresponding $K\alpha$ - lines, then the electrochemical analysis of particles from the same surface is carried out via their transformation into acidic mineral-organic background electrolyte with high solvating ability, which provides high selectivity of the quantitative determination (for example, the acidic sulphate dimethylsulphoxide electrolyte).

The areas of linear dependencies of the intensity of $K\alpha$ - lines of the components (Cu, Mo, W, Fe, Cr and others) of the coatings and their polarographic currents on the degree of a material wear and on the load upon the abraded surface have been established.

The method permits rapid determination of preffered wear of that or other component of coatings, the determination of the element composition of transitive zones and estimation of their wear-resistance.

L30

MODIFIED DILUTION-ADDITION METHOD FOR X-RAY FLUORESCENCE ANALYSIS: THEORETICAL BACKGROUND AND APPLICATION TO QUANTITATIVE ANALYSIS OF CLAYS

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Quantitative analysis by X-Ray Fluorescence presents a series of difficulties due to the interelemental effects which distort the analytic signal. The study of these effects and their possible correction is therefore a basic aim in quantitative analysis. This communication proposes a modification to the Dilution-Addtion method [1], which can compensate for the matrix and interelemental effects and is applied to the elemental determination of clays.

The proposed model permits the analysis of raw materials using standards of a similar raw materials. The interelemental effects affecting the various analytes are compensated for.

This methodology does not require the preparation of synthetic multielemental standards with the similar characteristics to those of the unknown, something which is difficult to achieve given the complex nature of these materials. It is sufficient to have a similar mineral containing the elements to be evaluated, even though they may be in very different concentrations to those of the unknown.

The results obtained by applying the mathematical equation deduced in the modified Addition-Dilution Method for the different analytes are highly satisfactory.

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L31

MOLECULAR CONECTIVITY, A WAY TO PREDICT MOLECULAR CHEMILUMINESCENCE

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Usually, the analytical work in direct chemiluminescence (CL) consists of to seek CL of the analytes themselves by examining their reaction with a range of oxidants (and reductants) under different reaction conditions, which result in time-consuming trial-error procedures. Although there are some empirical rules for predicting chemiluminescent behaviour, there are many exceptions to these guidelines too, and CL reactions cannot be predicted indeed.

The present paper deals with the first attempt to apply molecular conectivity calculations to predict the chemiluminescent behaviour of a molecule when recats with common oxidants in liquid phase. In QSAR (Quantitative Structure-Activity Relationship) studies, molecular conectivity is a topological method capable of describing the structure of a molecule by means of numbers called indices; subsequent regression in relation to the experimental values of the physical, chemical and/or biological properties yields a series of functions called conectivity functions. In recent years, molecular conectivity studies have been used to predict several parameters related to the biological activities and even chromatographic behaviour of drugs [1].

For the molecular conectivity study, discriminant analysis was applied to a group of more than 150 chemiluminescent and non-chemiluminescent substances (found either on the bibliography or in an experimental screening by continuous-flow CL), most of them pharmaceuticals. The method used for descriptors selection was a stepwise linear discriminant analysis (SLDA) from F-Snedecor parameter. The classification criteria used was the minimum value of Mahalanobis. The quality of the discriminant function was calculated through the Wilks'U-statistical parameter.

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L32

DIRECT DETERMINATION OF ANTIMONY IN ROADSIDE SOILS AND SEDIMENTS BY ULTRASONIC SLURRY SAMPLING AND ELECTROTHERMAL ATOMIC ABSORPTION SPECTROMETRY

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The natural low levels of antimony in the earth crust (0.2-0.3 µg/g) makes it a potential marker of metallic contamination. The high sensitivity of electrothermal atomic absorption spectrometry (ETAAS) makes it a suitable technique for this purpose which combined with the slurry sampling represents a powerfull methodology for trace analysis. This way is not without problems so the experimental conditions must be carefully checked for each analyte/matrix system. Therefore, the development of the automatic ultrasonic slurry sampling (Perkin-Elmer, USS 100) has avoided quite a lot of problems though this accesory is not available in most laboratories.

This work presents a rapid and reliable way for direct antimony determination in soils and sediments using USS-ETAAS. The experimental conditions were carefully optimized for slurry preparation, ultrasonic agitation, and ETAAS instrumental measurements. Slurries were prepared in nitric acid (0.5% v/v). Pyrolysis and atomization temperatures were set at 900° and 1700°C, respectively.

Sixteen roadside soils from a medium-size city, La Coruña (NW of Spain), and twelve sediments from two estuaries (La Coruña estuary and Ares-Betanzos estuary) were analyzed. The antimony content found in soils ranged from 0.30 to 8.81 µg/g. A clear relation between antimony concentration and motor vehicle intensity was observed. Regarding sediments, the levels of antimony amount from 0.22 to 1.51 µg/g for La Coruña estuary and 0.24-0.71 µg/g for Ares-Betanzos estuary. The antimony contents seemed to reflect, again, the anthropogenic influence.

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ACA P1

CAPACITIVE AFFINITY BIOSENSORS BASED ON ω-MODIFIED ALKYLTHIOLS

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ω-Modified alkylthiols form perfectly ordered dielectric monolayers on gold surface and thus provide a perspective base for preparation of affinity biosensors. Both stability of the monolayers in different conditions and analyte binding with the affinity biosensors can be sensitively monitored by capacitance measurements [1].

The stability of monolayers from alkylthiols with different length of the hydrophobic chain with terminal carboxy groups was studied at different pH and different electrode potentials. No stability range was observed for short chain ω-modified alkylthiols. Also, a strong desorption of monolayers formed by 3,3'-dithiodipropionic acid was measured. In contrast, a desorption of carboxyhexadecanethiol from the gold surface at optimal conditions was less than 0,005% from the total amount during four days.

Several examples of capacitive biosensors based on the long-chain ω-modified alkylthiols, including an immunosensor for HSA [1], a biosensor for LDL and a gene sensor, were developed. These sensors were built layer-by-layer and have a structure Au-S-$(CH_2)_{15}$-coupler-receptor. The detection limit of the immunosensor is about 15 nM. The immobilized minimal receptor for LDL demonstrated high selectivity to the receptor associated protein. A gene sensor of the structure Au-S-$(CH_2)_{15}$-coupler-avidin-biotin-oligonucleotide displays capacitive response to complementar olygonucleotide, the detection limit for 22-mer olygonucleotides is about 100 nM. A structure Au-S-$(CH_2)_{15}$-CO-NH-oligonucleotide results in higher sensor response.

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ACA P2

ANIONIC SURFACTANTS IN ACID MEDIA: A NEW CLOUD POINT EXTRACTION METHODOLOGY FOR THE DETERMINATION OF PAHs IN ENVIRONMENTAL SAMPLES

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Polycyclic aromatic hydrocarbons (PAHs) are a wide group of polluting compounds which are of anthropogenic and natural origin. They have carcinogenic and mutagenic properties, even at concentrations on the ppt level [1], so their occurrence in the environment has to be monitored. Because of their low concentration the analysis of PAHs in environmental samples requires always a preconcentration step prior to chromatographic separation. The most common procedures for the preconcentration of samples are these of either solid sorbents [2] or liquid-liquid extraction [3]. Although recently PAHs extraction with nonionic [4] and zwitterionic surfactants [5], based in the cloud point phenomenon, has been also proposed.

Advantages for the use of cloud point extraction include: 1) ability to concentrate a variety of analytes with high concentration factors, 2) safety and cost benefits; very small amounts of the relatively nonflammable and nonvolatile surfactant are required, 3) easy disposal of the surfactant, and 4) the surfactant-rich compatibility with micellar or hydroorganic mobile phase. Disadvantages of the nonionic surfactants employed to date include: 1) a high background absorbance in the ultraviolet region, 2) fluorescence due to the presence of the aromatic moiety, 3) large retention times which produces oberlapping with PAHs, and 4) thermally labile analytes can undergo degradation at the temperatures required for phase separation. The zwitterionic surfactants studied overcome some of these disadvantages but they are not commercially available.

In this work, we propose for the first time the use of anionic surfactants in the cloud point methodology. It has been checked that this kind of surfactants [*e.g.* sodium dodecylsulphate (SDS), sodium dodecanesulfonic acid (SDSA) and sodium dioctylsulfo succinate (Aerosol OT)] separate into two isotropic phases, in an acid medium. By using surfactants of linear chain (*e.g.*. SDS, SDSA and Aerosol OT) several advantages areobtained; 1) low background absorbance at the wavelength used to monitor PAHs, 2) no fluorescence signal, 3) low retention time due to their polar character, and 4) cloud points not dependent on the temperature which permits thermally labile analytes to be preconcentrated. In addition they are commercially available. These advantages have been exploited for the preconcentration of PAHs [*e.g.* pyrene, benzo(a)anthracene, benzo(a)pyrene, benzo(e)pyrene, benzo(b)fluoranthene, benzo(k)fluoranthene, indene(1,2,3-cd)pyrene, and benzo(b)naphtho(2,1-d)thiophene] in water samples an extraction of these pollutants from sewage sludge.

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ACA P3

DEVELOPMENT OF ELECTROCHEMICAL SENSORS FOR FLOW-INJECTION DETERMINATION OF SOME NOBLE METAL IONS

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The development of electrochemical ion sensors is one of the rapidly growing areas of electroanalytical chemistry that offers great potential for detection in flow-injection (FI) analysis. However, it should be pointed out that the utility of sensors based on the commonly used electrode materials is often limited by low surface stability, short life time, poor selectivity and slow charge-transfer kinetics at the sensor-solution interface. The choice of new effective ion-sensing electrode materials and the optimization of FI parameters play a critical role for solving this problem.

