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Abstracts of the contributions **List of participants**

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Abstracts

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9.15-10.00 **Invited lecture**

Howell G.M. Edwards, Ian J. Scowen, University of Bradford (United Kingdom)

Raman spectroscopy of extremophiles from hot and cold deserts: an astrobiological journey from Mars oasis, Antarctica, to planet Mars

10.15-10.35 **Susan Richardson, J. Jackson Ellington, F. Gene Crumley, John J. Evans, Benjamin C. Blount, Lalith K. Silva, Frederick L. Cardinali, Michael J. Plewa, Elisabeth D. Wagner,** U.S. EPA, National Exposure Research Laboratory, Athens GA (USA)

Occurence of IODO-acid and IODO-THM disinfection by-products in drinking water

10.35-10.55 **Jin-Ming Lin, Yuki Hashi, Min Liu, Fengyun Pan, Guanqun Song, Jianguo Yao,** State Key Laboratory of Environmental Chemistry and Ecotoxicology, Chinese Academy of Sciences, Bejing (China)

Automated on-line liquid chromatography-photodiode array-mass spectrometry method with dilution line for the determination of bisphenol A and 4-octylphenol in serum

10.55-11.15 **José B. Quintana, Thorsten Reemtsma ,** Technische Universität Berlin, Berlin (Germany)

The use of ion-pair liquid chromatography for analyzing strongly acidic environmental trace pollutants by electrospray mass spectrometry

11.15-11.35 **Heqing Shen, Niels E. Skakkebaek, Jorma Toppari, Karl-Werner Schramm,** GSF – National Research Center for Environment and Health, Neuherberg (Germany)

Chiral industrial pollutants in human samples

11.35-11.55 **Laure Malleret, Céline Gueydon, Gilbert Mille, Pierre Doumenq,** UMR 6171 – Equipe de Chimie Analytique de l'Environnement, Université Paul Cézanne, Aix en Provence (France)

Recent developments for the reliable quantification of total polychlorinated n-alkanes by using GC/EI-MS and GC/EI-MS/MS

11.55-12.15 **Alexandra Hütteroth, Martin Jekel, Anke Putschew,** Technical University Berlin, Berlin (Germany)

Selective detection of unknown organic bromine compounds by negative-ion electrospray ionization mass spectrometry with induces in-source fragmentation

14.00-14.45 **Invited lecture**

Helmut Becker-Ross, Stefan V. Florek, Uwe M. Heitmann, Mao D. Huang, Michael Okruss, ISAS – Institute for Analytical Sciences, Berlin (Germany)

Spectrographs with electronically photoplates – new possibilities for analytical and remote spectrometry

15.15-15.35 **Bohumil Dočekal, Hana Dočekalová, Veronika Řezáčová-Smetková**, Institute of Analytical Chemistry, Czech Academy of Sciences, Brno (Czech Republic)

Soil characterization by diffusive gradients in thin film (DGT) technique

15.35-15.55 **Werner Brack, Georg Streck,** UFZ–Center for Enrivonmental Research, Leipzig (Germany)

The rapid dialysis procedure: A novel clean-up method for complex environmental samples

15.55-16.15 **Isabella Bisutti, Ines Hilke, Jens Schumacher, Michael Raessler**, Max-Planck-Institute for Biogeochemistry, Jena (Germany)

Simulatenous determination of organic and inorganic carbon by a new dual temperature combustion (DTC) method

16.15-16.35 **Markus Lenz, Chris Roubos, Piet N.L. Lens**, Wageningen University, Wageningen (The Netherlands)

Role of sulphate reducing bacteria in the biological treatment of selenium containing wastestreams

16.35-16.55 **Torsten Spitzer,** Environmental, Industrial and Food Analysis, Helmstedt (Germany)

Natural occurrence of perylene in the environment

16.55-17.15 **Licia Guzzella, Claudio Roscioli, Andrea Binelli,** IRSA-CNR, Brugherio (Milan) (Italy)

PBDE analysis of sediments and Zebra mussel (*Dreissena polymorpha*) in the Lake Maggiore bisin (Italy) by GC-MS/MS and GC-ECD

RAMAN SPECTROSCOPY OF EXTREMOPHILES FROM HOT AND COLD DESERTS : AN ASTROBIOLOGICAL JOURNEY FROM MARS OASIS, ANTARCTICA, TO PLANET MARS.

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The survival strategies of extremophilic organisms in terrestrially stressed locations and habitats are critically dependent upon the production of protective chemicals in response to desiccation, low wavelength radiation insolation, temperature and the presence of toxins[1]. The adaptation of life to the prevailing conditions involves the control of the substratal geology ; the interaction between the rock and the organisms is critical and the biological modification of the geological matrix plays a significant role in the overall survival strategy[2,3,4] . The identification of the these biological and biogeological chemical molecular signatures in the geological record is, therefore, a crucial stage in the recognition of the presence of extinct or extant life in terrestrial and extraterrestrial scenarios.

Raman spectroscopic techniques have been identified as valuable instrumentation for the detection of life extraterrestrially because of the use of non-invasive laser-based excitation of organic and inorganic molecules and molecular ions with high discrimination characteristics ; the interactions effected between biological organisms and their environments are detectable through the molecular entities produced at interfaces, for which the vibrational spectroscopic band signatures are unique. Combination of spectroscopic and microscopic data acquisition from Raman microscopes gives an additional information category which is essential for the desription of heterogeneous specimens ; for geological specimens of significant transparency, the use of confocal microscopy for the spectroscopic analysis of subsurface inclusions in crystals is a significant development for the analytical detection of halotrophs[5] . A very important attribute of Raman spectroscopy is the acquisition of experimental data using remote optical flexible probes without the need for chemical or mechanical pre-treatment of the specimen ; this has been a major factor in the proposal for the adoption of Raman instrumentation on robotic landers and rovers – and this is now being advocated for the ExoMars programme [6].

In this paper, the merits of using Raman spectroscopy for the recognition of key molecular biosignatures from several terrestrial extremophile specimens will be illustrated and some recommendations made for the technical requirements of a miniaturised system and its evaluation for Martian exploration . The data and specimens used in this presentation have been acquired from Arctic and Antarctic cold deserts, a meteorite crater, and from a hot desert saltpan evaporite locations from which it will be possible to assess the advantages and current limitations of Raman spectroscopic techniques for the detection of extraterrestrial extremophilic life signatures.

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OCCURRENCE OF IODO-ACID AND IODO-THM DISINFECTION BY-PRODUCTS IN DRINKING WATER

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As part of a recent Nationwide Disinfection By-Product (DBP) Occurrence Study, iodo-acids were identified for the first time as DBPs in drinking water disinfected with chloramines. The iodo-acids identified included iodoacetic acid, bromoiodoacetic acid, (*E*)-3-bromo-3-iodo-propenoic acid, (*Z*)-3-bromo-3-iodo-propenoic acid, and (*E*)-2-iodo-3-methylbutenedioic acid. There is concern about these new iodo-acid DBPs because mammalian cell cytotoxicity and genotoxicity studies have revealed that iodoacetic acid is highly cytotoxic and genotoxic, with a genotoxicity potency 2X higher than bromoacetic acid, the most genotoxic of the regulated haloacetic acids. Also, many drinking water treatment plants in the United States have switched from chlorine to chloramines for treatment. New evidence indicates that the formation of iodinated DBPs will be higher in chloraminated drinking water than in chlorinated drinking water. The goal of this work was to develop an analytical method to quantify these five iodo-acids in drinking water and measure their occurrence in drinking waters treated with chloramination. Two iodinated trihalomethanes (iodo-THMs), dichloroiodomethane and bromochloroiodomethane, were also measured in these waters. These iodo-THMs were the most commonly found iodo-THMs in the previous Nationwide DBP Occurrence Study.

An analytical method similar to EPA Method 552.3 (developed for chlorinated and brominated acetic acids) was developed to extract and quantify iodo-acid concentrations in drinking water samples. Gas chromatography/mass spectrometry (GC/MS) with negative chemical ionization (NCI)-MS offered low detection limits (low and sub-ng/L). Iodo-THMs were extracted using solid phase microextraction (SPME) and were analyzed using GC with high resolution electron ionization (EI)-MS and stable isotope dilution (deuterated standards of each analyte).

Two samplings have been conducted to-date on drinking water plants using chloramination for disinfection. The first sampling took place in May 2005 (of five plants), and the second sampling took place in the fall of 2005 (21 plants). Iodoacetic acid and bromoiodoacetic acid were found in most of the plants sampled, at sub-ppb to low-ppb levels. (*E*)-2-iodo-3-methylbutenedioic acid was also found in many of the plants, and (*E*)-3-bromo-3-iodo-propenoic acid and (*Z*)-3-bromo-3-iodo-propenoic acid were found in a few of the plants sampled at sub-ppb levels. The two iodo-THMs sampled, dichloroiodomethane and bromochloroiodomethane, were found at all plants sampled, at low ppb or sub-ppb levels (with a high of 10.2 ppb for bromochloroiodomethane). Although this work was reviewed by EPA and approved for publication, it may not necessarily reflect official Agency policy.

AUTOMATED ON-LINE LIQUID CHROMATOGRAPHY–PHOTODIODE ARRAY-MASS SPECTROMETRY METHOD WITH DILUTION LINE FOR THE DETERMINATION OF BISPHENOL A AND 4-OCTYLPHENOL IN SERUM

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A novel on-line liquid chromatography-photodiode array-mass spectrometry (LC-PDA-MS) system was established by restricted-access media (RAM) precolumn and dilution line combined with a column-switching valve. The serum samples were directly injected onto precolumn under diluted condition by dilution line. After elution of proteins in the serum, the analytes were backflushed onto an ODS analytical column using a 6-port column-switching device. The influence of the composition of the mobile phase, for instance, organic modifer, ion strength, pH, dilution times, and the rotation time of switching valve have been investigated using bisphenol A (BPA) and 4-octyphenol (4-OP) as analytes. The evaluations for peak responses and sensitivity were conducted by MS, and proteins were removed by RAM-column with PDA monitoring at 280nm. By adding of dilution line, the shape of peak got improved especially in case of large volume injection (LIV), which resulted in high sensitive anaysis. The selective and sensitive quantification of bisphenol A and 4-OP in serum sample could be finished within 25 min. The method had linearity in the range 0.1–500 ng/mL with a limit of quantification for BPA and 4-OP of 0.1 and 0.5 ng/mL respectively. The recoveries were in the range of 80–101% with less than 9.0% RSDs. This on-line LC-MS method demonstrates potential application for evaluating the exposure and risk of BPA and 4-OP in human.

THE USE OF ION-PAIR LIQUID CHROMATOGRAPHY FOR ANALYZING STRONGLY ACIDIC ENVIRONMENTAL TRACE POLLUTANTS BY ELECTROSPRAY MASS SPECTROMETRY

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While electrospray ionization-mass spectrometry can detect highly polar and ionic environmental contaminants with high sensitivity and selectivity, it is often difficult to obtain adequate chromatographic retention in RPLC. This retention problem often hampers the development of LC-MS procedure for the quantitation of strongly acidic and highly polar environmental pollutants. The same is true for the enrichment of strongly acidic analytes from aqueous samples.

Ion chromatography may be applicalbe to retain and separate strongly acidic organic analyes, but the coupling of IC to ESI-MS requires the introduction of a suppressor system between the analytical column and the ESI-interface. These systems are often not very robust. Even though ion chromatography may be applicable the problem of analyte enrichment would remain unsolved.

Some years ago we have proposed to use volatile trialkyl amines as ion pairing agents to enhance the retention of strongly acidic aromatic sulfonates in RPLC [1]. These amines are sufficiently volatile to allow coupling in LC-MS procedures and they may significantly reduce the extent of multiple charging and adduct formation, which was otherwise often encountered in ESI-MS analysis of polysulfonates. Meanwhile we have successfully extended the IPLC-MS approach to many other classes of acidic environmental contaminants such acidic pharmaceuticals [2], phosphoric acid diesters used as plasticizers [3], as well as for some complexing agents. The IPLC-ESI-MS approach provides good sensitivity and often allows for the direct injection of many kinds of aqueous samples, without any preceeding enrichment steps [2, 3]. If higher sensitivity is required, ion-pairing is equally useful for the SPE enrichment of highly polar acidic analytes.

Besides that IPLC-MS is well suited for the determination of microbial and chemical metabolites, which tend to be even more polar then their parent compounds. This has been shown for dyestuff [4] and for bacterial metabolites of acidic pharmaceuticals [5] encountered in municipal wastewater. In this way the IPLC-MS approach contributes to our understanding of biodegradation pathways of many polar contaminants in the environment.

We conclude that IPLC with volatile amines is a substantial improvement for the qualitative and quantitative analysis of strongly acidic environmental pollutants by ESI-MS. It may well be applicable to several other classes of highly polar contaminants in water for which adequate LC-MS procedures are not elaborated, yet.

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CHIRAL INDUSTRIAL POLLUTANTS IN HUMAN SAMPLES

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Many industrial pollutants were mixtures when released into the environment. Most of these mixtures contained some chiral forms. For example, some endocrine disruptors like technical DDT, technical chlordane, toxaphene, PCBs, HCHs, nonylphenol and phthalates. Because the physical processes (leaching, volatilization, and atmospheric deposition) and abiotic reactions (hydrolysis and photolysis) for chiral compounds are believed to be unaffected (Bidleman et al., 1999), enantiomeric ratios (ERs) show only the information of biotransformation or biodegradation of these chiral pollutants. Therefore, chiral pollutants, for example, α-HCH, have been used as a versatile tool for process studies (Hühnerfuss, 2000). Therefore, we measured ERs of some chiral pollutants in human tissues to understand their possible fate of human exposure.
The study was approved by the local ethics committee and conducted according to the Helsinki II declaration. The sample collection, preparation, cleanup procedures and HRGC-HRMS analyses for organochlorine pesticide and chiral compounds have been described elsewhere (Shen et al., 2006). Some chiral compounds in 65 milk samples and 112 placenta samples from Turku, Finland, and 65 milk and 168 placenta samples from Copenhagen, Denmark, were analyzed. Similar to our recent report in placenta (Shen et al. 2006), the ER *vs.* (+)- or (-)-enantiomer concentration profiles of α-HCH, *c*-HE also showed the structural characteristics in milk samples, where the isomer concentrations generally changed depending on ERs. Contrary to *c*-HE, no structural characters of ER-concentration plots were found for chiral OXC. Only one Finnish milk sample had a detectable level of heptachlor, which showed an enantioselective residue for (+)-isomer. Due to the enantiomeric selective biodegradation of the chiral pollutants in fatty depot and the low level of recent uptake from environment, we propose the following equation to interpret structural characteristics of the ER-isomer concentration plots. Here C_{uptake} and C_s represent the recent uptake and the fatty tissue depot of the chiral pollutants, respectively.

$$ER = C_+ / C_- = (C_{uptake_+} + C_{s+}) / (C_{uptake_-} + C_{s-})$$

Although not all the differences reached the statistical significance, the results in most cases showed the ER deviated from the racemic ratio (ER = 1) more in the placenta than in milk for α-HCH and c-HE in Danish samples. The ER of OXC in placenta and milk were nearly the same. ER differences between paired placenta-milk samples suggested tissue specific pollutant biotransformation.

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RELIABLE QUANTIFICATION OF TOTAL POLYCHLORINATED N-ALKANES BY USING GC/EI-MS AND GC/EI-MS/MS.

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Short-chain polychlorinated n-alkanes (PCA) are industrial formulations commercialized as complex technical mixtures with a chlorination degree between 30 and 70% and a linear alkane RECENT DEVELOPMENTS FOR the chain with length of C_{10}-C_{13}. As a consequence of their numerous industrial applications, PCA were widespread dispersed in the environment, although their toxicological properties and their capacity to bioaccumulate are now well-established. Accordingly, PCA are included in the list of priority hazardous substances of the European Water Framework Directive. Hence, reliable routine analytical methods will be needed in the near future, as the Directive implies more intensive monitoring of the total PCA concentration in the aquatic environment since 2006. Nevertheless, due to the complexity of the technical mixtures (about 7000 congeners and homologues) and the lake of quantification standards, analysis of PCA is far from being well established [1]. To date, method developments were mainly based on the use of high resolution gas chromatography (HRGC) coupled to electron capture detector (ECD) or to mass spectrometry with electron capture negative ionization (ECNI/MS) [2]. Compared to HRGC/ECD, HRGC/ECNI-MS offers similar sensitivity together with better selectivity, justifying that today this latter technique is the most applied one. But the major drawback of ECNI/MS is the strong dependence of the response factors of congeners of on their degree of chlorination, resulting in the quantification of only congeners with 5 to 10 chlorine atoms. Additionally analyses performed by using technical standards of different chlorination degrees can lead to errors on the concentration of 65 to 940%. Compared to ECNI-MS, MS with electronic impact ionization (EI) was hardly ever investigated for the analysis of PCA.