In the present communication, the dynamic characteristics of a new type of carbon composite electrodes (CCEs) containing a silica carrier (SC) with covalently immobilized thiacrown-compounds were investigated. The thiamacrocycle-bound silica compounds shown to acquire strong complexing affinity properties to noble metal ions in flowing solutions. Desirable properties for this reagent are: water insolubility, stability in solutions of low pH and rapid formation of insoluble complex with the metal ions of interest. It was found that introduction of the modified silica matrix into the solid-state electrode composition strongly effected on the redox processes in the metal ion solutions. By choosing the most appropriate immobilized reagent it became possible to receive the best selectivity of amperometric signals to some noble metal ions in the presence of other non-complexing redox-ions. Thus, the immobilized macrocycles were found to be very attractive as solid-phase reagents in amperometric sensors for chlorocomplexes of Au (III), Pd (II) and Ir (IV). The complex response mechanism for the new sensors was obtained and the effect of macrocyclic ligand in the forming of the resulting dynamic signal was clarified. The selectivity of analytical signals under the fixed FI conditions were found to be dependent on the structure of a modifier as well as on the nature of a supporting electrolyte.

The FI scheme and optimal conditions of adsorptive voltammetric determination of ultratrace concentration of silver were found by using SC-CCE with 16-membered tetrathiacrown-compound . The new FI method for determination of silver in sea water was developed and its applicability for ship-board use was demonstrated.

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ACA P4

Ultrasensitive catalytic spectrophotometric detection of metal cations in flow analysis and ion chromatography

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Post column derivatisation is a routinely used method for post separation detection in flow analysis and ion chromatography. Recently, the main task of development of post column derivatisation is widening the universality and increasing the sensitivity of detection. Catalytic reactions are well known to enhance sensitivity of spectrophotometric determination of cationic and anionic species, so it is suitable for development of new high sensitive detection systems for flow analysis.
The system for sensitive catalytic spectrophotometric detection of manganese(II) was developed. This system is based on manganese(II) catalytic effect in oxidation reactions. Different catalytic systems were tested: oxidants – hydrogen peroxide, sodium periodate; reductants – alkylanilines, hydroxybenzoic acids, triphenylmethane dyes (basic fuchsine, malachite green, etc.). The sensitivity of this detection system allows to determine Mn(II) in sub-ppb level. Manganese(II) was analyzed using this system in several natural and technogenic water samples.
It is known that displacement complex-forming different metal cations with Zn-EDTA allows to extend universality of post column photometric reaction with PAR. The analogous system with Mn(II) complexes was proposed and tested for catalytic spectrophotometric detection of some alkaline earth and transition metal cations for ion chromatography.

ACA P5

DEVELOPMENT OF AN ENZYME-LINKED IMMUNOSORBENT ASSAY FOR BENALAXYL

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A rapid quantitative determination of pesticide residues in vegetable and fruit crops, or an estimation of distribution and persistence of pesticides in different parts of plants is possible using a sensitive, specific, simple and rapid analytical method as immunoassay.
We have developed a competitive enzyme-linked immunosorbent assay (ELISA) for the determination of benalaxyl (methyl N-phenylacetyl-N-2,6-xylyl alaninate), a fungicide widely used in grape and vegetables (peppers, tomatoes) cultivation.
The molecular structure of the pesticide was considered to obtain a highly specific antiserum: a derivative of benalaxyl (hemiglutarimido-N-phenylacetyl-N-2,6-xylyl alalinate, Bn-HG) was synthesised and linked to bovine serum albumin (BSA). The so obtained immunogen was used to immunise three mice and one chicken, which responded by producing specific antibodies to benalaxyl with negligible cross-reactivity to various structurally related pesticides. The binding capacity was studied by mouse and chicken antiserum titres obtained on Bn-HG-ovoalbumin conjugates (corresponding to different hapten protein reaction ratios) and on Benalaxyl-acid (Bn-COOH)-ovoalbumin conjugate immobilised on microtiter plates. Different concentrations of immobilised conjugates were considered to obtain highest sensitivity.
The optimised calibration curve in buffer has a working range of about 0.5 - 50 ng/ml, with a detection limit of 0.35 ng/ml (with mouse antibodies) and of 0.20 ng/ml (with chicken antibody). The assay has been applied for determination of benalaxyl in acqueous samples: tap and river-water samples spiked with benalaxyl show quantitative and reproducible recoveries ranging from about 80 to 120% in a working range of about 0.5 - 50 ng/ml. Further studies to determine benalaxyl in wine are in progress.

ACA P6

SELECTION OF A REPRESENTATIVE TRAIN SET FOR THE CLASSIFICATION OF DEMOLITION WASTE

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Nowadays, separation of demolition waste is done manually. Automation of this process is beneficial for reasons of increased throughput, better working conditions and reduced costs. In the E.C. supported *AUTOSORT* project, the goal is the separation of demolition waste into three fractions:
- (Un)treated wood, paper, and cardboard,
- Plastics, and a
- Rest fraction, mainly stone, glass, and ceramics.

From demolition waste objects, mini-spectra consisting of 6 spectral regions in the near-infrared range are recorded. Linear Discriminant Analysis (LDA) is used to do a classification. To obtain an LDA model, a representative train set has to be selected from a complete "real world" data set.

For a "practical" implementation, questions are: how many objects, which ratios of selected objects between the three fractions, how to generate a constant test set, and how to select the objects? Furthermore, the selected objects can be used to monitor the performance in time (quality control).

To obtain a train set, objects are randomly selected from a constant data set. Statistical tests are executed to check the reproducibility. This method is compared to the Kennard-Stone object selection method. Kennard-Stone is preferred, because the objects are equally selected in LDA-space.

The presentation will discuss the applied statistical tests, Kennard-Stone, and the results.

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5.2

INVESTIGATION FOR ORGANIC POLLUTANTS FROM HOUSE HEATING SYSTEMS USING BIOGENIC FULES

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Introduction

Biogenic fuels are an interesting alternative to reduce the CO_2 – emission and protection of the energy supply. In contrary to the fuel wood the biogenic fuels are much more critical because of their high content of chloride. But this compound is one requirement for the formation of chlorinated organic compounds.

Materials and Methods

The incineration experiments were carried out using a ``oekotherm compactanlage TYP CO`` with automatic charger and different biogenic fuels and wood. The manual heat efficiency was 50 kW.

The sampling was done by the filter-cooler method according to the VDI guide line 3499 page 2 and the VDI guide line 2066 page 1 and 2. For clean up the filter and glass wool was transferred into a soxhlet. After addition of the 17 $^{13}C_{12}$ - PCDD/F, 6 $^{13}C_6$ - PCBz and 5 $^{13}C_6$ – PCPhen a soxhlet extraction (24 h) with toluene was carried out. $^1/_{10}$ of the treated toluene extract was separate cleaned up after the addition by deuterated PAH-standardmixture for PAH-GC/MS-Analysis.

Each sample was analyzed for the 17 2,3,7,8-PCDD/F isomers and the sum parameters by HRGC/HRMS. The PAH, PCB, PCBz and PCPhen analysis were carried out by HRGC/LRMS in the SIM mode

Results and Discussion [1]

The concentrations of polychlorinated-dibenzodioxins/furans (PCDD/F), polyaromatic hydrocarbons (PAH), polychlorinated-phenols (PCPhen) and polychlorinated-benzenes (PCBz) in exhaust gas of burning wood and various other biogenic material are shown and discussed.

[1] T. Launhardt, A. Strehler, R. Dumler-Gradl, H. Thoma, O. Vierle; *Organohalogen Compounds* **1996**, *27*, 30.

A40

ASPIRIN DISSOLUTION STUDIES BY SEQUENTIAL INJECTION ANALYSIS WITH A SPECTROPHOTOMETRIC DETECTOR

A. N. Araújo, M. C. B. S. M. Montenegro and M. G. F. Sales

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The therapeutic effect of a pharmaceutical preparation is greatly dependent on its dissolution at the gastrointestinal tract. Additionally, the kinetics of the dissolution of a pharmaceutical gives major information about the rate of release of its main active ingredient, but needs to be determined at the first steps of the in vitro dissolution study.

Therefore, information's that may predict its dissolution in the human being, namely the in vitro evaluation of the amount of drug dissolved under specified conditions became nowadays a legal requirement for several pharmaceuticals. To fulfill the pharmacopoeias requirements, these dissolution studies need an operator to collect, at a certain period of time, treat and analyze the samples. This procedure may lead to erroneous results considering that the analyses step is not performed under real time conditions and, further, unable any kinetic studies.

Therefore, in order to perform, in real time, a complete dissolution profile, a new system based on the sequential injection analysis concept has been established. This system, in conjunction with a spectrophotometric detection has been applied to monitor the dissolution rate of Aspirin tablets. After optimizing all parameters, calibrations of a 30 µL volume of acetyl-salicylic acid standards from 0.06 to 1.00 g/L were of Abs = 1.093(±0.054) + 0.012(±0.006); Rsquared = 0.999. Under the optimized conditions, several dissolution profiles were performed collecting from the dissolution vassel, each 3 min and along a 30 minutes period of time, a 30 µL volume of sample. At the end of each trial, the United States Pharmacopoeia monograph procedures were performed, and the comparison between both methodologies at the 30 minutes dissolution period showed a good agreement.

Acknowledgments: The authors gratefully acknowledge PRAXIS XXI (Project nº 2/2.1/SAU/1190/95). One of us (MGFS) thanks a Ph.D. grant to Praxis program (PRAXIS XXI/BD/2958/94).

O29

IN-ELECTRODE TITRATIONS: DETERMINATION OF CHLORIDES IN WATER BY ANODIC STRIPPING COULOMETRY IN A SILVER-COATED POROUS ELECTRODE

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The determination of chlorides in waters is a common task in environmental analysis. Higher chloride concentration are usually determined by mercurimetric or coulometric titration which provide reliable results. Lower chloride concentrations can be managed by turbidimetry or more conveniently by cathodic stripping voltammetry with a silver working electrode.

Flow-through electrochemical analysers with porous working electrodes offer an unique approach for the determination of complexing substances and/or species forming negligibly soluble compounds such as sulphides, halogenides, chromates, etc. The principle of the method is as follows: The bulk of the porous electrode is coated with a metal by electrodeposition at a suitable potential. The electrode is then filled with the sample solution containing e.g. some chelating species or anions forming less soluble compounds with the metal ions. The deposited metal is galvanostatically stripped next and the corresponding chronopotentiogramm is registered. The presence of the above species in the sample gives rise to a shift of the stripping peaks to negative values, whereas the shift is governed both by the formation constants of the corresponding complexes and the solubility product of the precipitate. Moreover, the shift also depends on the concentration of the species in the sample. The peak area depends on the amount of the species in the sample volume captured in the electrode bulk.

Chlorides can be determined by making use of the above principle. The carbon porous electrode of inner volume of about 20 µL is coated with silver and the electrode is filled with the sample solution at a potential of -500 mV. Then silver is stripped by a constant current of -100 µA and the chronopotentiogramm is registered. The presence of chlorides in the sample is reflected in a pre-peak, the area of which is proportional to the chloride concentration in the sample. The influence of sample composition, various ions and organics on the results are discussed.

E65

ANALYSIS OF FLAME RETARDED POLYMERS ANS RECYCLING MATERIALS

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Introduction

Polymer samples were analysed as received from a recycling company. Recycling of the material was tested for the flame retarded polymers identified to occur most frequently. The concentrations of polybrominated dioxins and furans (PBDD/F), as well as of selected flame retardants, were monitored during the recycling process in order to characterize the reaction behaviour of the flame retardants. The results demonstrate that flame retarded poly-mers can be recycled under certain experimental conditions.

Experimental and Methods

Pyrolysis gas chromatography (py-GC/MS) with mass spectrometric detection for the determination of the flame retardancy class of the samples [1]. The polymer was identified by infrared spectroscopy (FT-IR) in combination with thermogravimetric methods. Energy dispersive x-ray fluorescence (ED-XRF) was used to identify the halogen containing samples. (HRGC/MSD) for quantifying the polybrominated dioxins and furans (PBDD/F) .A suitable clean up method had to be developed for the quantification of the PBDD/PBDF content in polymer extracts containing high concentrations of PBDE.

Results and Discussion

It has been shown that polybrominated diphenylethers (PBDE) are still frequently found in polymers originating from electrotechnical applications. During recycling processes flame retardants as well as PBDD/F tend to form lower brominated products. The recycling as a material is feasible for certain groups of materials.

[1] B. Danzer, M. Riess, H. Thoma, O.Vierle, R. van Eldik, *Organohalogen Compounds* **1997**, *31*, 108-113.

CHIMIA 52 (1998) Nr. 7/8 (Juli/August)

G29

MULTISENSOR WITH SYSTEM OF IMAGE ANALYSIS

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The report subject is the complex study tool of physical-chemical conversations in substance, taken in the microvolume, placed on the specially prepared surface.

Reactions (stimulated by different methods, catalytical, immunochemical...) conducted on the film sensor surface is a subject to study. The surface is formed from the compositional particles. Compositional particles are submicron conglomerates, containing primary nana-particularities (base material and sensor sensitive components materials). Conglomerates and conglomerate based film have the prescribed porosity. Miniature electrodes are formed from different materials on the film surface. They enable to measure electrical parameters of reacting environment, agents and products of reaction. Simultaneously the process flow is studied under microscope with digital video camera, linked to the computer.

Electrode system functions include the temperature and electrical influences and control: variation and measurement of temperature in the reactive microvolume; measurement of selectively sensitive to the studied substances surface fragments conductivity; integral environment parameters; other parameters of agents and process taken in the time perspective. All parameters are entered into computer data base through analogue-digital converters.

The researcher has the opportunity to study reactions digital processing of the varying images and electric signals.

The improvements in the image analysis [1] enable to efficiently allocate the assigned fragments of the image. The cryotechnology methods for the film multisensors [2] with following improvements take it possible to unite any given components of structure of multisensor.

We see the new tool application perspectives in the fundamental researches. A multisensor unit in the combination with various conditions of optical supervision (luminescence, polarisation), environment conditions (temperature, pH), methods of digital processing enable us to gain the parameters in different aspects, elaborate new analysis methods and new diagnostica on the same micro volume of substance. In the clinical laboratories the multisensors will be effective because their film elements with electrodes is produced under the chip group technology.

[1] Sokolovsky A. Efficient single connecting area double image clasterization algorithm// Proceedings of young scientists 1998, P. 52 - Ulyanovsk, UlGU
[2] Sokolovsky V. Thick film sensitive elements of microchip sensor: Abstract of PhD in Technical Sciences - Ulyanovsk, 1992

I17

QUALITY ASSURANCE IN ANALYTICAL CHEMISTRY - DREAMS AND REALITY

Jan Garaj, Trencín University, Slovak Republic

The responsibility of the analytical chemists producing wrong results can be enormous in many areas such as nutrition, environmental monitoring, trade, forensic analysis and so on. The huge costs, both in terms of financial and resources, and human misery that could be caused by such activity are one side of false results. At least so important is image not only of the particulare analytical laboratory but also of the analytical comunity as a whole.

The presure to improve quality of production and service has been increased rapidly in the last decade. In the field of chemical measurements the main ways to higher quality, to confidence in the validity of analytical results: are good laboratory practice and accreditation. Both these systems are involving mainly in the regulatory sphere and in the large entertprises, dealing with the export of products. However, the most field analytical laboratories operating in the home market area and also academic analytical laboratories work in a traditional way.

Very upsetting is reality in the last named area. Academic analytical laboratories operating with the highest qualified personal in the country, and educating young generation at the university level might not be representatives of progress but a hindrance for the today necessity.

One may be optimistic having in the mind, that the progress of Analytical Chemistry as a applied science is forced by two main resons: the development of the human knowledge, and the needs of the practice, the last named factor will rectify a contradiction betwen necessities and reality in the future.

In spite of enhancement of the analytical results confidence one should find possible reasons of the present situation. The reasons may be:

1. Low product competition within the country market and /or lack of the relevant legislation.
2. The little if any requirements from the international scientific journals (included the majority of analytical journals) to document experimental data and their evalution by elements of the quality assurance.
3. Absence of some quality system elements in the analytical books even in those thay operate on the top level. AOAC standars operation precedures dealing with standard deviations may serve as an example.
4. The concept of uncertainty, traceabitity, methods validation, proficiency testing requirements in analytical textbooks is seldom.
5. The explanation of new concepts is often too sophistic, time consumable and some times not unambiguous (*e.g.*validation, uncertainty).
6. The term uncertainty provokes reservation among managments of the firms. They require „confident" results.

Possible ways what should be done to improve the chemical measurements will be given on the poster.

L33

SPECTROPHOTOMETRIC DETERMINATION OF MANGANESE IN STEELS AFTER EXTRACTION OF PERMANGANATE WITH THE DIMETHYLDISTEARYLAMMONIUM CATION

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Manganese(VII) (0-120 μg) can be determined spectrophotometrically at 496 nm after its extraction as dimethyldistearylammonium permanganate into dichlorœthene.

Prior oxidation of manganese(II) to manganese(VII) is achieved by potassium periodate in acidic solution.

The calibration graph is linear up to 20 μg ml^{-1} Mn and the detection limit is 0.19 μg ml^{-1} Mn. The apparent molar absorptivity of the ion pair is 2.21×10^{4} l mol^{-1} am^{-1} at 496 nm.

The system has been applied to the determination of manganese in a range of certified standard steels.

C14

Packed-Column Supercritical Fluid Chromatography in Combinatorial Chemistry and High Throughput Screening

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Denis Berger, CHEMPUTEAM SA, 9, Route des Jeunes, CH-1211 Genève 26

Recent developments in drug discovery, using Combinatorial Chemistry (CC) and High Throughput Screening (HTS), exercise a new type of pressure on the analytical laboratories which test for new compounds identification and purity. In the past, the widely used analytical methods involved High Performance Liquid Chromatography (HPLC), since most of the drug substances are polar, non-volatile and/or thermo-labile. These screening methods are implemented to assess purity, in order to avoid false positives or negatives in the biological activity assays. Unfortunately, HPLC is a relatively slow technique. In order to decrease analysis times and increase throughput, higher than optimum flows, shorter columns and smaller particle are used. The first two decrease the resolution, the latter increases pressure drop across the column.

Packed-column Supercritical Fluid Chromatography (SFC) is a chromatographic technique in which most of the liquid solvent has been replaced with carbon dioxide. Since polar compounds are typically not soluble in CO_2, a polar modifier is usually added and solute retention is managed through composition gradient elution. Most of the hardware, including the column, is the same or similar to the one used in HPLC. However, the SFC pump has to cope with controlled delivery of a compressible fluid, which compressibility vary with temperature and pressure. Cooled traditional HPLC pumps are therefore not suitable to generate reproducible and accurate gradients. A SFC pump is thus designed and optimized to fully compensate for variable fluid compressibility.

In CO_2 based mobile phases, the optimum velocity is 3 to 5 times higher than in normal liquids, and the viscosity is 10 times lower. Both aspects favor higher throughput, and the re-equilibration of the column is extremely rapid. Full gradients at optimum velocities have produced cycle times as low as 3 minutes, thus allowing the process close to 500 samples per day and per SFC system. The chromatograms which are presented show that there is clearly room to further improve this performance. In addition, the cost of organic solvents waste disposal is reduced by 3 to 10 times in packed-columns SFC as compared to HPLC, while processing 3 times more samples per day.