The aim of this work was to evaluate the applicability of HRGC coupled to EI/MS in selected ion monitoring mode (SIM) and to EI/MS/MS for the reliable quantification of the sum of PCA in environmental samples. Special attention was drawn to develop method suitable for routine monitoring and also to obtain a quantification method independent from the quantification standard used. An original methodology was developed for the selection of the most judicious ions, which were used for the acquisition in SIM mode or for the MS/MS detection operated in the multiple reaction monitoring mode. For both developed methods, limits of detection were about tens pg/µL for pure compounds, 0.2 ng/µL for congeners mixtures and 1 ng/µL for C_{10}-C_{13} technical mixtures. Relative standard deviations ranged from 8 to 12%. The specificity of the developed methods was estimated on the one hand by calculating the relative error generated by the presence of interfering halogenated compounds (in the sample. On the other hand, the specificity was examined by analyzing sediment and biota extracts, fortified with a known amount of PCA. The accuracy of the methods for total PCA determination was tested by analyzing commercial formulations differing by their chlorination degree. Finally the capability of the developed method, compared to other techniques, to provide worldwide comparative data was demonstrated by quantifying the same samples with the use of three different technical standards. With the developed method, relative errors as low as 2 to 8% where obtained, whereas relative errors ranged from 22 to 144% and from 30 to 180% when applying HRGC/ECD and HRGC/ECNI-MS, respectively.

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SELECTIVE DETECTION OF UNKNOWN ORGANIC BROMINE COMPOUNDS BY NEGATIVE-ION ELECTROSPRAY IONIZATION MASS SPECTROMETRY WITH INDUCED IN-SOURCE FRAGMENTATION

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The detection of unknown organic compounds can be simplified if a characterization of the compound of interest by a functional group or a heteroatom is feasible. For organic halogen compounds the halogen atoms are adequate for their characterization. It could be shown that iodinated organic compounds can be traced via iodide by mass spectrometry after liquid-chromatography negative-ion electrospray ionization (LC-NI-ESI) if an induced in-source fragmentation (IISF) is used. Here the iodinated organic compounds are destroyed already in the source of the MS and m/z 127 is detected [1].

It was tested if that method is also suitable for tracing unknown brominated organic compounds. Infusion experiments performed with brominated organic compounds showed that bromide is a fragmentation product of the induced in-source fragmentation, which is induced by applying a high cone voltage. In contrast to iodide with an m/z of 127 the detection of bromide with m/z 80 is not possible because at that low mass many ions are detectable. For that reason the two natural occurring isotopes of bromine (^{79}Br : ^{81}Br, 1:1) have to be detected. Organic bromine compounds are definitely detected if the signal of m/z 79 and 81 has the same intensity and additionally if LC is applied the same retention time. The analysis of brominated organic compounds showed that even quantification is possible. Furthermore the LC-NI-ESI-IISF-MS analysis is more sensitive than the common used LC-ESI-MS/MS analysis. Thus LC-NI-ESI-IISF-MS is not only a method for tracing unknown brominated organic compounds it is also suitable to quantify the bromine content of known compounds.

The method was used to trace unknown brominated organic compounds, which were detected in a surface water in Berlin. Over several years seasonal (Sept- Oct) high concentrations of organic bromine compounds were detected by differentiation of the group parameter AOX into AOBr and AOI [2]. It could be shown that the bromine compounds are autochthonous produced by algae. After sample clean up brominated compounds were selective detected in lake water samples as well as in algae cultures. The retention times of unknown brominated organic compounds were determined by LC-NI-ESI-IISF-MS analysis. The same samples were analyzed by the non-sensitive classical LC-ESI-MS analysis in the scan mode. Due to the known retention times of the brominated compounds it was possible to determine the molecular weight, and based on the isotopic pattern the number of bromine atoms bound to the unknown compounds.

The novel application of in-source fragmentation MS is a tool for those who do not possess the facilities to perform ICP-MS.

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SPECTROGRAPHS WITH ELECTRONICALLY PHOTOPLATES – NEW POSSIBILITIES FOR ANALYTICAL AND REMOTE SPECTROMETRY

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Spectrometers based on linear solid-state detector arrays have been widely accepted for a lot of spectroscopic tasks during the last decade. As an example, one can use a multitude of combinations of optics and detectors, offered by the company Ocean Optics, for several applications. This company is nowadays the synonym for miniaturized spectrometer production.

The outstanding feature, common for all array spectrometers, is their capability for simultaneous recording of a certain spectral interval. The size of the interval and/or the achievable spectral resolution is determined by the total number of pixels used for a specific array. For spectrometric applications, linear CCD arrays with up to 3648 pixels (TCD1304AP, Toshiba, Japan) are applied, resulting in a resolution from 0.75 nm (for a 200-1100 nm interval) down to 0.03 nm (for a 56 nm interval). Nevertheless, the recording of a broad interval with high spectral resolution, which is desirable for analytical atomic and molecular spectrometry, surpasses the capability of a linear CCD array. Therefore, combinations of several array spectrometers or arrangements of multiple arrays in one spectrometer are used. In the majority of situations the better choice is the utilization of image detectors for the recording of two dimensional echelle spectra. The giant number of up to 85 million pixels (CCD 595, Fairchild, USA) enables the coverage of some hundred echelle orders arranged in more or less parallel rows by means of a cross-dispersing unit. Overall spectrum lengths of several meters are achievable.

At ISAS/Department Berlin echelle spectrographs were developed and applied for analytical spectrometry [1]. For example, spectrographs have been designed for High-Resolution Continuum Source AAS (HR-CS AAS) as well as for Laser-Induced Breakdown Spectroscopy (LIBS). The HR-CS AAS spectra of complex samples show, in addition to the expected atomic lines, a multitude of molecular lines. This way, very useful information concerning the sample matrix as well as some non-metals(S, P, Cl, F), which are normally not detectable by conventional AAS, can be obtained and the possibility for their quantitative determination is opened [2].

For the detection of extremely line rich LIBS spectra, an optical design was developed. Here, a high-speed chopper wheel is used to gate-out the initial continuum of the plasma with accuracy better than 1 μs. Moreover, telescope optics for laser focusing as well as for spectrometer illumination offers remote LIBS measurements over distances of several meters without a substantial loss in sensitivity.

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SOIL CHARACTERIZATION BY DIFFUSIVE GRADIENTS IN THIN FILM (DGT) TECHNIQUE

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The content of heavy metals in agricultural soils is gradually increasing from various processes such as utilization of sewage sludge, fertilizers, creation of landfills, atmospheric fall-out etc. These metals may transfer from contaminated soils into growing plants and may retard the growth of plants and soil microorganisms. Therefore, it is essential to assess and predict the biological relevance of heavy metals in soils. For this purpose, various leaching, basically operationally and functionally defined procedures are applied or proposed for estimation the relevance [1-3]. In fact, total mineral analysis cannot provide any information about the biochemical activity of heavy metals. Sequential extraction procedures are adopted for determination of distribution of heavy metals in different forms and phases, i.e. exchangeable cations, oxidizable phases, acid-soluble phases and reducible phases. No standardized chemical or biological methods are available to assess the mobilizable part of the metal in the solid phase.
The technique of *Diffusive Gradients in Thin films* (DGT) [4] was employed for characterization of sewage sludge amended soils in the Czech Republic, for assessment of mobile forms of heavy metals. GF AAS was used for determination of labile forms of heavy metals. The influence of the soil moisture content, the deployment time and the DGT-sink demand on *in situ* response of the soils were investigated. The maximum heavy metal re-supply fluxes were estimated. The yields of extraction of cadmium, chromium, copper, nickel and lead were also investigated by using *aqua regia*, ethylenediaminetetraacetic acid, iminodiacetic acid, acetic acid, sodium nitrate and water leaching agents and compared with those of DGT-experiments. Biological relevance, phytoavailability, and leachability of heavy metals are discussed.

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THE RAPID DIALYSIS PROCEDURE: A NOVEL CLEAN-UP METHOD FOR COMPLEX ENVIRONMENTAL SAMPLES

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The analysis of organic toxicants in complex environmental samples like sediments or tissues of organisms requires one or more clean-up procedures after the extraction. Target-oriented analyses allow for specific methods to remove matrix compounds. However, if an environmental study is effect-orientated and aims at a comprehensive detection of toxicants the clean-up methods must not only achieve the necessary separation of matrix compounds and analytes, but, regarding the toxicants, it should be non-specific at the same time. A non-preselecting clean-up procedure is demanded. Effect-directed analysis (EDA) is a powerful approach to determine which compounds may cause toxic effects in the environment [1]. It combines chemical analysis, fractionation and biotesting. Bioassays need large amounts of samples to be extracted. This results in large amounts of matrix components after extraction and stresses the necessity of a high-capacity clean-up procedure.

Methods based on size exclusion like gelpermeation-chromatography (GPC) fulfil these requirements. Another technique based mainly on size exclusion is dialysis using semipermeable membranes, e. g. made of low density polyethylene (LD-PE). Conventional dialysis methods have been successfully used for the clean-up of lipid rich samples [2, 3]. The Rapid Dialysis Procedure (RDP) is a new and innovative technique, which combines a dialysis procedure and a pressurised liquid extraction with an ASE 200. This results in a faster dialysis, a reduction in solvent consumption and in an automated procedure [4].

The efficacy of the RDP was assessed by dialysing sediment and fish tissue extracts which were spiked with compounds of different classes and physicochemical properties (pesticides, PCB, PAH, dioxins). The influence of various parameters on the recovery was investigated. While higher temperatures allowed speeding up the RDP, finally a temperature of 40 °C was chosen to minimize matrix permeation through the membrane. An inverse relationship was observed for recovery and pressure. A pressure of 3.45 MPa, membranes made of LD-PE with a thickness of 80 µm and 16 dialysis cycles with a duration of 10 minutes each proved to be best regarding high recoveries of analytes and low carry-over of matrix-components. The ability of the RDP to remove lipids from fish tissue extracts was high (lipid reduction > 97 %), while the recoveries were comparable to conventional clean-up methods.

Finally, this contribution presents examples for the application of the newly developed method. Sediments from the river Elbe, muscle tissues and hepatopancreas from chub (*Leuciscus cephalus*) were extracted and further treated by RDP. The results suggest that RDP may be a useful clean-up technique suitable for a broad range of organic toxicants having a high-capacity for matrix removal.

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SIMULTANEOUS DETERMINATION OF ORGANIC AND INORGANIC CARBON BY A NEW DUAL TEMPERATURE COMBUSTION (DTC) METHOD

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The quantification of organic (OC) and inorganic carbon (IC) in soils provides an essential tool for understanding biogeochemical processes. Examples of its application are the assessment of the humification degree of soil organic matter, the calculation of carbon fluxes and budgets in terrestrial systems on a regional and global scale and the investigation of the carbon storage potential of soils. The verification of changes in carbon stocks requires an extensive number of samples as well as precise and reliable analyses.

Due to the wide variation in the concentrations of the two forms of carbon in solid samples, the exact separation is very difficult. We investigated the method of dry combustion of the two carbon species at two different temperatures: 515 °C (for OC) and 925 °C (for IC). This method, which we called Dual Temperature Combustion (DTC), allows the simultaneous determination of OC, IC, and total carbon (TC) within one single analytical run. It is characterized by a significantly reduced variability and low operator bias as there is no need of chemical sample pre-treatment. The method is applicable for various OC and IC contents. Furthermore, with DTC, it is possible to recognize the presence of thermally instable carbonates, like magnesite. In this case, with the use of silver boats as a catalytic agent, it is possible to obtain an improved separation of OC from IC. Numerous synthetic soil mixtures with different OC and IC concentrations were prepared and analyzed by the method presented here. To examine the accuracy and reliability of the DTC method, it was compared to other techniques frequently used for carbon determination in soil samples: total combustion by elemental analysis to determine TC and acidification of the sample prior to combustion to determine OC. We could show that DTC is a promising alternative for reliable OC and IC determination in soil samples.

Role of sulphate reducing bacteria in the biological treatment of selenium containing wastestreams

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The importance of selenium in environmental research is related to the fact that it shows only a marginal line between the nutritious optimum (as an essential element) and toxic effects upon exposure. Selenium occurs in different oxidation states in organic and inorganic forms. The toxicity of selenium compounds varies greatly in dependence of its speciation. For instance, Lethal Doses 50 (LD_{50}) for oral administration in rats are reported to be much lower for selenite (4.8-7.0 mg / kg body weight) than for elemental selenium (6700 mg / kg body weight) according to U.S. Department of Health and Human Services [1]. A huge variety of both anthropogenic and geogenic aqueous waste streams call for an efficient low-tech cleanup solution.

Compared to adsorptive or precipitative techniques, the bioreduction of selenate is very promising. Therefore two Upstream Anaerobic Sludge Blanket Reactor (UASB) systems were tested towards their removal capacity for selenate. Due to chemical similarities and consequent utilization of the same metabolic pathways, enhanced selenate conversion might be possible by systematic stimulation of sulphate reducing bacteria (SRB). On the other hand selenate is described to be a specific inhibitor for SRBs. Consequently, an intensive investigation of the influence of sulphate on selenium conversions was conducted.

Anaerobic granular sludge was used to inoculate two continuous bioreactors with a working volume of 0.46 L, operated at a superficial upflow velocity of 1 m h^{-1} and a hydraulic retention time of 6 h. Lactate was used as carbon source at an organic loading rate of 5 g COD L-1 d-1. In order to enrich sulphate-reducing consortia, one rector received sulphate at diffrent COD/Sulphate ratios, while the second reactor received only lactate but no sulphate as a control. It was shown, that selenate removal is strongly dependent on sulphate load. In the sulphate free reactor, specific selenate reducing bacteria developed, which reduce selenate independent of sulphate present. The adaptation of both reactor consortia towards selenate was determined in batch inhibition experiments.

As the process considers not only total selenium removal but also the prevention of toxic metabolite formation, selenate, selenite dimethylselenide and dimenthyldiselenide were determined species specifically. The formation of elemental selenium was investigated by XRD.

It appeared that less total selenium was removed from liquid phase compared with selenate removed. As neither selenite nor dimethylselenide or dimethyldiselenide were detected, an unknown selenium species was indicated to be present. This clearly underlines the importance of species-specific selenium analysis.

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NATURAL OCCURENCE OF PERYLENE IN THE ENVIRONMENT

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Perylene is a minor component among polycyclic aromatic compounds released from combustion sources into the environment. It is therefore found in airparticulate matter and surface soil [1,2]. The concentration of perylene is less than 20% of benzo(e)pyrene in emission sources [3], and an even lower ratio is found in immission sources like airparticulate matter or surface soil, since perylene undergoes a more rapid degradation than benzo(e)pyrene in the environment.

Polycyclic Aromatic Compounds (PACs) are isolated from samples of soil and particulate matter. Isolation is done by an affinity based procedure being highly selective for this compound class. Hydrocarbons, ketones and nitroarenes display distribution patterns with quantitative ratios of compounds similar to those found in particulate emissions of fossil fuel combustion. Concentrations of PACs were in the range of 10-500 ppb. Details of the analytical procedure are being discussed and compared with the isotope dilution technique [5].

Several samples of deeper soil layers rich in organic matter display perylene contents of 1-10 ppm (Figure 1). Concentrations of all other PACs in these samples were below 10 ppb. 4,9-dihydroxyperylene-3,10-quinone is a degradation product of humic substances in soil [4]. It is concluded that high perylene contents were generated by reductive degradation of this precursor.

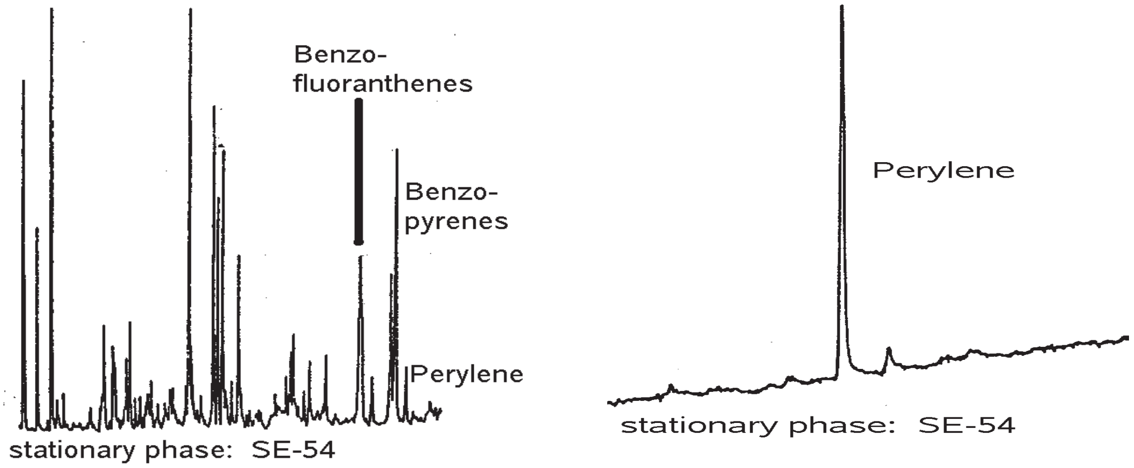

Figure 1. FID traces of PAC profiles by glass capillary gas chromatography ,
samples: PAC eluates after compound class selective clean-up
Left pattern: PACs from combustion sources Right pattern: PACs from certain soils

Thus, these high perylene concentrations are of natural origin.