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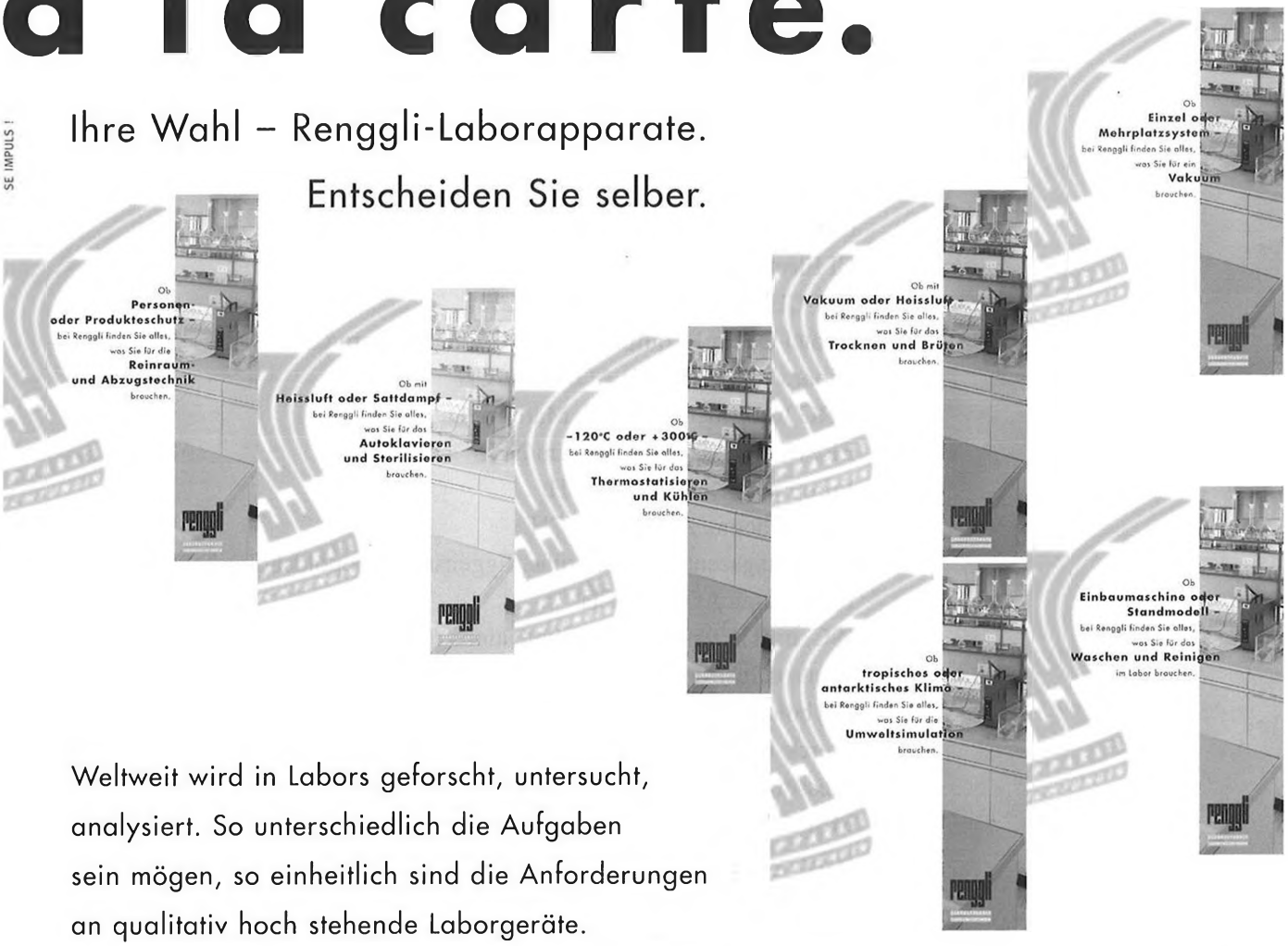

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'Just Add Water' der neue Standard in der Ionenchromatographie

'Just Add Water' ist der Begriff für die neue Technologie der Ionenchromatographie, die für die Herstellung der Eluenten und die kontinuierliche Suppression der Hintergrundleitfähigkeit lediglich Wasser in Kombination mit elektrolytischen Verfahren benötigt.

Seit der Einführung der kontinuierlich selbstregenerierenden Suppressoren der SRS-Serie im Jahre 1992 ist der Einsatz der chemischen Regenerationsmittel Schwefelsäure bzw. Tetrabutylammoniumhydroxid nicht mehr notwendig. Die zur Suppression benötigten Protonen bzw. Hydroxidionen werden durch Elektrolyse des Eluenten nach Verlassen der Leitfähigkeitszelle direkt im Suppressor erzeugt. Im Rahmen einer kontinuierlichen Weiterentwicklung der Suppressor-Technologie ist seit Frühjahr 1998 die Serie SRS-Ultra erhältlich.

Die elektrochemische Herstellung der Eluenten Kaliumhydroxid bzw. Methansulfonsäure wurde anlässlich der Pittcon 1998 eingeführt. Im Eluent Generator EG40 werden aus Wasser Hydroxid-Ionen bzw. Protonen gebildet, deren Konzentration durch entsprechende Regelung der Stromstärke exakt eingestellt wird. Die Zuführung der Gegenionen Kalium bzw. Methansulfonat erfolgt aus Elektrolyt-Kartuschen über eine selektive Membran. Die Herstellung der Eluenten in isokratischen oder Gradienten-Methoden wird über die PeakNet Chromatographie-Workstation gesteuert. Der EG40 kann in jedes bestehende oder neue IC-System der Serie DX-500 integriert werden, durch Kombination mit weiteren Modulen dieser Serie und der breiten Palette an Trennsäulen können unterschiedlichste Ionenchromatographie-Systeme individuell zusammengestellt werden.

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Leserdienst Nr. 22

Nitrogen Generator Selected to Supply New Mass Spectrometer at the Imperial College of Science, Technology and Medicine

A self-contained nitrogen generator and air compressor supplied by Whatman International has been installed in a new laboratory in the Chemistry Building at the Imperial College, South Kensington. It is to supply a Mass Spectrometer used in the process of analysing organic compounds.

The laboratory is sited on the eighth floor of the building and is designed to be self sufficient for the supply of nitrogen due to the distance from the cylinder store.

It is estimated that up to three cylinders of nitrogen a day might be required which will create undue cylinder manhandling.

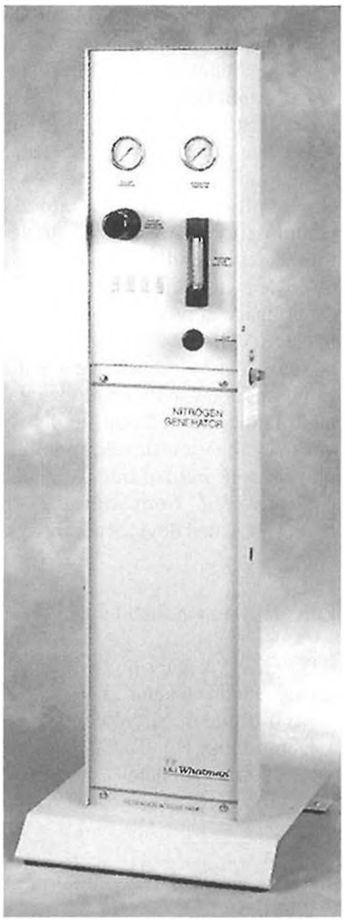
To produce nitrogen the generator requires a consistent supply of compressed air, but due to the location of the laboratory in-house compressed air was not available. To overcome this, Whatman provided a small compressor which is installed in an enclosed area nearby.

The compact and free standing Type 75-72 generator weighs 34 kg, measures only 1276×406×406 mm and is conveniently sited in the lab area close to the Spectrometer.

To safeguard the generator and the Spectrometer from any impurities in the air supply, two pre-filters with automatic drains are fitted to the generator to remove contaminants at up to 99.99% efficiency for 0.1 micron particles. Compressed air is then passed through hollow fibre membranes in the generator module to separate air into a concentrated nitrogen output.

Prior to entering the system the nitrogen is finally polished by a high efficiency filter to remove any possible migration of contaminants from the membranes. To maintain level pressures a flow controller is also fitted.

The nitrogen generator is capable of producing up to 42 lpm of nitrogen, but with the high purity levels required it is operating at about 7 barg to provide 6.2 lpm of nitrogen at a purity level of 99.5%.



The compact and free standing Typ 75-72

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Leserdienst Nr. 23

CHIMIA 52 (1998) Nr. 7/8 (Juli/August)

Microsystems for bio-analysis at IMT

Miniaturized system for coulometric titration in nanoliter volumes (courtesy of O. Guenat, IMT).

Miniaturization is the trend in most technologies these days, and chemical analysis is not exception. Improved analytical performance is the result, particularly with respect to shorter analysis times and added functionality. One of the strategies often used today to increase the speed of analysis is to incorporate a portion or all of the analysis into a flow system. The sample is injected into a flowing stream of carrier liquid, and is transported and manipulated automatically from one analytical procedure to the next. This approach of automation for chemical analysis first appeared in the early eighties, and is known as the total chemical analysis system, or TAS. Moreover, different functions can be integrated onto single devices not much larger than a matchbox, giving rise to the appealing idea of the lab-on-a-chip.

Construction of systems small enough to achieve these expectations are very difficult with classical engineering techniques. The past two decades have demonstrated the versatility of silicon chips technology, encompassing micromachining and thin-film technology, for making microstructures with not only electrical properties, but also mechanical, optical, electrochemical and fluid handling properties. More recently, efforts have been devoted to working with planar substrates other than silicon, such as glass, quartz, and plastics. It has therefore become state-of-the-art to use microfabrication technologies on the leading edge to construct microsystems for chemical analysis on a sub-µL scale.