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PBDE ANALYSIS OF SEDIMENTS AND ZEBRA MUSSEL (*Dreissena polymorpha*) IN THE LAKE MAGGIORE BASIN (ITALY) BY GC-MS/MS AND GC-ECD

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Polybrominated diphenyl ethers (PBDEs), characterized by chemical properties and toxicological profiles similar to other persistent synthetic organic compounds, are included in the E.U. Priority Pollutant List (2455/01/CE). They are considered to be environmentally persistent and their high lipophilicity indicates a strong bioaccumulation potential. Evidence of their toxic, carcinogenic and endocrine-disrupting effects was also suspected. PBDEs have been extensively used in European countries and U.S.A. over the past two decades as flame retardants in polymer additives for a variety of plastics (EPS, ABS, HIPS), furniture, building and textile materials, paints, electronics.

Lake Maggiore basin, a heavily industrialised and densely populated sub-alpine area, was selected for studying for the first time the PBDE contamination in the Italian aquatic ecosystems. The lake receives the inputs from seven main tributaries (Maggia, Verzasca, Ticino, Tresa, Margorabbia, Badello, Boesio and Toce) and has the main outlet in the Ticino effluent.

The PBDE contamination in the lake Maggiore basin was studied by analysing six sediment cores collected in September 2005 in the lake and grab samples collected from April 2005 to January 2006 every three months at the mouth of the main tributaries and in the emissary. We also collected several hundreds of Zebra mussel (*Dreissena polymorpha*) specimens from 14 sampling sites at the end of April 2005 to evaluate the PBDE levels bioavailable for the accumulation through the lacustrine food web.

PBDE analysis of sediment and biota samples was undertaken in GC-MS/MS for the quantification from tri-BDE to hepta-BDE congeners; a further step of MS/MS (MS/MS/MS) acquisition mode was employed to improve their peak identification. Specific chemical-physical characteristics of BDE-209 and consequently its chromatographic behaviour led to develop a specific analytical method by on-column injection and GC-ECD detection. Best chromatographic performance of BDE-209 analysis were obtained with a direct injection in a non polar-phase coated megabore retention gap coupled with a short narrow bore column. The influence of this retention gap on the BDE-209 peak shape have also been discussed. The analytical methods were validated through reference material analysis: CRM river sediment and fish tissue (flounder).

Results of sediment samples showed a prevalent presence of BDE-209 (> 95% of total-BDE) and a limited amount of BDE-47, BDE-99, BDE-100 BDE-153 and BDE-154. The lake core sediment profiles highlight a recent contamination of Lake Maggiore by these chemicals and an increasing trend of the BDE-209 since 1990. Between tributaries, Bardello and Boesio were the most contaminated rivers with concentration level up to 300 ng/g d.w.

Notwithstanding PBDE and PCB levels in lake sediments can be considered similar in the last fifteen years, we noticed an increasing and decreasing temporal trend, respectively.

Biomonitoring results carried out by Zebra mussel seem to confirm this pattern of contamination and the pollution condition of the lake because several point-sources were identified, mostly in the Southern area of the basin.

Oral contributions Tuesday June 6 2006

9.00-9.45 **Invited lecture**

Reinhard Nießner, Technische Universität München, München (Germany)

Immunochemical techniques for monitoring of contaminant traces

10.15-10.35 **Gesine Witt, Philipp Mayer, Gladys A. Liehr, Dörthe Borck,** Baltic Sea Research Institute, Rostock-Warnemünde (Germany)

Using solid phase microextraction to evaluate the bioavailability of sediment bound PAHs

10.35-10.55 **Agnieszka Kuczyńska, Jacek Namieśnik, Agnieszka Sagajdakow, Lidia Wolska,** Dept. of Analytical Chemistry, Gdańsk University of Technology, Gdańsk (Poland)

Simultaneous application of chemical analytics and bioassays in environmental studies

10.55-11.15 **Dolores Perez-Bendito, Soledad Rubio,** Dept. of Analytical Chemistry, University of Córdoba, Córdoba (Spain)

Coacervation of supramolecular assemblies for the extraction of organic pollutants

11.15-11.35 **Valerii D. Tonkopii,** Institute of Limnology, Russian Academy of Sciences, St. Petersburg (Russia)

A new purified cholinesterase for separate detection of organophosphates and carbamates

11.35-11.55 **Shuddhodan P. Mishra, Shailesh K. Prasad, Ram S. Dubey, Manisha Mishra, Diwakar Tiwari, Seung-Mok Lee,** Kwandong University, Kangwondo 215-802 (Republic of Korea)

Biosorptive behaviour of rice hulls for Cs-134 from aqueous solutions: A radiotracer study

11.55-12.15 **Hildegard Hoefler, Mihály Óvári, Christina Streli, Szilvia Szikora, Peter Wobrauschek, Gyula Záray ,** L. Eötvös University, Budapest (Hungary)

Development of TXRF method for determination of low Z elements in biofilms

14.00-14.45 **Invited lecture**

Koen Janssens, Bart Vekemans, Wout de Nolf, Roberto Terzano, Pacifico, Ruggiero, Ole-Christian Lind, Brit Salbu, Gerald Falkenberg, Centre for Micro- and Trace Analysis, University of Antwerp, Antwerp (Belgium)

Speciation of heavy metals by combined micro-XRF, micro-XANES and micro-XRD in polluted soil samples from the industrial site of Val Basento, Basilicata, IT and in U/Pu particles from Semipalatinsk, Kazakhstan

IMMUNOCHEMICAL TECHNIQUES FOR MONITORING OF CONTAMINANT TRACES

Reinhard NIESSNER

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The lecture likes to cover the status achieved by using antibodies (Abs) and light for qualitative and quantitative trace analysis.

Abs are proteins with strong binding properties directed to antigens, which are used to raise these Abs. For analytical purposes only those are of value possessing high affinity constants and of unlimited access. Beside polyclonal Abs, mainly monoclonal Abs are in use. Recombinant Abs are not used in analytical applications, yet. Nowadays Abs are available with broad selectivity (directed towards a common structural part of a target molecule) or a target analyte as whole.
Typically, interaction of Abs and analyte is achieved within seconds. A major restriction is the need for an aqueous surrounding.

Photons are needed to elucidate a quantitative measure of the interaction. Two main formats are known: homogeneous and heterogeneous immunoassays. Homogeneous means a mixture of Abs and analyte (antigen) molecule within a liquid, where a heterogeneous format is based on adsorbed Abs or analyte molecules. Depending on the size of the analyte molecule the direct observation of an immunocomplex formed is possible, e.g. by light scattering detection of the "colloid" suspension. In other cases, the surface coverage of limited bound Abs by excess tagged analyte or untagged analyte has to measured. From such a competition, the surface coverage directly reflects the concentration of analytes present.

Up to now more or less all possibilities of modern spectroscopy have been applied: absorption and emission techniques are in use.

Most promising are techniques in combination with array read-out capabilities, as used in chip technologies: fluorescence, chemiluminescence and surface plasmon resonance.

A series of typical examples will be discussed.

USING SOLID PHASE MICROEXTRACTION TO EVALUATE THE BIOAVAILABILITY OF SEDIMENT BOUND PAHS

Gesine WITT[1], Philipp MAYER[2], GladysA.LIEHR[1], Dörthe BORCK[1]

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Sediment-porewater partitioning of polycyclic aromatic hydrocarbons (PAHs) were measured in surface sediments and sediment cores of a dumping area in the western Baltic Sea compared to a reference site. The freely dissolved PAH porewater concentration was measured using solid phase microextraction (SPME). It was shown that matrix SPME is a very powerful method for the determination of freely dissolved PAHs. It was shown that the sampling technique is very sensitive because it can detect freely dissolved pore water concentration in the lower ng/L range for the PAHs in field sediments.

Elevated freely dissolved porewater concentrations were found in the core of the dumping site. The concentration peaks in the core correlate with the presence of the dumped material which was of conspicuous in colour and consistency. With the results it was possible to measure site and depth specific PAH distribution coefficients. The results show that the well established partitioning models from literature would underestimate the partitioning coefficient between solid phase and pore water. The elevated partitioning coefficients of the sediment-pore water systems could be explained through the distribution model which includes the soot-partitioning besides the organic carbon partitioning.

Furthermore chemical activity was calculated to predict the baseline toxic potential of the contaminant mixture [1]. The freely dissolved pore water concentration and chemical activity are important parameters for the prediction of the exposure of sediment dwelling organisms.

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SIMULTANEOUS APPLICATION OF CHEMICAL ANALYTICS AND BIOASSAYS IN ENVIRONMENTAL STUDIES

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Until recently, evaluation of the state of the environment was based solely on determining its level in water, sediment, the soil or biota samples, using “classical” methods of chemical analysis. Chemical analysis enables the detection, quantitation and identification of organic and inorganic pollutants, but does not provide information about the potential negative impact of environmental compounds on particular components of ecosystems. This is because chemical analysis does not consider:

- all the compounds present in the environment,
- the bioavailability of their different forms,
- and their different biological activities.

A complementary approach, taking into account the above-mentioned facts, can include the application of biotests. Moreover, usage of biotests enables the detection of toxic effects of the combination of many different pollutants in a sample. Synergistic as well as antagonistic effects can be observed.

Bioassays provide data about the effect, without pinpointing the substances and the potential source. Therefore, a tool is necessary for providing toxicity data as well as an identification of the compounds causing the effects. An integrated approach based on parallel application of bioassays and chemical analysis is the most powerful tool for the assessment of environmental pollution.

The combination of biotesting and chemical analysis was a valuable tool, successfully used in several research projects realized in the Department of Analytical Chemistry of the Chemical Faculty at the Gdansk University of Technology. Both the assessment of the effect of selected municipal waste dumps on the ecotoxicity of underground waters and the evaluation of the ecological state of Lake Turawskie (an artificial reservoir on the Mala Panew River) were performed using simultaneous application of chemical analytics and toxicity assays. As a result, it can be concluded that the application of the biotest approach provides valuable information that cannot be deduced from chemical analyses alone. However, the identity of potential problematic chemicals cannot be revealed by biotests and therefore chemical analyses and biotests should be used in combination in future monitoring programs.

COACERVATION OF SUPRAMOLECULAR ASSEMBLIES FOR THE EXTRACTION OF ORGANIC POLLUTANTS

Dolores PEREZ-BENDITO and Soledad RUBIO
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The development of solvent-less extraction techniques constitutes one important issue in chemical analysis. Coacervation, a phenomenon described by the Dutch chemists Bungenberg de Jong and Kruyt [1] and defined by IUPAC as the separation of colloidal systems into two liquid phases [2] (one rich in colloid, i.e. the coacervate, and the other containing little colloid) constitutes an excellent way for obtaining solvent-free extractions. A number of macromolecules including proteins, polysaccharides, synthetic polymers, drugs and supramolecular assemblies have been known to undergo liquid-liquid phase separation [3].

Application of the coacervation phenomenon to analytical extraction processes has invariably involved the use of dehydrating agent induced-coacervates made up of supramolecular assemblies [4]. The dehydrating agent is generally a salt, a non-solvent, the pH or the temperature. Coacervates made of reverse and aqueous micelles and vesicles have been recently used for the extraction/concentration of a variety of pollutants from surface water, wastewater, sludge, soil and sediment.

This presentation will discuss the state of the art of the use of coacervates for the extraction of organic pollutants from environmental matrices. Their ability to establish different types of interactions with analytes, the preconcetration factors that can be achieved and the practical aspects that should be considered in the implementation of this approach will be outlined. Their capacity to extract pollutants in a wide range of charge/polarity will be illustrated with some of the applications developed. The advantages/limitations associated to the use of coacervative extraction in environmental matrices and the problems that researchers need to overcome to make this approach extensively used in environmental analysis will be discussed.

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A NEW PURIFIED CHOLINESTERASE FOR SEPARATE DETECTION OF ORGANOPHOSPHATES AND CARBAMATES

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Among many xenobiotics entering aqueous media different anticholinesterase (antiChE) compounds (organophosphates and carbamates) notable for their high toxicity and selectivity are of particular hazard. At present, various types of purified commercial cholinesterases (ChE) are widely used to detect antiChE compounds. The detection is based on the property of xenobiotics to lower the activity of enzymes. However, this method is not universal because with using of ChE separate detection of organophosphorus CW, pesticides and carbamates is impossible. Carbamates belong to a group of compounds having a broad spectrum of toxicity – from relatively nontoxic to highly toxic compounds comparable with nerve agents. Potential threat of military and terrorism usage of carbamates connected with the high toxicity of compounds and difficulties of therapy of poisoning by carbamates. There is a real possibility that even more powerful CW that the nerve gases remain be discovered from the class of carbamates. It is well known that the cholinesterase of fish's brain is the typical acetylcholinesterase (AChE) with the same substrate specificity. On the other hand, the ChE of some fish's blood plasma has its own specificity. Some years ago for the first time we discovered that only the blood serum of freshwater fish from family of *Cyprinidae* (blue bream - *Abramis ballerus*, roach - *Rutilus rutilus)* contains nonordinary ChE with unusually high sensitivity to organophosphates - dipterex and DDVP and low sensitivity to carbamate neostigmine. This observation is of scientific and practical interest and so the fish’s blood plasma ChE of these species was purified for study of kinetic behaviour and sensitivity to antiChE compounds. After isolation and purification a stabilized lyophilized powder with activity of 5-10 units per mg of protein was obtained. The kinetics of choline and thiocholine ethers hydrolysis has been studied at the presence of new enzyme. The sensitivity of enzyme to 45 organophosphates (including sarin, soman and Vx) and carbamates has been determined. The Russian commercial purified lyophilized cholinesterases have been used for comparison: AChE from the erythrocytes of human, butyrylcholinesterase (BuChE) from the horse blood serum and propionylcholinesterases (PrChE) from the hen blood serum and from squid optic ganglion. We investigated the activity of new fish’s purified enzyme relatively to a choline and thiocholine esters hydrolysis as a function of substrate concentration. The results of this and the following experiments indicate that the new ChE from the blue bream and roach blood serum can be classified as BuChE, so the velocity of butyrylcholine and butyrylthiocholine hydrolysis is more than other substrates. At the same time, this type of new enzyme differs from other typical BuChE, so the hydrolysis rate of butyrylcholine by fish’s ChE is in 10 - 13 times more rapid as compared to hydrolysis of acetylcholine. The sensitivity of fish’s ChE to organophosphates is in 100-2000 times higher than the sensitivity of all types of commercial ChE. On the other hand a new enzyme has an extremely low sensitivity to carbamates. It is very important that with the help of a new purified fish’s ChE the separate identification of organophosphorus CW, pesticides and carbamates may be carried out. The extremely low sensitivity of new enzymes to carbamates and very high sensitivity to organophosphates is particularly valuable for these purposes.

BIOSORPTIVE BEHAVIOR OF RICE HULLS FOR Cs-134 FROM AQUEOUS SOLUTIONS : A RADIOTRACER STUDY

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Radiotracer techniques received an increased attention during last couple of decades in diverse areas of research as due to their higher sensitivity, absolute distinguish ability, sharp locality and also it provides the accurate trace level detection. Moreover, the environmental concerns related to water scarcity and degradation are growing problems for countries around the world, and global demand for fresh water is doubling every 21 years according to the FAO. The presence of radio cesium, particularly the ^{137}Cs (one of the major constituent of fission products [1]), in aquatic environment poses a serious threat as due to its high radiotoxicity value. Hence, in view of the important environmental implications and possible use of low cost dead biomasses in environmental remediation an attempt has been made to assess the removal behavior of rice hulls for Cs-134 at low levels from aqueous solutions by employing the 'radiotracer technique'.

The rice hulls were taken out mechanically from the seeds of *cv* Jaya in the laboratory in a usual way, crushed and washed repeatedly by double distilled water, dried at room temperature and then employed as an adsorbent. The sorption of Cs(I) on this rice hulls samples were carried out as a function of sorptive concentration (1.0×10^{-2} to 1.0×10^{-8} mol dm^{-3}) at constant temperature 298K and pH~6.40 and quantitatively, it was observed that the amount of Cs(I) adsorbed on this solid increased from 0.177×10^{-9} to 0.0852×10^{-3} mol g^{-1} with the increase in sorptive concentration from 1.0×10^{-8} to 1.0×10^{-2} mol dm^{-3}. Further, the concentration dependence data were utilized for analyzing the adsorption isotherm and it was found that these are fitted well for Freundlich adsorption isotherm. The Freundlich constants i.e., K and 1/n were found to be respectively $7.87 \pm 0.03 \times 10^{-3}$ mol g^{-1} and 0.949±0.004.

Temperature dependence study were carried out by increasing the bulk temperature from 298K to 328K, at constant sorptive concentration (1.0×10^{-5} mol dm^{-3}) and pH (~6.40), indicates that an increase in temperature apparently favored the uptake of Cs(I) on this biosorbent. It was also noted that the uptake of Cs(I) on this solid followed first order rate kinetics at different studied temperatures. Moreover, the thermodynamic parameters *viz*., the change in standard enthalpy (ΔH^0) and the activation energy (E_a) were optimized and were found to be 13.05±0.12 kJ mol^{-1} and 14.45±0.09 kJ mol^{-1} respectively. It was also observed that the uptake of Cs(I) greatly influenced with solution pH.