Aware of the numerous opportunities offered by microsystems, the European Community has recently launched the program Europractice directed to industries and academia to meet their future challenges and improve their competitiveness in the global market place. A network of services, including Competence Centers designated in different application areas, has been set up. The Sensors, Actuators, and Microsystems Laboratory, or SAMLAB, headed by Prof. Nico F. de Rooij, has been appointed Competence Center for Bio-analytical Microsystems. Fully equipped laboratories, including the newest technologies for the design and microfabrication of devices, together with the interdisciplinary approach of the group makes SAMLAB a highly qualified partner. This Competence Center can introduce you to the fundamentals of microfabrication, and help you to identify and develop applications in your field of interest which could benefit from the use of microfabricated devices and/or systems.

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Leserdienst Nr. 24

Applikationsunterstützung für die Planar-Chromatographie

Für wiederholt auftretende analytische Problemstellungen welche vorteilhaft mit Hilfe der Planar-Chromatographie gelöst werden können, hat CAMAG eine Sammlung von Applikationsschriften zusammengestellt. Bis zu zehn Kopien davon können von interessierten Kunden kostenlos angefordert werden.

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Leserdienst Nr. 25

Erhöhte Flexibilität bei der beschleunigten Lösemittelextraktion (ASE™)

Die beschleunigte Lösemittelextraktion ('Accelerated Solvent Extraction', ASE™) vereinigt die Anwendungsbreite konventioneller Lösemittel-Extraktionen von Feststoffen mit Automatisierung und Schnelligkeit. Durch die Anwendung von erhöhten und definierten Temperaturen und Drükken sind die Siedepunkte der Lösemittel nicht mehr limitierend. Sowohl Extraktionszeiten als auch Lösemittelverbrauch können dadurch deutlich reduziert werden.

Generell kann jede 'klassische' Extraktion von Feststoffen mit organischen oder wässerigen Lösemitteln auf dem ASE200 durchgeführt werden. Mit dem bereits bekannten Extraktionsmittel bestehen hervorragende Startbedingungen für die Optimierung der Methode, die z.B. durch Modifikation eines Gemisches durchgeführt werden kann. Hierfür ist der Solvent Controller besonders geeignet, der als Zusatz-Modul zu bestehenden oder zu Neugeräten erhältlich ist. Durch die Möglichkeit, Gemische aus bis zu vier Flaschen in jeweils 5%-Inkrementen zu definieren, können die reinen Lösemittel eingesetzt und Verluste durch nicht verwendbare Gemische vermieden werden.

Darüberhinaus bietet der Solvent Controller die Möglichkeit, die Automatisierung des ASE200 noch flexibler zu nutzen. Entweder können Proben einer Serie nacheinander mit verschiedenen Gemischen oder unterschiedliche Serien von Proben sequentiell mit dem jeweils zugehörigen Lösemittelgemisch extrahiert werden. Die Programmierung von Methoden und Sequenzen kann dabei entweder direkt am ASE200 oder über die AutoASE-Software mittels DX LAN-Kommunikation erfolgen.

Die U.S. EPA hat die ASE-Technik bereits bei ihrer Einführung 1995 nach einer Vergleichsstudie mit bestehenden EPA-Methoden (Soxhlet-, automatisierte Soxhlet- bzw. Schüttel-Extraktion) als normiertes Verfahren akzeptiert. Mittlerweile erfolgte die Veröffentlichung als U.S. EPA SW-846 Methode 3545. Die Möglichkeit, die ASE-Technik zur Zertifizierung von Referenzmaterialien einzusetzen, wurde kürzlich von der NIST publiziert (M. Schantz et al., *Anal. Chem.* **1997**, *69*, 4210–4219).

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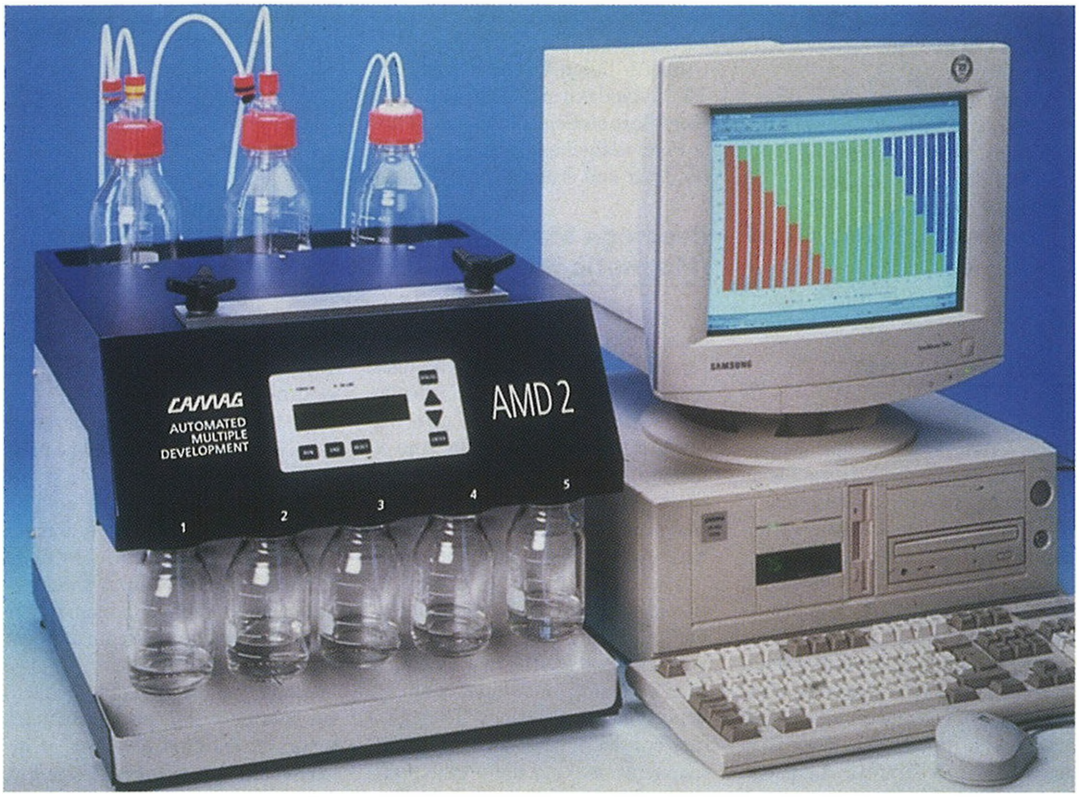
Leserdienst Nr. 26

AMD 2 – Computer-controlled multiple development of planar chromatograms



Automated multiple development (AMD), more particularly if performed as a gradient technique achieves the maximum resolution feasible within the limited separation distance available on a HPTLC plate. In terms of peak capacity it compares with HPLC while retaining the inherent benefits of planar chromatography:

- Many samples are chromatographed in parallel, e.g. unknowns and identification standards directly side by side.
- All fractions are stored on the plate, making them accessible both for selective evaluation using different parameters and for unproblematic post chromatographic derivatization.
- Nothing remains hidden on the planar layer. Substances which are strongly retarded and could occur in the next or an even later analysis run, stay in or close to the starting zone and are detectable.

The AMD method demonstrates its efficiency in, for example, the separation of complex natural substances containing heavy matrix.

Euroanalysis 10: Stand 131

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Leserdienst Nr. 27

Reagents for Bioanalytical Research

Fluka, as an integral part of the worldwide-operating Sigma-Aldrich-Group, is one of the leading producers of chemicals, biochemicals and molecular biology reagents.

Based on its focus on analytical techniques in chemical and biochemical research, Fluka offers a wide range of new product lines:

Fluorescent probes:

Luminescence techniques represent one of the fastest-growing and most widespread analytical tools in life sciences and analytical biochemistry.

They offer extraordinary sensitivity and selectivity and are thus suitable for direct analysis of analytes in complex biological matrices. Luminescence monitoring is usually rather staightforward and can be readily automated.

Fluka has now published a new brochure which lists more than two hundred new fluorescent probes, including a wide selection of fluorophores for carbohydrate analysis and a large number of enzymespecific substrates.

Electrophoresis:

Electrophoresis has become an indispensable tool for cell- and molecular-biologists and biochemists as it is simple, rapid and highly sensitive for both preparative and analytical separations. A wide range of techniques have been developed for the separation and analysis of nucleic acids and nucleic acid protein interactions.

Fluka offers a full range of specifically tested electrophoresis reagents (MicroSelect). The recently developed acrylamido buffer set (pI-Select) considerably extends the application potential of isoelectric focusing. Immobilized pH gradients can thus be produced for the first time in a broad pH range of 2.5–11. The Fluka electrophoresis program is comprehensive: reagents for gel preparation, standards, test reagents and buffers for all protein and nucleic acid electrophoresis techniques are offered. A series of ready-to use HPCE buffers for the most varied applications: protein separation, restriction fragment analysis, sequencing and the detection of inorganic anions and cations, is also available. The buffers are offered in a constantly high quality as sterile filtered solutions.

Standards for Food analysis:

Fluka has also introduced a variety of new standards for food analysis. This group contains certified reference material for the detection of genetically modified organisms Roundup-Ready®. Soya and Bt-176-(Maximizer)-Malze. The CRMs were produced by IRMM on behalf of Fluka in the frame of a project of the Environment Institute (EI) of the Joint Research Centre of the European Commission (Ispra Italy), aiming at the validation of the polymerase chain reaction (PCR) screening method for the detection of genetically modified food.