The radiation stability of rice hulls sample was also assessed by prior irradiation of this solid upto *ca* 72 hrs using a 11.1 GBq neutron source (Ra-Be) having an integral neutron flux of *ca* 3.2×10^6 n/cm^2/sec and associated with a nominal γ-dose of *ca* 1.72 Gy/h and the results showed that no significant change in sorption of Cs(I) took place on the surface of rice hulls, hence the solid was found to be radiation stable, at least, for the removal of Cs(I).

[1] Mishra, S. P., Tiwari, D., Prasad, S. K., Dubey, R. S., and Mishra, M., J. Radioanal. Nucl. Chem. 268: 191-199 (2006).

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DEVELOPMENT OF TXRF METHOD FOR DETERMINATION OF LOW Z ELEMENTS IN BIOFILMS

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Biofilms (periphyton communities) are complex associations consisting bacteria, algae, fungi and their secretions, building up a mucous cover on all immersed surfaces in the aquatic environment. Since the biofilms are important nutritive sources for many organisms in the aquatic ecosystem, the trace elements bound by them can be directly introduced into the food chain. For the complex understanding of the biofilm formation and to judge better the effects of pollution on biofilms, it is necessary to determine not only the polluting trace elements, but also the major biogenic elements (C, N, P, S) in biofilms. The objective of the research was the development and use of a low energy TXRF method for determination of low Z elements (from carbon to calcium, Z=6 to 20). For this, a TXRF spectrometer with Cr anode, multilayer monochromator (excitation Cr-Kα, 5.4 keV), vacuum chamber and ultrathin window detector was used. As the determination of low Z elements requires that the sample spot thickness is definitively less than a few µm, the reference material NIST1643c (Trace elements in water) was used to check the linearity between analyte amount and analytical signal intensity. It has been established, that this linearity can be guaranteed for the elements C to F (Z=6 to 9) up to an absolute amount of 600 ng, above Na ($Z \geq 11$) this limit was at around 1000 ng. In this step, the obligate internal standard element was Ti. Biofilms were grown directly on the quartz carrier plates of the spectrometer. In the framework of this, the plates were taken out of the water (Velence Lake) after 3, 6, 7 and 11 days. There was a direct relationship between the absolute amount of C and growth time, however, the biofilm thickness became too thick after 6 days, so the signal intensity did not increase considerably beyond this limit, and the inhomogeneity of the biofilm on the carrier became too strong (as was visibly). On the other hand, the shorter growth time is more useful for bio-monitoring, since short-term pollution plumes can be better detected. The colonization process of biofilms has been also investigated, however, the signal intensities of C were too low in the first two days of the biofilm growth. For bio-monitoring, about 6 days growth time is recommended. As biofilms contain a considerable but variable amount of Ti, a two-stage internal standardization was used. Ag-L_α was the primary internal standard having a 2.9 keV line, where Ar-K_α line should be under atmospheric conditions, but this latter is not present in vacuum. This was applied for Ti determination, which was subsequently used for determination of the low Z elements.

SPECIATION OF HEAVY METALS BY COMBINED MICRO-XRF, MICRO-XANES AND MICRO-XRD IN POLLUTED SOIL SAMPLES FROM THE INDUSTRIAL SITE OF VAL BASENTO, BASILICATA, IT AND IN U/PU PARTICLES FROM SEMIPALATINSK, KAZAKHSTAN

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The bioavailability and toxicity of heavy metals in soil are strongly connected to their solubility and therefore to their geochemical forms. The correct identification of the physico-chemical forms in which heavy metals are present in soil is of extreme relevance for a proper risk assessment and to formulate effective remediation strategies. In the first part of this paper, results from soil samples from the industrial site of "Val Basento" (Basilicata, Italy), studied by means of a combination of synchrotron X-ray microanalytical techniques will be reported. This polluted site showed concentrations of toxic elements such as Hg, Pb, Cr, Zn, Cu, and V strongly exceeding the Italian legislation limits. The same sample areas of thin soil sections (20-60 micrometer thick) have been characterized by EPXMA (Electron Probe X-ray Microanalysis), and a combination of micro-XRF (micro X-ray Fluorescence), micro-XRD (micro X-ray diffraction) and micro-XANES (micro X-ray Absorption Near Edge Spectroscopy). The latter methods employ a focussed beam of synchrotron radiation (SR) X-rays with a diameter of typically 15-20 micrometer, available at Beamline L of HASYLAB, Hamburg.

The results obtained up to now show that, despite a very high heavy metal total concentration in the investigated soils, these heavy metals appear to be present as scarcely mobilisable geochemical forms, indicating that the environmental risk connected to their presence in these soils is much lower than expected.

The second topic covered in the paper will deal with three-dimensional analysis of U- and Pu-rich particles. Radioactive particles containing refractory radionuclides such as uranium and plutonium have been more frequently released to the environment during severe nuclear events than previously anticipated. Particle characteristics such as the activity concentrations and activity or isotopic ratios are source dependent (depending on fuel burn-up), while properties such as size distribution, shape, crystalline structures and oxidation states of matrix elements also depend on specific release conditions. Information on particle characteristics influencing weathering rates is essential to estimate the ecosystem transfer for particle associated radionuclides.. Particles in samples collected from the Semipalatinsk nuclear test site, Kazakhstan, were characterized by conventional and micro-X-ray fluorescence analysis (XRF) at HASYLAB BL-L. Since this investigation revealed the particles to be strongly heterogeneous with respect to their overall major-element composition, while simultaneously a very high correlation between the U and Pu abundance was observed, additional investigations by means of absorption X-ray microtomography, confocal micro-XRF and scanning micro X-ray diffraction at HASYLAB BL L were performed.

These techniques proved very valuable for characterizing internal structures and elemental distributions in micrometer-sized particles, of relevance for environmental impact assessments.

Oral contributions Wednesday June 7 2006

9.00-9.45 **Invited lecture**

Gary M. Hieftje, Francisco J. Andrade, Gerardo Gamez, Steven J. Ray, Gregory D. Schilling, Michael R. Webb, William C. Wetzel, James H. Barnes IV, M. Bonner Denton, Roger P. Sperline, David W. Koppenaal, Charles J. Barinaga, Dept. of Chemistry, Indiana University, Bloomington, IN (USA)

Progress in atomic spectrometry methodology for measurements in the environment

10.15-10.35 **Alexey Kamyshny, Irina Ekeltchik, Tamara Voitsekovski, Jenny Gun, Ovadia Lev**, Max-Planck-Institute for Marine Microbiology, Bremen (Germany)

Speciation of inorganic polysulfide in environmental aquatic samples

10.35-10.55 **Daniel Kremer, Michael Kersten, Institute for Geosciences**, Johannes-Gutenberg-University Mainz, Mainz (Germany)

Determination of organometal(loid) compounds in landfill gas and landfill leachate by GC-ICP-MS

10.55-11.15 **Nalini Parthasarathy, Michael Pelletier, Heliana Kola, Jacques Buffle**, Dept. of Analytical Chemistry, University of Geneva, Geneva (Switzerland)

Supported liquid membrane preconcentration device for multielement speciation studies in natural waters: Assessment of Cd(II) speciation in comparison with Cu(II)

11.15-11.35 **Danuta Barałkiewicz, Dept. of Trace Elements Analysis**, Adam Mickiewicz University, Poznań (Poland)

Simultaneous determination of Zn, Pb, Cd, Cu, Ni and Cr in seawage sludge by slurry sampling

11.35-11.55 **Xiao-quan Shan, Shuzheng Zhang, Bei Wen**, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Bejing (China)

Speciation of metals and metalloids in soils and plant using X-ray absorption spectroscopy

11.55-12.15 **Victor G. Mihucz, Enikö Tatár, István Virág, Chen Zhang, Jao Jun, Gyula Záray**, Hungarian Academy of Sciences, Environmental Chemistry Research Group, Budapest (Hungary)

Leaching of arsenic before consumption in Chinese rice

14.00-14.45 **Invited lecture**

James W. Readman, Plymouth Marine Laboratory, Plymouth (United Kingdom)

Biogeochemistry of the marine environment: Examples of recent trends in environmental analytical chemistry

PROGRESS IN ATOMIC SPECTROMETRY METHODOLOGY FOR MEASUREMENTS IN THE ENVIRONMENT

Gary M. HIEFTJE[1], Francisco J. ANDRADE[1], Gerardo GAMEZ[1], Steven J. RAY[1], Gregory D. SCHILLING[1], Michael R. WEBB[1], William C. WETZEL[1], James H. BARNES, IV[4], M. Bonner DENTON[2], Roger P. SPERLINE[2], David W. KOPPENAAL[3], Charles J. BARINAGA[3]

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In this presentation, the focus will be on new instrumentation for optical and mass spectrometric measurements in the environment, especially novel sources and spectrometer systems. The sources will largely be based on glow-discharge approaches, with some at reduced (conventional) pressure and others at atmospheric pressure. They offer new possibilities not only for sample fragmentation, atomization, excitation and ionization, but also for sampling. The spectrometers to be described are predominantly based on mass detection, but a method for imaging-based atomic-emission detection will also be described.

One new source, based on a glow discharge, samples metallic species directly from solution, and at atmospheric pressure. Similar to the "ELCAD" device described by others, this source offers a simplified design and outstanding detection limits. Unlike most other plasmas employed for atomic spectrometry, it requires no gas flow and is therefore particularly attractive for field measurements. Fundamental characteristics of the discharge will also be outlined.

Another glow discharge, also operated at atmospheric pressure, is intended for ionizing species directly from solid or gaseous samples for mass-spectrometric detection. This discharge employs a flowing afterglow, to enable samples to be desorbed and ionized, after which they are extracted into the sampling cone of a time-of-flight mass spectrometer. This source is unusually stable, and can generate spectra that range in degree of fragmentation, from free atomic ions to clusters, to molecular fragments, to the molecular ion, depending on the chosen operating conditions.

The first sort of mass spectrometer is based on time-of-flight technology. Because of its speed, it can be coupled with switched or modulated ion sources, which can generate atomic, molecular, and fragmentation mass spectra on a time scale compatible with even the fastest chromatographic schemes. Further, when appropriately modified, it can be coupled to two or more ion sources at a time, to yield even more information about complex samples. The data to be presented here are from the dual-source TOFMS coupled simultaneously to an ICP and to an ESI source, the first to produce elemental mass spectra and the second to be used for speciation information.

The second form of mass spectrometer is based on a sector-field arrangement. However, it is fitted with a simultaneous-recording 128-channel detector array, so a broad range of molecular fragments, elements and isotopes can be measured at once, and continuously. Its sensitivity exceeds that of quadrupole mass filters, and its isotope-ratio performance rivals that of thermal-ionization mass spectrometry. To illustrate the ability of the new instrument to measure mass spectra simultaneously and rapidly, it has been coupled to transient atomization sources, including laser ablation and electrothermal vaporization.

SPECIATION OF INORGANIC POLYSULFIDE IN ENVIRONMENTAL AQUATIC SAMPLES

Alexey KAMYSHNY*,**, Irina EKELTCHIK*, Tamara VOITSEKOVSKI, Jenny GUN* and Ovadia LEV*

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Inorganic polysulfides, S_n^{2-} and their protonated forms are important compounds in natural aquatic systems. They are intermediates of hydrogen sulfide oxidation under neutral and basic conditions. These compounds have been found in anoxic and oxic aquatic systems. A novel method of inorganic polysulfide speciation by rapid single-phase derivatization with methyl trifluoromethanesulfonate in methanol-water medium followed by HPLC-UV quantitative detection of dimethylpolysulfanes allows determination of the individual concentration of all polysulfide with $n \leq 8$ [1].

The method has been adapted for analysis of natural aquatic samples with pH>6.8 by preconcentration of the dimethylpolysulfides mixture by dodecane extraction. The different polysulfide species can be detected at concentrations as low as 100-400 nM [2]. The method has been applied for inorganic polysulfide speciation in three natural systems: Lake Kinneret (Sea of Galilee), underground water from nine sulfide rich wells in southern and central Israel and in seawater spiked with polysulfide precursor (K_2S_5). Additionally we traced the dynamics of the evoluition of the individualk polysulfides during the oxidation of hydrogen sulfide by hydrogen preroxide at moderately basic pH.

Current detection limit of the process did not allow speciation of polysulfides in the hypolimnion of Lake Kinneret, where they had been previously detected in nanomolar levels [3]. The highest concentartions of polysulfides have been found near the the chemocline and not near the bottom as predicted by thermodynamic calculations.

Results of the measurements in anoxic water wells were compared to those predicted by thermodynamic calculations assuming supersaturation (with respect to sulfur) and equilibrium conditions. The deviation of the experimental findings from the thermodynamic distribution allowed us to evaluate if the water source meets our assumptions. Total polysulfide sulfur has been also detected by an independent method - reaction with cyanide followed by detection of thiocyanate by ion chromatography.

For the hydrogen sulfide oxidation by H_2O_2 the total polysulfide concentration increases immidiatly after initiation of the reaction with dominance of the shorter polysulfide species (S_3^{2-} and S_4^{2-}). After the solution becomes supersaturated by sulfur, the longer polysulfides (S_4^{2-}, S_5^{2-} and S_6^{2-}) become more dominant, and at the final stages of the reaction polysulfides concentration decreases to yield sulfur and sulfate.

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DETERMINATION OF ORGANOMETAL(LOID) COMPOUNDS IN LANDFILL GAS AND LANDFILL LEACHATE BY GC-ICP-MS

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Organometal(loid) compounds are molecules bearing at least one metal(loid) – carbon bond. Their occurrence in landfill sites is known for quite a while [1] and they can be found both in landfill gas [2] and leachate [3]. These compounds are formed in sanitary landfills from inorganic and organic precursors by microbiological activity or transalkylation reactions. Many of these products can be more toxic than their precursors, e.g. alkyltin or alkylmercury compounds.

A powerful tool for analysing organometal(loid)s is the coupling of capillary gaschromatography (GC) with inductively coupled plasma - mass spectrometry (ICP-MS) [2]. It combines good trace-matrix separation of GC with ICP-MS as a sensitive detector having multi-element capability and the option of isotope analysis.

Gaseous samples are analysed by our self-made cryotrapping (CT) - cryofocussing (CF) - GC - ICP - MS system. Samples are stored in 5 L Tedlar® bags and about 50 mL are directly injected into the system with a glass syringe. The use of Tedlar® bags for sampling and storing is more convenient in comparison to cryo-techniques and provides good results for thermodynamically unstable organometal(loid)s [4]. We found more than 10 volatile organotins, with tetramethyltin having concentrations up to 22.59 ng L^{-1}. In addition, mercury, selenium and tellurium species were found in landfill gas.

Landfill leachate is analysed using GC-ICP-MS for liquid injections of solvent extracts. Hence, water soluble compounds have to be transferred into volatilizible species for GC analysis. This is achieved by in-situ derivatization with sodium tetra-(n-propyl)-borate ($NaBPr_4$) and extraction with n-hexane. The popylated derivates of ionic organometal(loid) species can cause problems as they can have high boiling points which complicates the transfer from GC to ICP-MS. To overcome this a heatable transferline was used. Next to one organolead compound only organotins were found in landfill leachate.

Comparing landfill leachate and gas, it seems that more organometal(loid)s can be found in the gas phase; the water phase might be a temporary reservoir until further alkylation to volatile organometal(loid) species takes place.

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SUPPORTED LIQUID MEMBRANE PRECONCENTRATION DEVICE FOR MULTIELEMENT SPECIATION STUDIES IN NATURAL WATERS : ASSESSMENT OF Cd(II) SPECIATION IN COMPARISON WITH Cu(II)

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Chemical speciation studies are important for understanding the biogeochemical cycling of trace metal ions. In natural waters, trace metals e.g. Cu, Pb, Cd and Zn exist in various chemical forms and their bioavailability and toxicity to the micro-organisms depend on the specific form, in particular the free metal ions are the most toxic form. Trace metals in natural waters, are present at low total concentration (<100 nmol/L) and their free concentrations are still lower(<10 nmol/L). Very few methods, which combine both speciation capability and high sensitivity are available. Carrier assisted supported liquid membrane (SLM), an emerging analytical method based on liquid-liquid extraction principles, allows the determination of free metal ions or bioavailable species. The attractive features of SLM are: - separation and preconcentration of target species can be achieved in one step, thus minimizing sample handling and contamination risks; - it somewhat mimics biological membrane, - it can be used readily for in situ speciation measurements. The speciation capability of SLM, comprising of didecyl 1,10 diaza crown ether in phenyl hexane/toluene (1:1), was demonstrated previously by measuring fluxes in the presence and absence of complexing ligands (e.g. sulphosalicylic acid, hydroxyquinoline sulphonic acid, fulvic acid etc.) [1].