Fluka also stocks: standards for the detection of food irradiation, standards for the detection of phytoestrogens, standards for the detection of BADGE and similar compounds, as well as antibiotics and sulfonamide standard solutions.

Combinatorial Chemistry:
This technique is finding immense application, mainly in pharmaceutical reseach for drug discovery. Fluka has complied a new and comprehensive program for this technique, containing the following product groups: polymer supoports, polyethylene glycols, Tentagels® polymer-bound protected amino acids, linkers, functionalized reagents (dinucleophiles, dielectrophiles, electro-nucleophiles), and reagents for special reaction types (Suzuki, Ugi).

Euroanalysis 10: Stand 130

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  http://www.Sigma-Aldrich.com/fluka

Leserdienst Nr. 28

Cyclodextrine von Cyclolab Ltd. Budapest

Cyclolab steht für: sachkundige Experten über jegliche Art der Verwendung von Cyclodextrinen in Produkten und Technologien.

1973 gegründet und ab 1979 ausschliesslich auf Cyclodextrine spezialisiert (in der Folge als 'CD' erwähnt), ist Cyclolab seit 1991 durch Management buy-out sowie Beteiligung des Personals in Privat-Besitz. Die einzigartige Spezialisierung basiert auf mehr als 20-jähriger Forschungs- und Entwicklungsarbeit, sowie auf weltweiter, vertraglicher Zusammenarbeit mit einer Vielzahl von Firmen, deren Produkte CD enthalten.

Cyclolab besitzt eine Datenbank für CD, die ihresgleichen sucht, indem seit mehr als 20 Jahren alles und jedes über CD gesammelt, gesichtet, abstrahiert und klassifiziert wird. Daraus ist eine nützliche Dienstleistung geworden: wer etwas über CD wissen oder suchen möchte, ist bei Cyclolab an der richtigen Adresse. Mit Recht sagt die Firma, wenn es ums Suchen geht: 'wir finden für Sie auch die Stecknadel im Heuhaufen.'

Aus eigener Feder stammen einige Bücher und über 200 wissenschaftliche Papiere. Cyclolab besitzt mehr als 70 Patente und hat 14 Doktoranden-Themen aufgestellt. Cyclolab war Initiantin des 1. Internationalen Symposiums über CD, das 1981 in Budapest abgehalten wurde und mit über 200 Teilnehmern aus 18 Ländern ein grosser Erfolg wurde. Seit 1984 finden diese Symposien im Zweijahres-Zyklus statt. Nebst Europa wurden auch Übersee und der Ferne Osten für Tagungsorte mit einbezogen.

Cyclodextrin News ist das allmonatlich von Cyclolab herausgegebene Neuheiten-Zirkular, das jeden Monat mindestens 100 Sonderaufzeichnungen enthält über CD (Forschungs-Papiere, Patente, Präsentationen, neue CD enthaltende Produkte usw.). Diese wertvolle Informationsschrift kann abonniert werden (USD 275.– für 12 Ausgaben inkl. Postgebühren).

Das Dienstleistungsangebot von Cyclolab ist sehr umfangreich. Nebst Vermittlung von ausführlichen, weitreichenden Informationen über CD, Patente, Produkte usw. werden auch die Entwicklungs-Stufen verschiedenster Produkte beschrieben u.a. die Entwicklungs-Stufen eines Arznei/Cyclodextrin-Komplexes mit allen dazu gehörenden Abklärungen, auch hinsichtlich bestehender Techniken, Patente usw. und diesbezüglichen Empfehlungen.

Durch die vertraglich abgesicherte Zusammenarbeit mit allen einschlägigen Instituten der Universitäten Budapest hat Cyclolab sicheren Zugang zu allen dortigen Forschern, zu den modernsten Einrichtungen, zu Fachzeitungen usw. und diverse Versuchsanordnungs-Möglichkeiten.

Die Hauptgebiete der Aktivitäten von Cyclolab betreffen: Pharmazeutika; Nahrungsmittel; Kosmetische Produkte; Analytische Chemie/Diagnostika; Umweltschutz; Biotechnologie; Agrar-Chemikalien und -Produkte.

Hiefür liefert Cyclolab mehr als 70 Cyclodextrine, Derivate und Komplexe als Feinchemikalien. Diese sind weitgehend sofort ab Lager lieferbar und erreichen die Abnehmer per Kurierpost auf dem schnellsten Wege.

Euroanalysis 10: Stand 123

- Ammann-Technik AG
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  Telefax 062 723 51 58

Leserdienst Nr. 29

Promega MagneSil™ (Magnetic Silica Separation Technology)

Promega was among the first companies to introduce magnetic separation for molecular biologists with the PolyATract® mRNA Isolation Systems. To meet the growing needs of researchers for this kind of technology, Promega has developed proprietary magnetic silica MagneSil™ Particles that can be used in a wide range of applications.

These silica-coated paramagnetic particles are easily manipulated with a magnet in a single well, 96 well, or automated format. Promega offers a variety of compatible magnetic separation devices. The particles consist of 45% SiO2 and 55% magnetite making them extremely responsive in a magnetic field. The particles are also paramagnetic in nature. They will respond when placed in a magnetic field but have no 'magnetic memory' and will not remain magnetized when removed from the magnet. This characteristic prevents clumping, making them easier to handle. MagneSil™ particles have a median diameter of 5.0–8.5 µm and a pore size > 500 angstroms. This combination of particle size and macroporous structure results in enhanced surface area characteristics (27 m^2/gram material) and improved binding capacity over other materials of this type. A unique manufacturing process results in complete encapsulation of the magnetite, which eliminates the possibility of leaching and nonspecific binding to the iron. The particles are stable in a wide variety of organic solvents, detergents and chaotropic salts.

The composition of these particles makes them a suitable extraction media for purifying many biomolecules such as nucleic acids from bacteria, tissue lysates, blood, foodstuffs, water and soil.

Since the particles can be completely resuspended during the purification wash steps the risk of clogging associated with column extraction methods is substantially reduced. This also results in more efficient washing of adsorbed materials and eliminates contaminants that can affect downstream applications.

Binding of the target molecule to the mobile solid phase particles occurs in solution resulting in increased capture efficiencies at low concentrations and allows extractions to be scaled to suit individual needs. There are numerous applications for magnetic separation in the life science research, diagnostic and industrial laboratory.

Catalys AG was established as a Promega branch office in Switzerland in 1991. It is our pleasure to always supply you with highest quality products and up-to-date information.

Please contact Dr. Jürg Gysi or any member of our technical service group to discuss your specific requirements.

Euroanalysis 10: Stand 155

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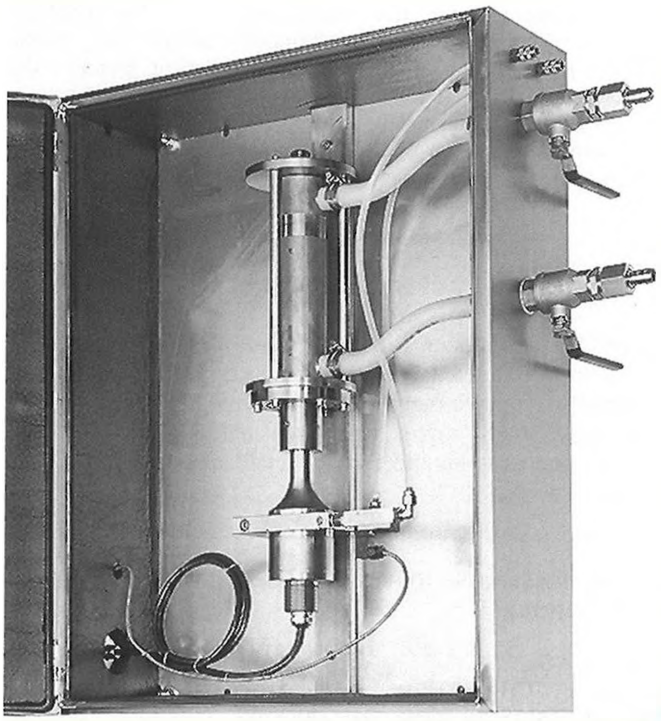
Leserdienst Nr. 30

Ultraschall Hochleistungs-Durchflussreaktor für sonochemische Anwendungen und Prozesse

Mit Ultraschall-Druchflussreaktoren lassen sich eine grosse Vielfalt chemisch/physikalischer Prozesse realisieren wie z.B. Desintegration von Mikroorganismen, Herstellung von Emulsionen und Dispersionen, Beschleunigung chemischer Reaktionen, Extraktion von Wirkstoffen, Homogenisieren, Entgasen von Flüssigkeiten und vieles mehr. TELSONIC Ultraschall-Durchflussreaktoren werden einerseits für Untersuchungs- und Forschungsarbeiten im gesamten Bereich der Sonochemie und andererOseits für sonochemische Produktionsprozesse auf kontinuierlicher Basis eingesetzt. Die Produktepalette umfasst Ultraschallgeräte für Laboranwendungen im niedrigen Leistungsbereich (30–100 W) bis hin zu kundenspezifischen, massgeschneiderten Spezialausführungen mit einer Leistung von mehreren Kilowatt.

Die zur Anwendung kommenden Resonatoren können die unterschiedlichsten Formen und Grössen aufweisen und werden applikationsspezifisch aufgrund der erforderlichen Leistungsdichte festgelegt. Im wesentlichen unterscheidet man zwischen Stabresonatoren mit radialer, einseitiger Abstrahlung nach aussen oder stirnseitiger Abstrahlung am Stabende, Rohrresonatoren mit radialer, doppelseitiger Abstrahlung nach innen und aussen. Schwingplatten mit horizontaler Abstrahlfläche oder Hochleistungs-Radialresonatoren mit Abstrahlung nach innen und zusätzlichem Fokussierungseffekt.