In this paper, the speciation capability of the designed SLM for Cd(II) has been investigated. The Cd(II) speciation measurements were done in the absence and presence of complexing ligands such as oxalate and diglycolic acid. The results showed that free metal ions are only transported, like Cu(II). Measurements of Cd(II) fluxes in the presence of small organic ligands, forming neutral Cd(II) complexes (e.g. hydroxyquinoline, diethyldithiocarbamate...), were made to see if these complexes are transported across the membrane, as they are known to be assimilated by microorganism. The results showed that Cd(II) - DDC complex passes through the membrane like the Cu(II)-DDC complex [2], but in significantly higher proportion. Thus, information on bioavailable fraction can be obtained from SLM data. Finally, the SLM was tested for its bioavailability prediction in the exudate of green algae Chlamydomonas Reinhardtii. The results demonstrated indeed that free metal ions are measured by SLM [3].

The application of SLM for in situ speciation measurement of Cu, Pb and Cd in natural water, using a specially designed hollow fibre supported liquid membrane (HFSLM), will be presented. The limit of detection is in the few picomolar range, demonstrating the capability of SLM for multi-element trace metal speciation analysis.

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Simultaneous determination of Zn, Pb, Cd, Cu, Ni and Cr in seawage sludge by slurry sampling ICP OES method.

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Zinc, lead, cadmium, cooper, nickel and chromium can be presented as a trace contaminant in all environmental compartments as a result of both natural and anthropogenic activities, determination of those elements being of considerable interest because of its toxicity and ability to bioaccumulate in many organisms [1]. The knoweledge of the toxicological implications of those elements in the environment has encouraged the development of very sensitive methods for their determination.

Decomposition of organic and inorganic matrices is a critical stage in trace metal analysis, since it largely determines the precision and accuracy of the results obtained. A wide variety of combinations of strong acids, oxidants, ultrviolet irradiation and elevated temperatures and pressure has been used and ecommended. Main concerns are voltility and absorption losses during elevated temperature digestion procedures, sample contamination, and the problem of using a large amount of reagents during pretreatment, which gives rise to increased blank values and higher detection limits.

A significiant increased level of heavy metals in the sludge is a strong argument against their use for fertilising purposes. And mineralisation of sludge during its treatment does not decrease but increases the concentration of heavy metals. Facing increasing demands as to the properties of sludge admissible for agricultural use in Europe [2] including Poland [3], the amount of sludge used for the purpose has decreased. The admitted amounts of Zn, Pb, Cd, Cu, Ni and Cr in sewage sludge, which can be used in agriculture are:2500 – 4000;750 – 1200; 20 – 40; 1000 – 1750; 300 – 400 and 100 – 1750 mg kg^{-1} respectively [3]. In this context, an accurate, precise sludge and quick determination of zinc, lead, cadmium, cooper and nickel in sewage has become an important analytical task.

The introduction of solid samples as slurries into ICPOES system can greatly reduce the time required for analysis by avoiding sample decomposition by wet or dry oxydation methods with the reduced risk of Zn, Pb, Cd, Cu, Ni and Cr losses and sample contamination.

In this research, a procedure for rapid and simultaneous determination of six elements in sewage sludges discussed using this approach. The special condition of using a suspension medium containing different concentration of HNO_3, solid particle size distribution measurements, influence of slurry concentration, calibration techniques and optimisation of operating variables were researched.

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SPECIATION OF METALS AND METALLOIDS IN SOILS AND PLANT USING X-RAY ABSORPTION SPECTROSCOPY

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Combined use of batch equilibrium methods and FTIR, NMR and XAS has enabled one to study the mechanisms of adsorption of metals and metalloids onto soils, the speciation and the coordination environment within plants. When arsenate was adsorbed onto goethite and soil three different complexes are formed: mononuclear bidentate, binuclear bidentate and monodentate complexes. In such complexes one As atom is coordinated to 4 oxygen atoms, and the As-O bond length is 1.68 Å. For the second shell coordination environment the As-Fe bond lengths for these complexes are 2.77, 3.25 and >3.50 Å, respectively [1]. XAS study revealed that Pb and Cu were bonded to peat predominantly *via* carboxylic moieties without excluding the hydroxyl groups, elucidating the mechanism of competitive adsorption of Pb and Cu on peat [2]. Heavy metals and organic contaminants often coexist in soil. However, there was very little information regarding the effect of metals on the adsorption of organic contaminants on soils and vice versa. XAS identified that Cu and Pb formed inner-sphere complexes with soil minerals and soil organic matter. Cu and Pb were coordinated to siloxane surface, carboxyl and hydroxyl groups. FTIR study indicated that these groups also reacted with *p*-nitrophenol and 2,4,6-trichlorophenol. Overlapping of these adsorption sites of Cu, Pb, *p*-nitrophenol and 2,4,6-trichlorophenol in part was one of the reasons responsible for the observed competitive adsorption [3, 4]. Organic acids increased the uptake of La, Pb and Cd by barley, wheat and corn roots, respectively. In case of La, XAS provided evidence of La-oxygen environment and established that one La(III) atom was coordinated to 11 oxygen atoms that are likely to be involved in the binding of La(III) to barley roots via carboxylate groups and hydration of La(III) [5]. XAS provided the evidence that the local environment of Pb in wheat roots is similar to that of lead(II) acetate [6].

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LEACHING OF ARSENIC BEFORE CONSUMPTION IN CHINESE RICE

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It is important to study the effect of As-polluted ground water used for cultivation of terrestrial plants. Little is known about the leaching and speciation of As before consumption. Moreover, rice preparation traditions can vary with different cultures [1]. In some countries, rice is boiled with an excessive amount of water and the remaining water after cooking is discarded. However, in other countries, rice is cooked with less water and the grains absorb it all. Therefore, in order to assess the effect of the cooking on the leaching of the arsenic species in rice, 50 g of raw Chinese rice grains were washed with 3 × 100 mL water and subsequently boiled with 300 mL water for 15 minutes. The aliquots of the cold and boiled starch suspensions were freeze-dried, digested and analysed their As concentration by double focusing sector field inductively coupled plasma mass spectrometry (DF-ICP-MS). Total As concentration of the milled rice sample was also determined by the same method after microwave-assisted digestion employing Ge as internal standard. The total concentration of the sample was 155.3 ng/g. Accuracy was checked by analysing also a NIST1568a rice sample. The arsenic distribution between water used for rinsing, boiling as well as in the cooked rice was 7.7 %, 29.3 % and 63.1 %, respectively. The arsenic recovery compared with the total As of the milled rice grains was 96.0 %. Moreover, as it is important to be able to determine the distribution of the arsenic species, a speciation study was carried out by a hyphenated high performance liquid chromatography (HPLC) and ICP-MS. In water samples resulted by rinsing and boiling, arsenite, dimethyl arsinic acid and arsenate were identified by an anion-exchange HPLC-ICP-MS method. Thus, the processes applied (cold washing or boiling with water) did not affect the leaching of the arsenic species from the rice sample investigated. More details will be given during the lecture.

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BIOGEOCHEMISTRY OF THE MARINE ENVIRONMENT: EXAMPLES OF RECENT TRENDS IN ENVIRONMENTAL ANALYTICAL CHEMISTRY

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Understanding the cycling of carbon within marine systems is complex but is necessary if we are to assess how mans' activities can impact these systems. Examples of how combined isotopic and molecular organic marker research can aid in this task will be presented [1, unpublished data]. More specific examples of strategies to investigate marine contaminant biogeochemistry will follow. These will include investigations of environmental pollution resulting from the Gulf War [2, 3]; assessment of the impact of antifouling agents in marine paints [4, 5]; evaluation of agrochemical run-off entering marine environments [6]; corals as recorders of contamination [3]; and the photo-oxidation of the anti-microbial triclosan which forms a dioxin [submitted]. Novel applications of techniques such as solid phase micro-extraction (SPME) to evaluate the behaviour of MTBE [7] and the bioavailability of PAHs [8]; immunoassays to screen prior to high resolution analyses [9] and to quantify bioavailable contaminants in invertebrate biological fluids [10]; combined chemical and biological "Rapid Assessments of Marine Pollution" [11]; and flow cytometry/high resolution HPLC of pigments to investigate responses of phytoplankton to toxicants [4, 5] will be presented. A comprehensive review of this topic is in press [12].

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Oral contributions Thursday June 8 2006

9.00-9.45 **Invited lecture**

Peter Brimblecombe, School of Environmental Sciences, University of East Anglia, Norwich (United Kingdom)

Atmospheric chemistry and urban pollution

10.15-10.35 **Julien Dron, Nicolas Marchand, Henri Wortham,** Laboratoire de Chimie et Environnement, Université de Provence, Marseille (France)

Functional group analysis for the particulate organic matter: An innovative approach applying neutral loss scanning mass spectrometry

10.35-10.55 **Pasquale Avino, Maurizio Manigrasso,** DIPIA-ISPESL, Rome (Italy)

Investigations on primary and secondary pollutant evolution by DOAS methodology in urban and industrial environments

10.55-11.15 **Kamil Motyka, Zbyněk Večeřa, Pavel Mikuška**, Institute of Analytical Chemistry, Academy of Sciences of the Czech Republic, Brno (Czech Republic)

Wet-effluent diffusion denuder–FIA method for nitrous acid determination in air

11.15-11.35 **Vinod Kumar Jena, Khageshwar Singh Patel, Suresh Chandra Patel,** School of Studies in Chemistry, Pt. Ravishankar Shukla University, Raipur (India)

Bioabsorption of heavy metals with menthe arvensis

11.35-11.55 **Jürgen Wess**, PANalytical, Kassel (Germany)

Measurement of toxic elements in secondary fuels with XRF

11.55-12.15 **Monica Culea, Ristoiu Dumitru, Aurel Mocanu**, Dept. of Biomedical Physics, Babes-Bolyai University of Cluj-Napoca (Romania)

Interlaboratory analytical methods for THMs determination in drinking water

12.15-12.35 **René Van Grieken, Katleen Van Meel, Yaroslava Makarovska**, Dept. of Chemistry, University of Antwerp, Antwerp (Belgium)

Monitoring of heavy metals in aerosols by the new high-energy polarized-beam XRF

14.00-14.45 **Invited lecture**

Wittko Francke, Stephan Franke, Institute of Organic Chemistry, University of Hamburg, Hamburg (Germany)

Non-target screening: identification of new organic pollutants

15.15-15.35 **Christina Caliebe, Wolfgang Gerwinski, Michael Haarich, Heinrich Hühnerfuss, Norbert Theobald**, Federal Maritime and Hydrographic Agency, Hamburg (Germany)

Occurrence of perfluorinated organic acids in the marine environment

15.35-15.55 **Vesna Furtula, Basil Hii**, Pacific Environmental Science Centre, Vancouver, British Columbia (Canada)

Groundwater analysis in Abbotsford Aquifer, British Columbia, Canada

15.55 -16.15 **Peter Hancock, Timothy Jenkins, Jean-Marc Joumier, Keith Worrall**, Waters EHQ, St Quentin en Yvelines (France)

Multiresidue analysis of priority pollutant in surface waters using exact mass GC-TOF

16.15-16.35 **Markus Scheurell**, **Stephan Franke, Heinrich Hühnerfuss,** Institute of Organic Chemistry, University of Hamburg, Hamburg (Germany)

Effect-directed analysis – a powerful tool for the surveillance of aquatic systems

16.35-16.55 **Jun J. Ding, Liushui Yan, Qun Cao, Rong R. Shi, Xiao Y. Yang**, Nanchang Institute of Aeronautical Technology, Nanchang (China)

Simultaneous determination of 15 trace organic pollutants in drinking water by solid-phase extraction-liquid chromatography-ion trap mass/mass spectrometry

16.55-17.15 **Norbert Theobald,** Federal Maritime and Hydrographic Agency, Hamburg (Germany)

Monitoring of organic contaminants in the marine environment – special analytical and other challenges

Atmospheric chemistry and urban pollution

Peter Brimblecombe
School of Environmental Sciences,
University of East Anglia,
Norwich NR4 7TJ UK

Atmospheric chemistry and urban pollution have become closely linked because so much of our contemporary understanding of air chemistry has been driven by a need to understand air pollution. The modern science began with the pioneering work of Leighton and his group in California in the 1950s. Gas-phase chemistry is dominated by the hydroxyl radical and photo-chemically induced reactions. It was paralleled by an interest in regional chemistry initiated by C.E. Junge. The last half century has greatly expanded our understanding of reactions in the gas phase. Despite early interest in the heterogeneous chemistry of sulphur dioxide oxidation in rain droplets, there has been less progress in our understanding of the chemistry of dissolved in rain drops or on atmospheric aerosols. In recent years the awareness that particles in urban atmospheres are a key driver of health affects has renewed interest in heterogeneous chemistry, with an increasing focus on radical reactions in solution and the production of low volatility organic compounds (secondary organic aerosol, SOA). The shifting interest poses not only difficult theoretical questions, but also severe analytical demands as we have to understand on the chemistry of single particles which can have elaborate structures. The compounds or their mixtures are sometimes so complex that it may not be possible to specify chemical formulae. Here it can be necessary to describe properties of the materials (e.e. Humic like substances, HULIS) or their functional groups.

FUNCTIONNAL GROUP ANALYSIS OF THE PARTICULATE ORGANIC MATTER: AN INNOVATIVE APPROACH APPLYING NEUTRAL LOSS SCANNING MASS SPECTROMETRY

Julien DRON, Nicolas MARCHAND and Henri WORTHAM
Laboratoire de Chimie et Environnement (Case 29), Université de Provence, 3, place Victor Hugo, 13331 MARSEILLE Cedex 03 (France)

Particulate organic matter (POM) in atmospheric aerosols results from primary emissions as well as in situ formation through oxidative processes of gas-phase organic compounds, and contributes in approximately 20 to 50% of the total fine aerosol mass at continental mid-latitude [1]. It has been well established that this class of particulate material has a high potential impact on both human health and climate change. In order to better estimate the influence of organic aerosols, a good knowledge of its organic fraction is required. However, considering the degree of complexity of POM, conventional analytical methods lead to its incomplete characterization [2]. Thus, molecular analysis performed by gas chromatography / tandem mass spectrometry (GC/MS/MS) identifies only a small part of the organic fraction [3] while organic and total carbon determination provides very poor information relative to the chemical nature of the POM. Functional group determination is a complementary approach in the field of POM analysis which is commonly achieved by Fourier Transform InfraRed spectroscopy (FTIR). This technique makes it possible to characterize a larger fraction of the aerosol mass as well as to provide information on the chemical nature of the aerosol. Nevertheless, the performances of FTIR spectroscopy suffer from poor accuracy, excluding consequently reliable quantitative measurements [4].

The aim of this work is to propose a new method for the analysis of functional groups. This method is based on tandem mass spectrometry, operating in constant neutral loss scanning mode (CNLS). The samples are directly injected into the atmospheric pressure chemical ionization chamber (APCI) of a triple quadrupole mass spectrometer. The quantification of the functional groups relies on the ability of the compounds bearing the same functional group to loose an identical and characteristic neutral fragment into the collision cell. The application of this technique to the determination of oxygenated functions, i.e. carboxylic acids and carbonyl compounds, revealed that their preliminary derivatization was required. Performance tests were carried out with numerous mixtures of different compositions and containing each up to 30 standard compounds. The results demonstrated the reliability of the method for the analysis of several oxygenated functional groups.

Compared to FTIR spectroscopy, the analytical strategy proposed by this study provides major benefits because it offers an overview of the molecular weight of the detected compounds and it enables the quantification of the functional groups with a high accuracy. For the determination of carboxylic acid functional group, a relative standard deviation (RSD) as low as 12% was reached and linear calibration curves ranging from 0.01 to 1 mmol/L were obtained with coefficients of correlation, $R^2 > 0.985$. More widely, this new approach for functional group quantification would offer great perspectives because it is particularly well adapted to the characterization of complex matrices, which are prevailing in the field of environmental analysis.

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INVESTIGATIONS ON PRIMARY AND SECONDARY POLLUTANT EVOLUTION BY DOAS METHODOLOGY IN URBAN AND INDUSTRIAL ENVIRONMENTS

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The Differential Optical Absorption Spectroscopy (DOAS) is a remote-sensing analytical technique finding strong consents as demonstrated by numerous paper published during these last years. The DOAS analytical method is based on the UV and Vis light absorption (from 240 nm to 340 nm) of species with fine vibrational structures like SO_2, NO_2, ozone, nitrous acid, formaldehyde, benzene and toluene; the Lambert-Beer's law regulates the relationship between the adsorbed light intensity and the concentration of each species.

The DOAS system is constituted from the following parts: a light source, a receiver, an spectrophotometer equipped with a optical fiber and a computer for the system management (data elaboration and data storage). The light source is a Xenon lamp (at high pressure and 150W): a transmitter sends the light to the receiver that transmits the beam through the optical fiber in the analyzer.

The absorption spectra of each monitored chemical species are acquired at their relative typical wavelength ranges; subsequently, the interferences are eliminated by comparison with the reference spectra.

This technique furnishes the concentrations related to a portion atmospheric environment varying also for some kilometers. In fact, these "integrated" concentrations represent the average area pollution level better than the measurements obtained by traditional analyzers which are considered "punctual".

This communication reports two different DOAS system applications in urban and industrial areas. For the urban investigations a DOAS equipment (mod. AR500. Opsis, Sweden) was installed at the ISPESL's Pilot Station located in downtown Rome (near St. Maria Maggiore Cathedral), an area characterized by high autovehicular traffic: the optical length (distance between transmitter and receiver) was 280 m at 10 m-height. For the industrial area studies (a very complex area characterized by different anthropogenic sources) a DOAS located on the roof of the ISPESL's Mobile Laboratory was involved: the optical length was about 180 m at 4 m-height.

The levels of SO2, NO2, ozone, nitrous acid, formaldehyde, benzene and toluene measured during different intensive campaign in 2003 and 2004 are extensively discussed. The daily trends of the primary and secondary pollutants are compared with those acquired with UV point-source analyzers and interpreted according to the natural beta radioactivity used to investigate the dynamic of the boundary layer. It is evidenced that the secondary pollution, and in particular that derived from NO2 and ozone, is not influenced by emission intensity and consequently assumes homogenous values in the entire urban area.

The DOAS technique is an advanced measurement system useful for integrating information coming from monitoring networks: furthermore, it allows to investigate and understand the complex mechanisms of formation and transformation of atmospheric pollutants through the contemporary measurements of gaseous primary and secondary species.

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WET-EFFLUENT DIFFUSION DENUDER - FIA METHOD FOR NITROUS ACID DETERMINATION IN AIR

Kamil MOTYKA[a,b], Zbyněk VEČEŘA[a] and Pavel MIKUŠKA[a]
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Significance of nitrous acid (HONO) in atmospheric chemistry lies especially in its accumulation in atmosphere at night and quick photolysis at sunrise by absorption of sun light to form the hydroxyl radicals [1]. In addition, nitrous acid has a mutagenic property, it is a precursor of cancerogenic nitrosoamines [2] and takes part in the acidification of the environment [3].

This contribution describes results of study aimed to compare various absorption solutions (carbonate, bicarbonate, phosphate) as well as deionized water from the point of view of the collection efficiency of HONO in the cylindrical wet effluent diffusion denuder (CWEDD) and selectivity and sensitivity of nitrous acid detection**.**

The method combines a pre-concentration of nitrous acid in CWEDD from air into a thin film of absorption liquid and on-line analysis of denuder concentrate with collected nitrous acid employing a flow-injection analysis (FIA) where nitrous acid is oxidized into peroxynitrous acid and a chemiluminescent light emitted during the reaction of peroxynitrite with luminol is detected.

We found that HONO is quantitatively collected in the CWEDD (absorption liquid flow rate of 400 µl/min) up to air flow rate of 1 l/min and then CE decreases with increasing air flow rate for all studied absorption liquids.

No intereference was observed for alkanes, terpenes, BTX, acetone and ammonia. The presence of NO, NO_2 and the mixture of NO_2/SO_2 influence the HONO determination more significantly. The lowest interference of NO, NO_2 and NO_2/SO_2 mixture was observed for 1×10^{-4} M $NaHCO_3$ (pH 6.4; 0.07%, 0.18%, 0.93%) and 1×10^{-5} M $NaHCO_3$ (pH 4.7; 0.07%, 0.36%, 1.27%). Interference for water is at comparable level. In the presence of SO_2 measured results confirm a formation of secondary nitrite in the denuder concentrate as a result of decay of a relatively stable intermediate $[NO_2\text{-}SO_3]^{2-}$ formed in aqueous phase [4].

Absorption solutions (with exception of 1×10^{-2} M Na_2CO_3 which reduces the sensitivity by 10 %) do not influence the sensitivity of nitrite detection.

In spite of matter that the nitrogen oxides interference was the lowest for 1×10^{-4} M sodium bicarbonate, from the practical point of view we choose deionized water as the absorption liquid for the collection of HONO in the CWEDD. The proposed method was applied to the HONO measurement in a background area at Bílý Kříž (Czech Republic). Detailed results will be presented.

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BIOABSORPTION OF HEAVY METALS WITH MENTHA ARVENSIS

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Plant extracts of medicinal value have gained considerable importance in alternative medicine in recent times [1]. The herbal plants are rich in the essential oils and used as potential bio-absorptive for removal of the heavy metals [2]. However, there is an inherent health risk associated with many of these medicines due to presence of contaminating heavy metals. The medicinal herbs are one of potential source of toxic metal exposure for man and animals. Mentha arvensis (Pudina) is a well known medicinal herb in India. It is a downy perennial herb with running rootstocks and running branching stem. The leaves are lanceolate or oblong, sharply toothed, shortly petioled or sessile with minute hair. Menthol is one of the main component of the mint oil. It is planted in home gardens for various purposes. Many species of Mentha are cultivated in the Chhattisgarh, central India. The objective of this work is to determine the heavy metal contents (i.e. Cr, Mn, Fe, Ni, Cu, Zn and Pb) in the leaf, stem and root in different varieties of mentha arvensis, and the rhizospheric soil. Both the available and total concentration of the heavy metals in soil and accumulation factor in different part of different varieties of mentha arvensis is discussed.

Acknowledgement: We are thankful to CSIR, New Delhi and Alexander von Humboldt Foundation, Bonn for financial support.

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MEASUREMENT OF TOXIC ELEMENTS IN SECONDARY FUELS WITH XRF

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Increasing prices for primary fuels (natural gas/oil) opens the discussion for alternatives solutions. Secondary fuels like wastes with high caloric value, liquid hazardous waste, used lubrication oil or biomass are getting more and more important as a traded product.

Cement plants or power generation plants, using these secondary fuels, need to comply with strong governmental legislation. Especially some toxic elements like Hg, Cd, Tl etc. have to be controlled to reduce the emission. The limits of these elements are depending on local administrations but are normally at low ppm levels.

However, there are some preconditions important for this kind of analyses: Speed, sample preparation, homogeneity etc.

An approach to measure directly the concentration of these pollutions is X-ray spectrometry. This technique is able to work with solid or liquid samples with limited sample preparation and with a bigger amount of specimen like approx. 10 g of the representing sample. All elements can be analysed in one single analysis program. X-ray spectrometry doesn’t suffer from contamination or memory effects.

The used spectrometer works with high excitation energies (max. 100kV) so that the K-lines of heavier elements can be analysed with the highest sensitivity. A Ge-detector measures these lines with a 100 % efficiency.

A polarised configuration allows the reduction of background signals from the tube and offers possibilities to excite the elements of interest with optimised secondary targets.

Of course, the matrices of this kind of samples are very different and can vary from sample to sample.

In XRF, generating element specific fluorescence signals from the specimen is a physical process, which can be described mathematically very well. By a given composition of the sample and with the knowledge of the physical parameters (Fundamental parameters) the count rates can be predicted. Based on these fundamental parameters so called standardless methods normally need set-up samples so that the instrument factors can be determined accurately. Adding matrix relevant standards can increase the accuracy.

The presentation shows how far this energy dispersive technique allows getting correct results even in low ppm levels in unknown secondary fuel samples.

INTERLABORATORY ANALYTICAL METHODS FOR THMs DETERMINATION IN DRINKING WATER

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An interlaboratory study is described for trihalomethanes, chlorinated by-products in drinking water, determined by some analytical methods, based on the following techniques: liquid–liquid extraction–gas chromatography–mass spectrometry (LLE–GC–MS), headspace-gas chromatography–mass spectrometry (headspace–GC–MS), purge and trap–gas chromatography–mass spectrometry (purge and trap–GC–MS); and headspace extraction–gas chromatography–electron capture detection(headspace–GC–ECD). The compounds studied were chloroform, bromodichloromethane, dibromochloromethane and bromoform. The MS was operated in the SIM mode. The quantitative methods were validated and demonstrate the ability to identify and to measure reliably the yields of these toxic compounds.

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MONITORING OF HEAVY METALS IN AEROSOLS BY THE NEW HIGH-ENERGY POLARIZED-BEAM X-RAY FLUORESCENCE

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We have optimized and evaluated the new high-energy polarized beam energy-dispersive X-ray fluorescence (XRF) spectrometer Epsilon 5 (PANalytical, Almelo, The Netherlands) for quantitative analysis of aerosol samples deposited on filters. The advantages and the limitations of this spectrometer, relative to other relevant commercial XRF units, will be discussed briefly.

Concerning heavy metals in atmospheric aerosols, there are serious concerns whether wavelength-dispersive XRF, applied nowadays by several national environmental agencies in Europe, will be capable of providing the detection limits necessary for assessing the decreasing “limit values” imposed by national authorities or foreseen by the EU Directive 96/62/EC towards 2010. Conventional EDXRF can normally not measure e.g. Cd and Hg via their less spectrally interfered K-lines. The potential of the new high-energy energy-dispersive XRF was therefore studied.

The detection limits were around 1 ng/cm² for most heavy metals, i.e. sufficiently low to meet the present Flemish and future European limits for e.g. Pb, Cd, As and Ni, with a 100-200 counting time, for common sampling conditions. Other analytes usually present in very low concentrations (e.g. V, Cr, Sb) could be assessed as well. The natural background levels of many heavy metals could be measured.

NON-TARGET SCREENING: IDENTIFICATION OF NEW ORGANIC POLLUTANTS

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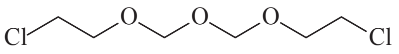
An unbiased comprehensive qualitative recording of organic pollutants (non-target screening) as well as reliable quantitative (target) analyses of any environmental compartment (surface- and groundwater, sediment, soil) form the basis for the description of the state of pollution at selected sites and are, thus, prerequisite for risk assessment, control measurements and decision making with respect to treatments.

Structure elucidation of new pollutants that are frequently found in complex multicomponent mixtures may not only require application of the whole range of modern analytical techniques but also

- formation and investigation of appropriate derivatives prepared through micro reactions
- independent syntheses of authentic reference samples.

Some new chlorinated compounds[1] that deserve special attention are represented by groups of acetals (1 or 2) showing formaldehyde or chloro- and dichloroacetaldehyde as well as chloroethanol or ethanol as substructures. Others are propene- or epichlorohydrin-derived chlorinated bis(propyl)ethers (3) or chlorinated 2-propyl phosphates (4). Further new chlorinated compounds are the styrene-derived 4-phenyl-5-chloromethyl-1,3-dioxane (5), the diphenylurea (6), and 1,2,3,4,7,7-hexachloro-5,6-bis(methylene)bicyclo[2.2.1]hept-2-ene (7), an obvious degradation product of the pesticide endosulfan.



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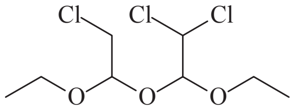

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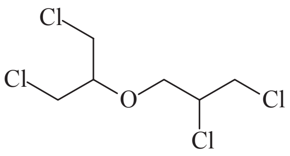

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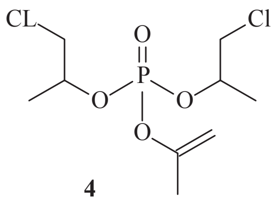

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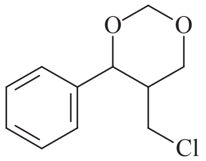

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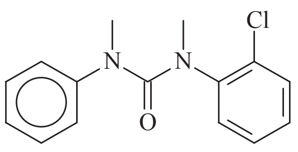

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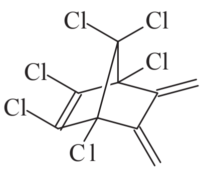

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OCCURRENCE OF PERFLUORINATED ORGANIC ACIDS IN THE MARINE ENVIRONMENT

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Perfluorinated organic acids (PFC) and their derivates have been industrially produced for several decades and are used for many purposes. They are applied as stain and water repellents for surface treatment of textiles, carpets, leather and paper products. Perfluorooctanoic acid is a processing aid in the production of fluorpolymers (e.g. PTFE, PVDF). Due to the large production quantities and their persistence in the environment, perfluorinated compounds are meanwhile globally distributed. Perfluorooctanesulfonic acid (PFOS), Perfluorooctanoic acid (PFOA) and other long chain perfluorocarboxylic acids have been detected in blood of ringed seals, in polar bears, arctic foxes, mink, birds, and fishes collected in the USA, at the coasts of the Baltic and Mediterranean Sea and in the Arctic. [1-4]

An analytical method consisting of SPE extraction/ enrichment and HPLC-neg.-ESI-MS-MS has been developed to determine a number of perfluorinated organic acids in river, coastal and marine water samples. In addition, two methods for the determination of PFC in sediments and biota (fish muscle and fish liver) were developed. Extreme care has been taken for blank control and prevention of contamination. In particular, the perfluorinated carboxylic acids are susceptible to contamination, e.g., by Teflon^R and Viton materials.

All three types of samples were taken from the North and the Baltic Seas and were analysed regarding to PFC. The predominant perfluorinated substances found were PFOA and PFOS. However, their concentration patterns varied in different matrices and areas. The concentrations of PFOS in fish liver samples were higher compared to fish muscle samples.

The investigations started in the estuary of the river Elbe, which is one of the most important sources for pollutants entering the German Bight, and continued to the open sea.

The concentrations of the major occurring PFOA and PFOS determined in sea water samples are in a similar range as other polar pollutants such as phenylurea, triazine or phenoxyacetic acid herbicides. [5] Compared to classical, lipophilic POPs their water concentrations are considerably higher.

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GROUNDWATER ANALYSIS IN ABBOTSFORD AQUIFER, BRITISH COLUMBIA, CANADA

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The Abbotsford aquifer is the Canadian half of the transboundary Abbotsford-Sumas aquifer in south-western British Columbia, Canada and north-western Washington, USA. The aquifer is comprised of mainly sand and gravel deposits which are unconfined and permeable and therefore vulnerable to land-based contamination. Land use on the aquifer is mainly agriculture and the sources of nitrate contaminants in the Abbotsford aquifer have been attributed to surface application of manure and chemical fertilizers [1].

Environment Canada in partnership with the Fraser Health Department, BC Ministry of Environment and University College of the Fraser Valley conducted a groundwater quality survey of about 150 wells in the Abbotsford aquifer. Contaminants such as nitrate and fecal bacteria were detected in many samples. The survey found that the nitrate concentrations in nearly 40% of the wells were over the Canadian Drinking Water guideline of 10 mg N/L. High nitrate concentration in groundwater may also be a good indicator of other contaminants such as pesticides leaching from agricultural lands [2].

Ten wells of different depths and with elevated nitrate concentrations greater than 30 mg N/L were selected for organic pollutant analysis. A new approach to groundwater analysis was used in order to detect pesticides and other organic contaminants. Water samples were prepared by liquid/liquid extraction using dichloromethane (DCM) as an extraction solvent and analyzed by gas chromatography mass spectrometry in scan mode (GC-MS). To increase sensitivity for pesticides detection, acquired scan data were further analyzed by Automated Mass Spectrometry Deconvolution and Identification Software (AMDIS) incorporated into the Agilent Deconvolution Reporting Software (DRS), which also includes mass spectral libraries for 567 pesticides. Extracts were reanalyzed by gas chromatography mass spectrometry single ion monitoring (GC-MS-SIM) to confirm and quantitate detected pesticides. Pesticides: atrazine, simazine, propazine, metalaxyl, heptachlor epoxide and endosulfan sulphate were detected at some sampling sites at concentrations higher than allowed by current drinking water standards. BTEX and PAHs were also detected. Detection and identification level for each pesticide found was also discussed. The proposed approach of monitoring organic pollutants in ground water enables their detection and identification at ng/L levels.

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MULTIRESIDUE ANALYSIS OF PRIORITY POLLUTANT IN SURFACE WATERS USING EXACT MASS GC-TOF

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The Dangerous Substances Directive (76/464/EC) lists 132 compounds that have legislated levels in drinking and surface waters, of which, more than 100 are amenable to GC analysis. A method has previously been published[1] employing single quadrupole mass spectrometry using selected ion recording (SIR) for screening of the GC amenable compounds. The compound groups analysed represent a wide range of polarities and types, and include benzidines, chloroanilines, chloronitrobenzenes, chloronitrotoluenes, chlorophenols, chlorotoluidines, OCs, OPs, PAHs, PCBs, phenylureas, triazines and volatile amines.

SIR allows for targeted screening of a finite number of compounds to be achieved. However, much of the chemical information is discarded so full spectrum techniques are still required in so-called “open” or untargeted screening environments.

Exact mass Time Of Flight Mass Spectrometry (TOF-MS) is a full spectrum technique capable of both the targeted and the untargeted screening approaches.

A method will be introduced for the targeted screening of 107 GC amenable compounds in surface waters down to the legislated concentration of 0.1 μg/L. The use of exact mass TOF-MS will be shown to improve the selectivity of the analytical method using exact mass chromatograms, reduce the chromatographic separation whilst maintaining the sensitivity compared to scanning quadrupole instruments and maximise the chemical information obtained from a single experiment with good accuracy of mass measurement.

A new method will also be introduced for the untargeted screening of other GC amenable compounds in surface waters using automatic peak detection, deconvolution and library searching with exact mass confirmation.

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EFFECT-DIRECTED ANALYSIS – A POWERFUL TOOL FOR THE SURVEILLANCE OF AQUATIC SYSTEMS

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Within the next decade more than half of the world´s population are expected to live in large metropolitan centres, due to increasing migration from rural areas. Limitation of pure drinking water and insufficient sanitation will be one of the upcoming problems in the growing process of these megacities. According to U.N. policy, measures have to be taken in order to overcome these problems.[1] Existing resources have to be protected from contamination and a closed drinking water cycle, including waste water treatment, has to be established.