Der abgebildete Universal-Ultraschall-Durchflussreaktor beinhaltet eine rostfreie Durchflusskammer (Nettovolumen 2,5 l) mit Ein- und Auslaufanschlüssen, einen innenliegenden, stabförmigen Titanresonator für radiale Abstrahlung mit aufgeschrumpftem Nullpunkt-Lagerungsflansch sowie einen PZT-Ultraschallwandler in Ex-Schutz Ausführung für Dauerbetrieb. Der Ultraschallgenerator weist eine Arbeitsfrequenz von 20 kHz auf und erzeugt eine maximale Leistung von 1000 W. Da die Schwingungsamplitude und Frequenz charakteristische Prozessparameter darstellen ist es unerlässlich, diese Parameter entsprechend zu überwachen und prozessbezogen zu beinflussen. Aus diesem Grunde zeichnet sich der Generator einerseits durch eine Konstantregelung der vorgegebenen Amplitude (im gesamten Lastbereich von Leerlauf bis Nennlast und bei Netzspannungsschwankungen) und andererseits durch eine vollautomatische Frequenznachlaufregulierung aus. Ferner kann die Schwingungsamplitude mit einem externen Analogsignal prozessbezogen (z.B. in Funktion der Beschallungszeit, Durchflussmenge, Temperatur oder Viskosität) simultan in einem Bereich von 50–100% reguliert werden. Standardmässig stehen folgende Betriebsarten zur Verfügung: Normalbetrieb 'RUNSTOP', Timer-Betrieb 'TIMER' und Puls-Betrieb 'PULSE' bei Labordesintegratoren. Die in der Frontplatte integrierten Überwachungs- und Anzeigeelemente geben jederzeit Aufschluss über den momentanen Betriebszustand und die aktuellen Prozessparameter.



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Leserdienst Nr. 31

Latest Literature Report on Planar Chromatography

The CAMAG Bibliography Service No. 80 was issued on schedule in March 1998. It contains abstracts of 167 recent TLC publications, as usual arranged in 38 classification sections for easy reference.

The special features section is devoted to Planar Chromatography in Practice. All of the applications featured in CBS 80 were collected from outside. They are commercially used, partly by contract laboratories who earn their money with these, partly by the industry rationalizing their analytical procedures. The applications are:

- HPTLC analysis of dye intermediates
- Assay of celandine alkaloids by HPTLC, another example of the analysis of herbals, a rapidly growing domain for planar chromatography.
- The third application is a method used by a large chemical producer for process monitoring. Here quantitative results are required within 30 minutes after sampling, which is readily fulfilled with planar chromatography.

The 52-page brochure is available from CAMAG free of charge via Internet: http://www. camag.ch.

Euroanalysis 10: Stand 131

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Internet http://www.camag.com

Leserdienst Nr. 32

Company Profil NResearch

Foreword

Neptune Research & Development Incorporated, founded in March 1975, is a highly specialized precision fabricator and designer of solenoid-operated valves and associated accessories.

With the increased demand for computerization of laboratory, analytical and medical processes, we have developed our range of valves to satisfy the need greater miniaturization and lower power consumption.

We work with high-performance engineering plastics, for example, Teflon®, Kel-F®, whilst at the same time maximizing the use of Aluminum (low weight), Stainless Steel (corrosion-resistance), Steel (magnetic properties) and Delrin® (low cost).

Our in-house design and manufacturing expertise in these materials allows close-tolerance and precision machining, ensuring quality of components. Our strict control is also reflected in our assembly procedures resulting in an end-product which is tested 100 percent at least three times.

Design Engineering

The design process begins with the components designed and functionally tested using our Computer-Aided Design workstations (CAD).

Prototypes are subsequently built for evaluation. With this advanced development tool, we are able to offer custom designs with very short lead times.

Machining

Manufacturing of all critical and precision components is achieved with our own specially developed tooling and state-of-the-art machines, being either computer-controlled machining or milling centers.

All the diaphragms and bodies of our valves, (our own patented designs), are made using premium quality, highest-density Teflon® rods or Kel-F® rod stock. The manifolded valves are milled from Virgin-grade Teflon® sheets, as are piping, connecting manifolds and connectors.

All accessories fittings are machined, not moulded, to ensure consistent precision component accuracy.

During manufacture we apply many of our own proprietary techniques, and our vigorous inprocess quality inspection ensures that dimensions for each component is carefully monitored. Ninety percent of all components are made in-house. Bought-out components are subjected to prior vendor approval and the same stringent standards of quality control/assurance is also imposed.

The assembly process is initiated with a 100 percent inspection of dimensions, to quality control components. The components are then ultrasonically-cleaned. The solenoid bobbin is individually 'Hi-potted' at 1000 Volts AC, to check dielectric integrity.

Our inspection is extended to completed sub-assemblies and assemblies with a final check for electrical and mechanical characteristics as well as flow and leak-testing.

Euroanalysis 10, Stand 159

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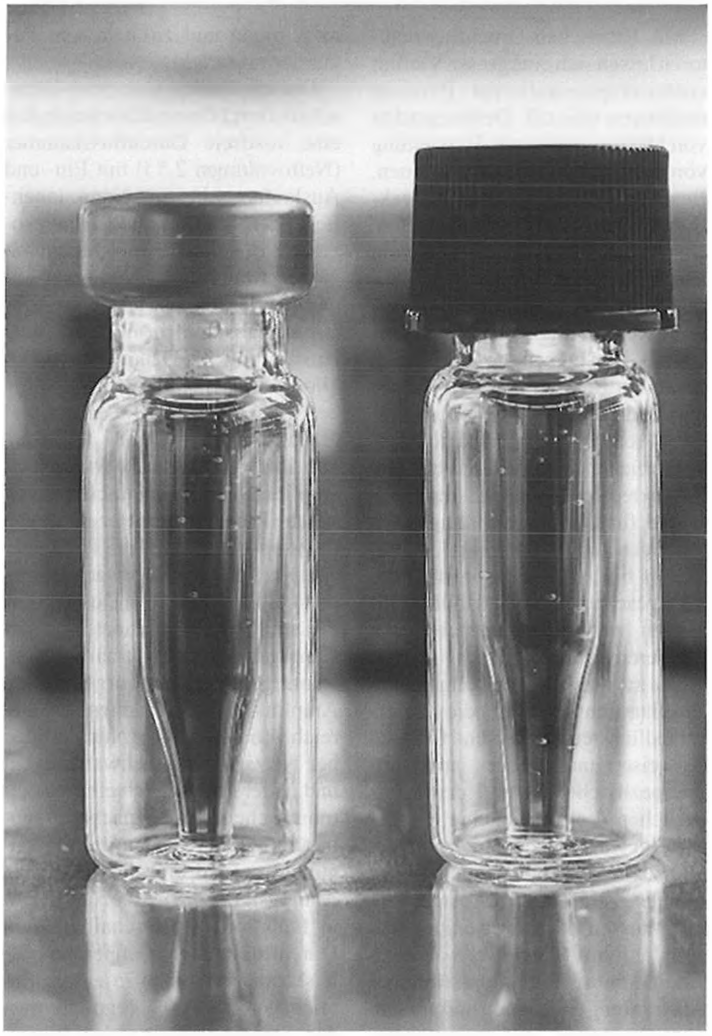
  E-Mail nreurope@nresearch.com
  Website nresearch.com

Leserdienst Nr. 33

µ-Vial



Infochroma AG bietet ein umfassendes Programm an Autosampler Vials, Sample Vials und HPLC-Spritzenfiltern an. Für kleine Probenmengen führen wir z.B. das µ-Vial, ein 12 × 32 mm Autosampler Vial mit integriertem 350 µl Insert. Zentrierprobleme gehören mit dem µ-Vial der Vergangenheit an. Das Zusammensetzen von Vial, Insert und gegebenenfalls Zentrierhilfen wie Plastikfüsse oder Federn entfällt. Das µ-Vial ist für alle Autosampler geeignet und wurde insbesondere auf den GC- und LC-Autosamplern von Hewlett-Packard zu voller Zufriedenheit erprobt. Das µ-Vial ist in klarem oder braunem Borosilikatglas mit Snap/Crimp, Crimp oder Wide-Mouth Schraubverschluss zu einem vorteilhaften Preis erhältlich.

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Seit 1. Juni können Sie das gesamte Zubehörprogramm von Hewlett-Packard bei uns beziehen. Gerne berät Sie Herr Floderer zu Fragen rund um GC und HPLC Säulen, sowie Verbrauchsmaterial für die Chro-matographie und für Hewlett-Packard Analysengeräte.

Besuchen Sie den Stand Nr. 106 an der Euroanalysis 10 oder fordern Sie telefonisch Muster an.

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  Sumpfstrasse 3, CH–6300 Zug
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Leserdienst Nr. 34

CHIMIA 52 (1998) Nr. 7/8 (Juli/August)

Varian Introduces World's Fastest Simultaneous ICP-AES

New Vista CCD Simultaneous ICP-AES Measures 73 Elements in Just 35 Seconds.

The world's fastest simultaneous inductively coupled plasma – atomic emission spectrometer (ICP-AES), based on the next generation of charge-coupled device (CCD) detector technology, is being introduced by Varian Associates, Inc. The new Vista CCD Simultaneous ICP-AES uses Varian's patented VistaChip detector technology to measure 73 elements in just 35 seconds, with a detector read-out speed up to 80 times faster than competing instruments.

'The VistaChip was custom designed to provide full wavelength coverage from continuous arrays of pixels (photosensitive detectors) rather than grouping pixels in segments to cover only selected wavelengths. This allows both trace and major concentrations to be measured simultaneously by using alternative wavelengths.