In the focus of an upcoming transdisciplinary project lies Karachi, Pakistan, and its drinking water supply as a classical example for a megacity. Object of the part of the project presented here is the analysis of the current state of the drinking water, its resources and waste water effluents regarding contamination with organic substances. The method developed for this purpose consists of a combination of chemical and biological methods based on the TIE (Toxicity Identification Evaluation) concept by the US-EPA.[2] This integrative method, also known as EDA (Effect-directed analysis) is a holistic approach to characterise an environmental sample including a first assessment of the risk.[3] In contrary to solely analytical approaches the sample extract is not only being fractionated and characterised by chromatographical analytical methods (NP/RP-HPLC, GC-MS), but from each step an aliquot is examined by accompanying bioassays. Thus information about the status and possible risks of the aquatic ecosystem is gained, including mixture toxicity effects which can be overlooked by subsequent single substance toxicity testing.

The aqueous sample is extracted through a SDB-Copolymer solid phase, the resulting lipophilic and hydrophilic eluates are fractionated by NP- or RP-HPLC, respectively. Before GC-MS analysis aliquots of the more hydrophilic fractions are additionally derivatised to extend the range of detectable substances. From each separation-step aliquots of the fractions are examined by the luminescent bacteria test which is sensitive to different kinds of unspecific modes of toxic action and well suited as a rapid screening bioassay. Positive results in this screening bioassay will guide further effort concerning fractionation or identification. In cooperation with partners further testing of toxicity with a battery of assays is possible regarding specific modes of toxic action such as mutagenicity. At laboratory level the analytical method has been developed and verified succesfully with 80 different substances, from classical POPs to acidic pharmaceuticals representing a log $K_{O/W}$ range from 1,7 to 7,2. In order to meet the requirements of real-life aquatic matrices many local samples (Elbe river, WWTP-effluents) have been analysed and the results are promising with regard to forthcoming applications. Orienting sampling and analyses in a comparable drinking water system of a megacity (Shanghai tap water, Tai Hu lake) during a precedent project have shown remarkable results.[4] Many classical POPs have been encountered in large concentrations, but also new contaminants have been identified. Yet the most interesting phenomenon was the highly mutagenic potential of the tap water, which shows the exceptional advantage of accompanying bioassays.

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Simultaneous Determination of 15 Trace Organic Pollutants in Drinking Water by Solid-phase Extraction-Liquid Chromatography-Ion Trap Mass/Mass Spectrometry

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It has been demonstrated that, because of incomplete removal or forming of an active form during the process of sewage treatment, endocrine-active chemicals are released in surface water like rivers, lakes, and seas. Exposure to endocrine disrupting chemicals (EDCs) can cause sterility or decreased fertility, impaired development, birth defects of the reproductive tract and metabolic disorders. Therefore, more and more attentions have be paid to monitoring EDCs in drinking water in these years, because it is essential for the risk assessment on endocrine disruption regarding human health.

EDCs usually exist in drinking water in trace or ultra-trace levels（ng /L and even lower）and with a wide range of structural diversity. The most commonly employed methods for analysis of EDCs are GC-MS and LC-MS. In recent years LC–MS and LC–MS–MS have become more and more important method for the purpose due to no use of derivatisation steps and wider application range. However, most published procedures dealt with determination of a few structurally analogous EDCs or detection by the same ionization mode in one run, which hardly meet the demands to rapid analysis.

In this paper, a high performance liquid chromatography-ion trap tandem mass spectrometric method has been developed for the simultaneous determination of 15 trace organic pollutants in drinking water in one run, including bisphenol A, phthalates, insecticides such as carbamates and organic phosphorous, herbicides such as triazines and phenylureas, and acrylamide from water treatment reagent polyacrylamide. Eight of them are suspected endocrine disruptors.

The proposed procedure includes an off-line solid-phase extraction of 250-mL water samples with a C_{18} cartridge, followed by liquid chromatographic separation with gradient elution, and then detection by ion trap tandem spectrometry in consecutive time segments corresponding to the elution window of the different analytes. Good linear range was obtained for all analytes with the correlation coefficients of 0.9975 ~ 0.9998, and detection limits were 0.2 ~ 20 ng/L with less than 1 ng/L for all the tested eight EDCs. The average recoveries of 15 analytes in spiked tap water samples with low, medium and high levels ranged from 75.1 % ~ 99.5 %, and the relative standard deviations were between 4.6 % ~ 12.3 %。 The proposed method has been applied to the analysis of 15 trace organic pollutants in five types of drinking water samples from Nanchang city and its suburb with satisfactory results. It shows that the method has advantages of high efficiency and high sensitivity, and can be used for monitoring EDCs and pesticide residues in drinking water.

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Monitoring of Organic Contaminants in the Marine Environment – Special Analytical and other Challenges

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Because of the very low concentrations observed in the open sea, monitoring of organic contaminants in the marine environment needs some special requirements concerning sampling and analytical techniques. On the one side, very constant procedures at ultra-trace level with a good quality control system over many years are necessary to enable the investigation of time trends. On the other side, a continuos up-date and development of methods is needed for implementing surveys for new emerging contaminants [1 –3]. Examples will be shown for both aspects. Long time series are available for HCH-concentrations in sea water, demonstrating the success of political measures for pollution reductions. The investigation of new polar compounds was possible only after the availability of new analytical procedures like HPLC-MS-MS. Thus, it was shown, that new pesticides and other xenobiotics are meanwhile spread into marine waters and are observed in part at much higher concentrations than classical non-polar pollutants. Examples are shown for triazine, phenylurea and phenoxyacetic acid herbicides in the North and Baltic Seas.
In addition to analytical challenges, administrational, logistic and financial characteristics have to be considered and optimized for monitoring strategies.

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A 1 Mohammad Abedi, Seyed Morteza Talebi, Iranian Research Organization for Science and Technology (IROST), Tehran, Iran

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A 2 Esteban Alonso, Manuel Callejón, Irene Aparicio, Juan Carlos Jiménez, Antonio Santos, Dept. of Analytical Chemistry, University of Seville, Seville (Spain)

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A 3 Muhammad Ali Awan, Paul Thomas, School of Chemical Engineering & Analytical Science, University of Manchester, Manchester (United Kingdom)

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A 4 B.K. Kanungo, Minati Baral, Rati K. Bera, Dept. of Chemistry, Sant Longowal Institute of Engineering & Technology, Longowal Punjab (India)

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A 5 Mohamed Benkrid, A. Noureddine, Centre de Recherche Nucléaire D'Alger (CRNA) Algiers (Algeria)

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A 6 Arne Kiera, Nicolas Bings, Institute for Inorganic and Applied Chemistry, University of Hamburg, Hamburg (Germany)

Evaluation of a novel orthogonal plasma-source time-of-flight mass spectrometer hyphenated with laser ablation for the simultaneous determination of metals in gels

A 7 João Canário, Miguel Caetano, Carlos Vale, INIAP/IPIMAR – Dept. of Aquatic Environment, Lisboa (Portugal)

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A 8 Pavel Diviš, Lukáš Brulìk, Hana Dočekalová, Institute of Chemistry and Technology of Environmental Protection, Brno University of Technology, Brno (Czech Republic)

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Liquid chromatography – mass spectrometry determination of acrylamide in drinking water according to the European Union directive 98/83

A 10 Ursula E.A. Fittschen, José A.C. Broekaert, Gerald Falkenberg, Stephan Förster, Stephan Hauschild, Gerhard Lammel, Florian Meirer, Giancarlo Pepponi, Christina Streli, Peter Wobrauschek, Institute for Inorganic and Applied Chemistry, University of Hamburg, Hamburg (Germany)

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A 11 Stephan Franke, Christiane Meyer, Institute for Organic Chemistry, University of Hamburg, Hamburg (Germany)

GC/MS of 2,4-diethyl-3-*n*-propyl-5-pentanolides

A 12 Stephan Franke, Jörg Grunenberg, Jan Schwarzbauer, Institute for Organic Chemistry, University of Hamburg, Hamburg (Germany)

GC/FT-IR analysis of Di-*iso*-propylnaphthalenes

A 13 Carlos Guitart, Trish Frickers, James W. Readman, Plymouth Marine Laboratory,

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A 14 Simone Griesel, Antje Kakuschke, Andreas Prange, Institute for Coastal Research, GKSS Research Centre, Geesthacht (Germany)

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A 15 Thorsten Hoffmann, Senchao Lai, Julia Muenz, Nicola Springer, Institute for Inorganic and Analytical Chemistry, Johannes Gutenberg-University, Mainz (Germany)

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A 16 Amarawan Intasiri, Anne Boos, Tuanjai Yubolpas, Dept. of Chemistry, Faculty of Science, Chulalongkorn University, Bangkok (Thailand)

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A 17 Abdulrahman Kassem, Dept. of Geology, Syrian Atomic Energy Commission, Damascus (Syria)

Determination of trace elements in soil and plants in the Damascus basin of Syria by using instrumental neutron activation analysis

A 18 Vojtech Adam, Jiri Baloun, Miroslava Beklova, Ladislav Havel, Jaromir Hubalek, René Kizek, Christoph Singer, Karel Stejskal, Bernd Sures, Josef Zehnalek, Ondrej Zitka, Dept. of Chemistry and Biochemistry, Mendel University of Agriculture and Forestry, Brno (Czech Republic)

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A 19 Vojtech Adam, Ladislav Havel, Ales Horna, René Kizek, Bohumila Kulichova, Andrea Kleckerová, Jiri Petrek, Jitka Petrlova, Karel Stejskal, Josef Zehnalek, Ondrej Zitka, Dept. of Chemistry and Biochemistry, Mendel University of Agriculture and Forestry, Brno (Czech Republic)

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A 20 Pavel Krejci, Bohumil Dočekal, Institute of Analytical Chemistry, Brno University of Technology, Brno (Czech Republic)

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A 21 Anuj Kumar, Ivan Viden, Institute of Chemical Technology, Praque (Czech Republic)

Global assessment of volatile organic compounds in ambient air

A 22 Jong-Ok Lee, Kum-Soon OH, Kyoung-Mo Kang, Seung-Soo Park, You-Sub Sho, Gun-Zo Woo, Department of Food Safety Evaluation, Seoul (Korea)

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A 23 Gerhard Lammel, Darrel G. Baumgardner, José A.C. Broekaert, Graciela L.B. De Raga, Ursula E.A. Fittschen, Birgit Peschel, Max-Planck Institute for Meteorology, Hamburg (Germany)

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A 27 Georgeta Burtica, Florica Manea, Ciprian Radovan, Ilie Vlaicu, Faculty of Industrial Chemistry and Environmental Engineering, Politehnica University of Timisoara, Timisoara (Romania)

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A 28 Fevzi Gumrah, Larisa M. Melita, Maria Popescu, Chemistry and Science Materials Dept., Technical University of Civil Engineering of Bucharest, Bucharest (Romania)

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A 33 Liubov Oliferova, Mikhail Statkus, Grigoriy Tsysin, Analytical Chemistry Division, Chemistry Department, Lomonosow Moscow State University, Moscow (Russia)

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A 34 Nevenka Mikac, Baghdad Ouddane, Li Zhenxuan, Laboratory of Analytical and Marine Chemistry (CNRS), University of Sciences and Technology of Lille, Villeneuve d'Ascq (France)

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A 35 Innocent J.K. Aboh, Dag Henriksson, Jens Laursen, Eva Selin-Lindgren, Magnus Lundin, Niels Pind, Thomas Wahnström, Dept. of Chemistry, University of Aarhus, Aarhus (Denmark)

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A 36 Antje Kakuschke, Elizabeth Valentin-Thon, Simone Griesel, Ursula Siebert, Andreas Prange, Institute for Coastal research, GKSS Research Centre, Geesthacht (Germany)

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A 39 Cecilia Regnault, Masanori Kanasawa, Ichiro Kano, Stéphane Mabic, Research and Development, Bioscience Division, Millipore, St Quentin-Yvelines (France)

New challenging organic contaminant in high purity water; endocrine disrupters

A 40 Henning Rosenfeld, H.-Burkhard Erbslöh, Bernd Niemeyer, Andreas Prange, Institute for Coastal Reseach, GKSS Research Centre, Geesthacht (Germany)

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A 42 Robert Byrne, Dermot Diamond, Kim K.T. Lau, Christina M. McGraw, Aleksandar Radu, Conor Slater, Adaptive Sensor Group, National Centre for Sensor Research, Dublin City University, Dublin (Ireland)

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A 43 Habibollahi Saeed, Talebi S. Morteza, Dept. of Chemistry, Isfahan University, Isfahan (Iran)

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A 45 Kishore K. Tiwari, Girdhar L. Mundhara, Vinay K. Gupta, School of Studies in Chemistry, Pt. Ravishankar Shakla University, Raipur (India)

A new reagent system for spectrophotometric determination of cerium in environmental and geological samples

A 46 Milada Vávrová, Radim Lána, Institute of Chemistry and Technology of Environmental Protection, Brno University of Technology, Brno (Czech Republic)

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A 47 Stefan Weigel, Eurofins Analytik GmbH, Hamburg (Germany)

Evaluation of an optical biosensor for the drug residue screening of environmental water samples

A 49 Hassan A. Zamani, Dept. of Chemistry, Islamic Azad University, Quchan (Iran)

Cd(II) PVC-based membrane sensor based on N’[1-(2-furyl)methylidene]-2-furohydrazide

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Novel PVC-based Cobalt(II)-selective membrane electrode based on N’-[1-(2-thienyl)ethylidene]-2-furohydrazide

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Zinc(II) PVC-based membrane sensor based on 5,6-benzo-4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8,8,8]hexacos-5-ene

A 52 Balázs Berlinger, Miklós Náray, Gyula Záray, Hungarian Institute of Eccupational Health, Fodor József National Center for Public Health, Budapest (Hungary)

Distribution of metals between the aerosol size fractions in welding fumes

A 53 Gábor Muránszky, Mihály Óvári, István Virág, Gyula Záray, Dept. of Analytical Chemistry, Eötvös Loránd University, Budapest (Hungary)

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A 54 Barbara Cittadini, Giovanni Citti, Emanuele Ferretti, Daniela Maresca, Massimo Ottavini, Enrico Veschetti, Istituto Superiore di Sanità, Dept. of Environment and Primary Prevention, Rome (Italy)

Determination of chlorine dioxide generator performances with suppressed ion chromatography applied to on-line reduced and purged effluents

A 55 Joanna Wilga, Agata Kot-Wasik, Jacek Namieśnik, Gdańsk University of Technology, Gdańsk (Poland)

Possibilities of using of Solid Phase Extraction (SOE) to determination of fluoxetine in water environment

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Monitoring of POP and related compounds by PDMS-coated stir bars in air

A 57 Michael Raessler, Kristin Lober, Annika Lenz, Max-Planck-Institute for Biogeochemistry, Jena (Germany)

Fast and reliable determination of trace concentrations of Ti and Zr in soil samples

A 58 Ana M. Ballesteros, Dolores Pérez-Bendito, Soledad Rubio, Dept. of Analytical Chemistry, University of Córdoba, Edificio Anexo Marie Curie, Córdoba (Spain)

Use of decanoic acid reversed micelles-based coacervation for the extraction of PAHs from surface water and wastewater samples

A 59 Diwakar Tiwari, Hyoung U. Kim, SeungM. Lee, Jae K. Yang, Kwandong University, Yangyang (Korea)

Ferrate(VI) for the oxidation of cyanide in aqueous solutions: a green chemical

A 60 Kamil Motyka, Pavel Mikuška, Zbyněk Večeřa, Antonije Onjia, Institute of Analytical Chemistry, Academy of Sciences of the Czech Republic, Brno (Czech Republic)

Flow-injection chemiluminescence determination of formaldehyde in water

A 61 Barbara Siegfried, Monica Culea, Ristoiu Dumitru, Urs von Gunten, Dept. of Biomedical Physics, University of Babes-Bolayi, Cluj-Napoca (Romania)

Trihalomethane formation kinetics by chlorination of raw water

SUPERCRITICAL FLUID EXTRACTION OF MERCURY FROM AIRBORNE PARTICULATE MATTER

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Mercury (Hg) is an extremely toxic metal, having no biochemical or nutritional function. The majority of toxic effects that can result from exposure are on the central nervous system [1]. Hg exists in a large number of physical and chemical forms with a large variety of properties that determine its complex distribution, biological enrichment and toxicity. Although mercury exists both in particulate and gaseous phases in the atmosphere, but more attention focused on gaseous mercury because of higher concentration and residence time in the air [2]. The various chemical forms of mercury could absorb on surface of airborne particulate matter, Therefore investigation about extraction and its chemistry has important role in the consideration of regional pollution of environment.