Fast, accurate results are produced from a single plasma configuration, without having to re-analyze samples as is necessary with alternative dual-viewing technology.'

I-MAP, Varian's image mapping technology is a key feature of the VistaChip CCD detector. With I-MAP, 70,000 pixels are arranged on the CCD in uninterrupted angled arrays to match exactly the two-dimensional image from the thermostatted echelle optical system. The VistaChip detector provides full wavelength coverage from 167-785 nm so that spectral interferences can be eliminated easily. The VistaChip also creates the high speed performance of the Vista. Read-out circuitry has been duplicated on each side of the detector and one million pixels can be processed each second.

Vista's software employs a unique 'worksheet' concept modeled on the analyst's workbook. The software features a range of tools making operation easy. These include AutoMax, a routine which automatically determines the optimum conditions for the analysis when the user presents a sample.

Vista's Adaptive Integration Technology (AIT) allows intense and trace signals to be measured simultaneously at the optimum signal-to-background ratio. AIT automatically allocates shorter integration times to more intense peaks and longer integration times to less intense peaks. Unlike conventional 'simultaneous' ICPs which sequence these steps, Vista can measure these readings simultaneously.

Vista also features smart data Quality Control Protocols with a programmable language so that customers can meet any regulatory requirements. The 32-bit, multitasking software operates under Windows 95/98 or Windows NT for simplified data transfer and industry standard networking and includes on-line video Help of routine maintenance and operational tips.

Applications for the Vista ICP-AES include the analysis of organic solvents in the chemical and petrochemical industries, pollutants and trace elements in waters, effluents, soils, and sludges for environmental laboratories, and the analysis of rocks and minerals for geochemical exploration.

For additional information or literature, contact:

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  CH–4002 Basel
  Telefon +41 61 295 80 00
  Telefax +41 61 295 80 80
  E-Mail
  varian.spectrom@ch.varian.com

Leserdienst Nr. 35

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CHIMIA-Leserdienst 7·8/98

Chimia-Report (Talon 3 Monate gültig)
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UNIVERSITE DE LAUSANNE

'Maître-Assistant' (Senior Demonstrator)

A position of 'Maître-Assistant' is becoming vacant on March 1999 at the Institute of Organic Chemistry, University of Lausanne. The appointment covers a period of 2 years and can be extended to a total of 6 years.

The person in charge of the position is responsible for a number of teaching and tutorial duties in practical organic chemistry. In addition, she/he is expected to develop an intense research activity partially in collaboration with research groups at the Institute in the field of bioorganic/peptide chemistry. In this sense, the position can offer an entry to an academic career.

Only candidates having a doctoral degree in chemistry of biochemistry and postdoctoral experience will be considered. Knowledge of French and English is desirable.

Applications and all pertinent documents (CV, diploma copies) should be sent before October 1st, 1998 to

Prof. Manfred Mutter
Institute of Organic Chemistry, BCH
CH–1015 Lausanne-Dorigny (Switzerland)
Voice: +41 21 692 39 50, Fax: +41 21 692 39 55
E-Mail: Corinne.Dentan@ico.unil.ch or Manfred.Mutter@ico.unil. ch

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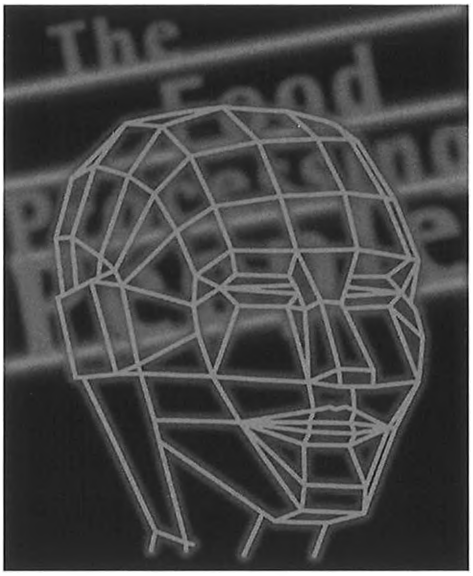

Industrielle Verfahren und Automation

Automation Mess-, Steuer- und Regelgeräte, Prozess-Visualisierungen sowie kundenspezifische MSR-Systeme für alle industriellen Prozesse sind der Schlüssel zur sicheren Qualität.

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Industrie-Planung Die Produktionsprozesse stehen bei unserer Planung im Mittelpunkt und setzen die Bedingungen für Bauten und dazugehörige Infrastruktur. Prozessorientierte Gesamtplanungen sind der Schlüssel zu Ihrem Erfolg.

Prozess- und Verpackungstechnik Apparate, Systeme und Anlagen für die Lebensmittel-, Chemie-, Pharma-Industrie von renommierten Herstellern. Der Schlüssel zu Ihrem Markt sind unsere bedürfnisgerechten Prozess- und Verpackungsanlagen.

Service Unsere gut ausgebildeten Servicetechniker sind der Schlüssel zur Erhaltung der Einsatz- und Leistungsfähigkeit der von uns gelieferten Teile und Maschinen.

Halle 224 · Stand M70
S.A.W. SWISS AUTOMATION WEEK
Basel, 1.– 4. Sept. 1998

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Halle 212/Stand L30 und Halle 205/Stand E20
S.A.W. SWISS AUTOMATION WEEK
Basel, 1.–4.9.1998

Mit dem MASSFLO® MASS 2100 DI 1,5 bietet Danfoss einen kompakten und robusten Masse-Durchfluss-messer zur Messung sehr geringer Mengen an.
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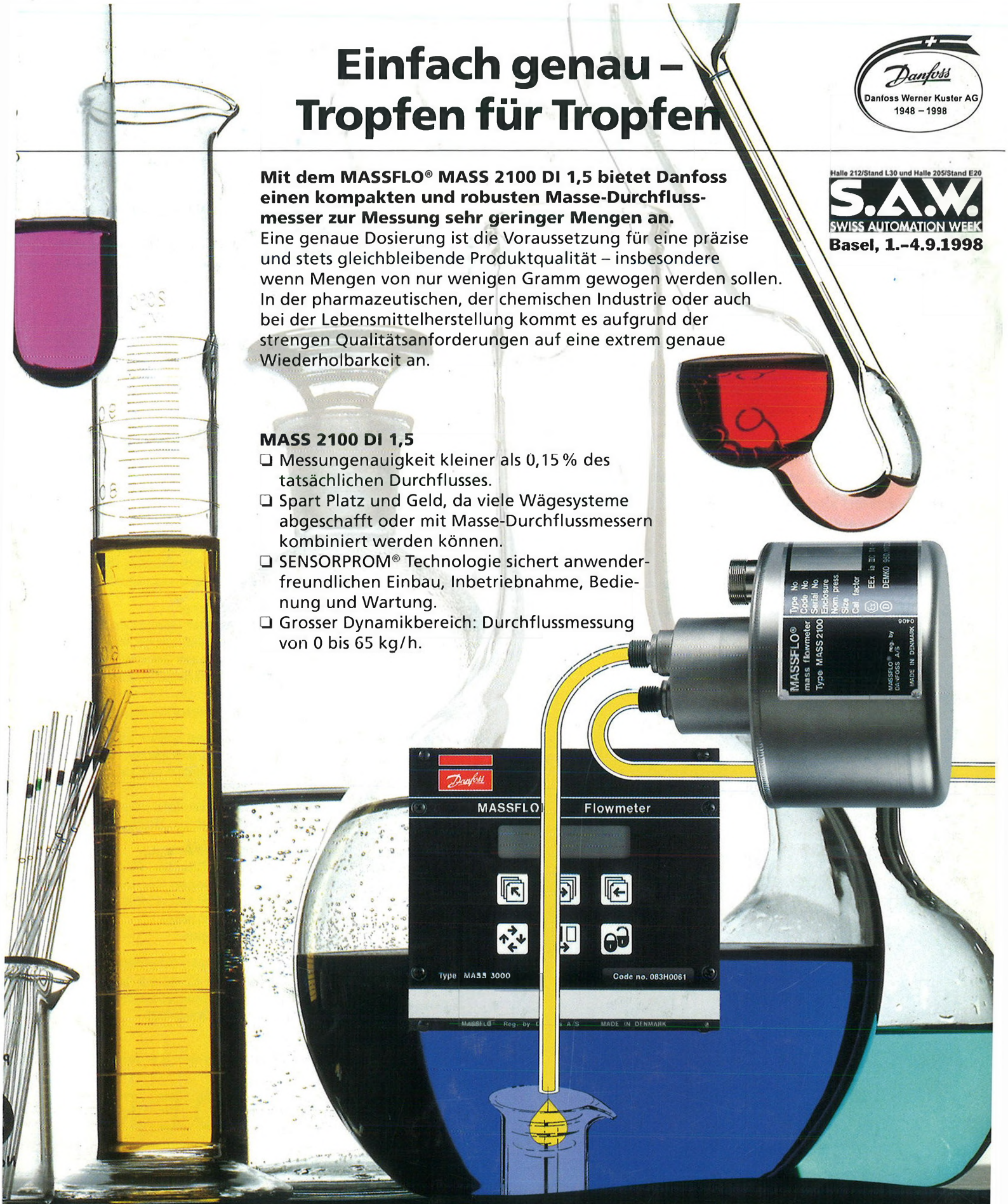
- ❑ Messungenauigkeit kleiner als 0,15 % des tatsächlichen Durchflusses.
- ❑ Spart Platz und Geld, da viele Wägesysteme abgeschafft oder mit Masse-Durchflussmessern kombiniert werden können.
- ❑ SENSORPROM® Technologie sichert anwender-freundlichen Einbau, Inbetriebnahme, Bedie-nung und Wartung.
- ❑ Grosser Dynamikbereich: Durchflussmessung von 0 bis 65 kg/h.



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