In this work, Supercritical fluid extraction (SFE) of mercury from airborne particulate matter has been investigated using supercritical CO_2 and sodium diethyldithiocarbomate (NaDDC) and dithizone (DT) as chelating agents. The samples were collected on quartz fiber filter using a high volume air sampler from the atmosphere of Isfahan city. The extraction was performed with supercritical CO_2 containing chelating agent at 60°C temperature and 160 bar pressure. The extracted samples were then subjected to determination of mercury by gold amalgamation cold vapor atomic absorption spectroscopy (CVAAS). Table 1 summarizes the percent recovery of mercury from airborne particulate matter. As it seen, NaDDC is more efficient than Dt for extraction of mercury from airborne particulate matter.

Table 1: Percent recovery of mercury from airborne particulate matter by SFE using NaDDC and DT as chelating agents

Sample	NaDDC	DT
1	47.3	27.8
2	41.9	28.4
3	35.2	25.7
4	38.6	25.4

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HEAVY METAL EXTRACTABLE FORMS IN GUADIAMAR RIVER SEDIMENTS (SW SPAIN)

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In April 1998, the spill of 6 million cubic meters of mining wastes (acidic waters and piritic sludge) severe polluted the Guadiamar River basin with heavy metals which caused serious damage to the local ecosystem. High levels were found for the following metals: Fe, Zn, Pb, Cd, Cu and Mn, among others.

Studies of the heavy metal pollution in the area have involved determination of total metal levels. Although these data are very useful to take immediate action to prevent the spread of pollutants, they do not provide enough information about their impact on the environment. However, sequential extraction procedures provide information about the different reactive binding strengths of the metal in the different solid phases and about their potential reactivity under different physico-chemical environmental conditions. With these extraction procedures the mobility of metals in the environment can be evaluated.

This work describes a distribution study of the metals Zn, Cd, Pb, Cu, Mn, Fe and Al by fractionation analysis of sediments in eleven samples of the Guadiamar riverbed. The samples were collected in the summer of 2002, four years after the spill and after the area had been cleaned.Total metal contents and metal fractions were determined following a protocol of sequential extraction (ESMTP, 1993) and final determination with the ICP-AES method. Fractionation analysis resulted in the definition of four categories: exchangeable metal (the most available), reducible metal (bound to hydrous oxides of Fe and Mn), oxidizable metal (bound to organic matter and sulfides) and a residual fraction (bound to minerals). Significant increases in the available fraction of some potentially toxic metals like Zn, Cd and Mn were found. The distribution pattern was variable along the river. At the site closest to the mineworks, the soluble forms of Zn, Cd and Mn, were significantly more abundant that those downstream. Pb and Cu were present mostly in the reducible fraction while Fe was present associated in the residual fraction. The fractionation results for the most characteristic metals Zn, Cd, Pb and Cu presented a similar distribution of metal extractable forms to that obtained for surface waters [1-3].

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OPTIMIZATION OF DERIVATISATION METHOD FOR PUTRESCINE AND CADAVERINE (BIOGGENIC AMINES)

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This work describes the systematic optimization of a new derivatisation method for the determination of putrescine and cadaverine; two important biogenic amines of biological and environmental significance. Putrescine and cadaverine are biochemical markers for a range of diseases including cancer, diabetes, arthritis and cystic fibrosis whereas, in food and meat products they are related both to food spoilage & food safety and as such are quality indicators. Previous approaches to the determination of these biogenic amines have used aqueous based derivatisation procedures, followed by evaporation to dryness of the products with resolvation prior to analysis by HPLC, and in some cases GC. Such approaches are not amenable to automation or integration within instrumental systems and so this studies as sought to develop a non-aqueous approach. The pre-column derivatisation of amines by trifluoroacetylacetone (TFAA) with the subsequent analysis by GC/FID & GC/MS is an important first step in moving towards in-trap derivatisation techniques. The derivatisation occurred in a single reaction step between TFAA and biogenic amines in methanol and/or ethanol. The study indicated that the optimized mole ratios for TFAA/putrescine and TFAA/cadaverine reactions are 5.0:1.0 and 5.8:1.0 respectively with a reaction time of 15 min at 95^{o}C. GC/MS methods have also been developed for analysis of the derivatised products. The retention times for the derivatised putrescine and cadaverine were 11.2 and 12.1 minutes respectively using capillary column, CP-Sil 8CB; 30m length x 0.25mm i.d. x 0.25μm film and GC oven programme 150^{o}C for 2 minutes, ramped 15^{o}C/min to 280^{o}C, and finally held at this temperature for 3.3 minutes (total 14min). The main mass fragments 69, 96, 110, 138 (for derivatised putrescine) and 69, 96, 152, 305, 334 (for derivatised cadaverine) are used in MS ionization mode, Electron Impact Selective Ion Storage (EI-SIS). Similarly, Chemical Ionization Selective Ion Storage (CI-SIS) methods employed molecular ions 361 and 375. The calibration curves for putrescine and cadaverine demonstrated linear trends with correlation coefficients (R^2) ranging from 0.9846 to 0.9996 over concentration ranges of 0.1 to 12μgcm^{-3}. The developed methods are useful in the trace level quantitation of both the amines down to 0.3μgcm^{-3}. The derivatisation method reduced the overall sample preparation time from 90-120 minutes to 30 minutes whereas, the GC/MS methods are very selective and take 14 minutes only. This research (a part of PhD programme) is an important first step in moving towards in-trap derivatisation techniques.

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DEVELOPMENT OF A NOVEL BIPYRIDYL BASED FLUORESCENT SENSOR FOR THE DETECTION OF NICKEL(II) IN ENVIRONMENT

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Nickel is one of the most toxic elements among transition metals. Allergic contact dermatitis, is the most frequent effect of exposure to nickel(II). Nickel hypersensitive may also cause pulmonary asthma, respiratory disorders, including bronchitis. Due to this exposure a considerable amount of nickel(II) is found in urine and other biological samples of the workers working in nickel refineries, welding shops and electroplating industries. Therefore, the determination of nickel(II) in biological fluids is very important and researches are on for finding efficient method for its determination. Molecular fluorescence is an important method because of its high sensitivity of detection down to a single molecule, recognition and/or self-assembly directed selectivity, on–off switchability, sub-nanometer spatial resolution with submicronvisualization, and sub-millisecond temporal resolution [1, 2]. In the present study, we have designed a new fluorescence chemosensor suitable for nickel ion detection in aqueous medium. The new bipyridyl based molecule N,N′-bis(2-aminoethyl)-2,2′bipyridine-3,3′dicarboxamide ($BNA(en)_2$) (Fig 1) has been synthesized and characterized through elemental analyses, UV-VIS, IR, ^1H NMR and ^{13}C NMR spectral data.

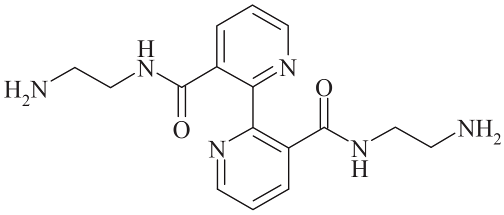

Fig 1. *N,N'-bis(2-aminoethyl)-2,2'bipyridine-3,3'dicarboxamide* ($BNA(en)_2$).

It was observed that $BNA(en)_2$ is highly specific in selectivity and gives sensitive response of fluorescence enhancement towards nickel(II) in aqueous medium due to dixotetraaza unit. $BNA(en)_2$ shows fluorescent enhancement on binding with nickel(II) whereas Ca^{2+}, Mn^{2+}, Fe^{2+}, Cu^{2+}, Zn^{2+} have little effect on fluorescence enhancement, when excited at λ_{ex}=364 nm. Stoichiometric studies indicate that $BNA(en)_2$ forms 1:1 and 3:2 types of complexes with nickel ion. The fluorescent intensity for the system 3:2 was found to be higher than that of 1:1. Potetiometric and spectrophotometric titration were carried out to study the co-ordination properties of $BNA(en)_2$ with the metal ions Ni^{2+}, Mn^{2+}, Fe^{2+}, Cu^{2+}, Zn^{2+} at an ionic strength of 0.1M $NaClO_4$ at 25±1°C in aqueous medium and the stability constant of the various species were determined. $BNA(en)_2$ acts as a potential fluorescent sensor for the nickel ion in aqueous medium.

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PLUTONIUM ISOTOPES CONCENTRATION IN SEAWATER ALONG THE ALGERIAN COAST

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Abstract

The International Atomic Energy Agency has organised in the framework of the regional project RAF/7/004, in collaboration with COMENA and ISMAL, during august 2001, a scientific campaign along the Algerian coast, on board of the research vessel M.S. Benyahia of ISMAL. Three stations, at the centre, east and west, were selected to collect five seawater samples for each water column reaching a maximum depth of 2000 m, using a stainless steel water sampler of a volume of 250 litres. After recording the marine environment parameters (T°C and S), seawater samples were conditioned and preconcentrated to precipitate plutonium isotopes using $MnCl_2$, in order to proceed to plutonium extraction by radiochemical separation. Concentration results in µBq/l of plutonium isotopes were obtained in the range of 26 to 102. Distribution of Pu through the plot of its profile was studied and the inventory was estimated. The obtained results were compared to those found by other authors in the same Mediterranean sea area.

Key words : Marine Environnement, Pu isotopes, nuclear fallout, inventory.

Evaluation of a novel orthogonal plasma-source time-of-flight mass spectrometer hyphenated with laser ablation for the simultaneous determination of metals in gels

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Mass spectrometry in combination with the inductively coupled plasma (ICP-MS) as ionisation source has become the most important tool in atomic spectroscopy for the determination of trace elements in various matrices. Conventional MS-systems, equipped with scanning-based analysers like quadrupole or sector field MS, are hampered by their limited multielemental detection capability for the measurement of short signals. In such systems the measurements are performed sequentially, only one mass at a time, which results in a loss of precision and/or sensitivity with an increasing number of isotopes monitored. In contrast to those systems, a time-of-flight mass analyser is operated in a truly simultaneous fashion, providing several important advantages over conventional ICP-MS detection systems. It not only permits the measurement of almost all elements and isotopes in a transient sample pulse, but also enables a great number (up to 30,000) of complete atomic mass spectra to be recorded each second. This high spectral-generation rate makes TOFMS ideally suited for the measurement of very short transient signals, resulting e.g. from electrothermal sample evaporation or laser ablation of solid material. Furthermore, because each complete mass spectrum is derived from the same brief pulse of ions, high precision can be achieved by using either isotope-ratioing or internal standardization techniques. As a result the compromise between mass coverage and sensitivity and precision inherent to scanned systems does not apply to the TOFMS.

To underline the aforementioned advantages, the analytical performance of the novel system was compared with data obtained by a PerkinElmer “Elan6000” quadrupole ICP-MS. To investigate the influence of the monitored mass range on the limits of detection and isotope ratio precision during the detection of transient signals, the integration interval was kept at 500 ms while the number of monitored isotopes was successively increased.

In biochemistry one of the most powerful tools for protein-analysis is represented by a combination of protein separation using gel electrophoresis prior to a detection step using gel staining or marker techniques. As a disadvantage, these techniques do neither allow a reliable quantification nor a simultaneous detection of heteroelements in proteins, such as e.g. metals, within a single protein-spot on the electrophoretic gel.

Due to its characteristics, ICP-MS is ideally suited for protein analysis. A second focus of this presentation is the development of a method for the direct determination of metals in agarose gels through the coupling of laser ablation with the novel ICP-TOFMS. Wet gels, spiked with Mg, Co and Mn were ablated and detection limits in the lower µg g^{-1} range were achieved. Advantages and disadvantages of this approach will be explored, and future developments in ICP-TOFMS will be outlined.

SIMPLE METHODOLOGY FOR MONOMETHYLMERCURY DETERMINATION IN AQUATIC PLANT TISSUES

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Large number of studies has been carried out on the toxic impact of the neurotoxin monomethylmercury (MMHg) [1]. Several analytical methods have been proposed to determine this compound in water, sediments, seston, and fauna but fewer efforts have been done with aquatic plants. An assessment of monomethylmercury may be of great relevance in salt marsh plants due to the tendency of accumulating high levels of contaminants in belowground biomass [2].
A simple method to determine MMHg in aquatic plants, involving microwave acid digestion ($HBr/CuSO_4$), toluene extraction, H_2S cleaning procedure and preconcentration of MMHg in dithizone was developed. Separation as well as quantification was performed by GC-ECD. Obtained and certified MMHg concentrations for an international certified reference material (AIEA-104/TM) showed no statistically differences (α=0.05). Low detection limits (0.54 pmol g^{-1}), good repeatability (CV< 2%) and recoveries (96-101%) made this method a useful tool for rapid MMHg determination in roots, stem and leaves of aquatic plants. No statistical differences ($p<0.05$) were found in MMHg concentrations by spiking samples with different concentrations of Hg^{2+}. This indicates that no artifact formation of MMHg occurs during the analytical procedure.
The method was applied to tissues of *Halimione portulacoides, Arthrocnemum fruticosum* and *Spartina maritima* from marshes with different anthropogenic pressures. It was found a broad concentration range: from 0.80 pmol g^{-1} in aboveground tissues to 3760 pmol g^{-1} in roots. The determination of MMHg partitioning in plants is of great importance to better understand the Hg cycling in wetlands, and also to assess toxicity since marshes are breading fields for many benthic fauna, fish juveniles and birds.

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APPLICATION OF WATER SAMPLING TECHNIQUES FOR ASESSMENT OF BIOAVAILABLE METAL CONCENTRATIONS IN THE SVITAVA RIVER

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During the April 2005 and October 2005 concentrations of Cd, Cu, Cr, Pb, Ni and Zn were monitored in Svitava River (Czech Republic, South Moravia). Except of commonly regular water sampling providing information about the total dissolved and total metal concentrations, the diffusive gradient in thin films technique (DGT) [1] was used for sampling of kinetically labile metal species. All of measured concentrations were compared with an amount of accumulated metals in the *Fontinalis antipyretica* moss species [2] deployed in the Svitava River together with DGT sampling units. Accumulated mass of Zn, Cr, Cd and Pb in *Fontinalis antipyretica* corellated very well with the measured DGT concentrations, while accumulated mass of Cu corellated rather with the dissolved concentration. No corellation between all of measured Ni concentrations and accumulated mass of Ni in *Fontinalis antipyretica* was found.

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LIQUID CHROMATOGRAPHY - MASS SPECTROMETRY DETERMINATION OF ACRYLAMIDE IN DRINKING WATER ACCORDING TO THE EUROPEAN UNION DIRECTIVE 98/83.

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The first liquid chromatography-mass spectrometry (LC-MS) method suitable for quantification of acrylamide monomer (AA) in drinking water according to the requirements of the European Union Directive 98/83 [1] has been developed.

Pre-concentrated samples of drinking water have been directly injected in a Zorbax NH2 column, eluted with a mobile phase consisting of acetonitrile-isopropanol (50:50, v/v) containing 0.1% of formic acid and analysed by positive TurboIonSpray-MS in the selected ion monitoring (SIM) mode. ($13C_3$) Acrylamide (I.S.) was used as internal standard.

The method was validated (linearity, precision, trueness, limit of quantification, limit of detection, specificity) according to the requirements defined by the European Community [1]. Good linearity over the concentration ranges tested (0.02-1.0 $\mu g \cdot L^{-1}$, $r^2 > 0.99$) was achieved. The limit of detection (LOD) and limit of quantitation (LOQ) are estimated at 0.01 and 0.05 $\mu g\ L^{-1}$, respectively. The results for precision (repeatability and reproducibility) and trueness fell within the ranges specified.

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ELEMENTAL ANALYSIS OF AEROSOLS WITH SR-TXRF: DIRECT CALIBRATION WITH PICO-DROPLETS GENERATED BY INK-JET PRINTERS

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The impact of the chemical composition of airborne particles and its particle size dependence on air quality and on climate has become apparent in recent years [1]. Particle sources and sinks are strongly related to their size and so is the chemical composition of most aerosols e. g. automobile traffic aerosols with regard to Pb, Pd and Pt [2]. Multiphase processes in the aerosol are highly variable both in time and space. A number of metals and also non-metals like P, S, Cl and Br undergo chemical transformations typically on the time scale of hours. These requirements translate to 10-1 pg and even less of trace elements to be determined. TXRF is a very sensitive method for element determinations which has been successfully used for size-resolved aerosol analysis [3] e.g. direct analysis of airborne dust collected with an impactor on glassy carbon and Si-wafer carriers using conventional x-ray tube excitation. Even more sensitive is SR-XRF. Its combination with size-resolved aerosol sampling is promising, as already shown in Ref. [4].

An accurate and reliable calibration of SR-TXRF of aerosol samples collected is necessary but difficult: The addition of standard solution with micropipettes may suffer from destroying the sample spots or lines as a result of the relatively high amount of liquid. On the other hand external calibration requires time-consuming scanning measurements to obtain good precision. Indeed, in SR-TXRF the diameter of the exciting beam is limited (~1 mm at 17 keV at the HASYLAB beamline L). Here we present the results of a study into the suitability of a calibration in aerosol sample analysis by SR-TXRF using pico-droplets (i.e. 5-130 pL), generated by inkjet printers. The procedure could be made compatible to aerosol particle sampling using a Berner impactor. In the latter the aerosol particles are collected in different complex patterns on the impaction stages. The device is known to exhibit excellent characteristics for size separations. The diameter of the dried droplets ranges from 50-200 μm for ink droplets printed on hydrophobic surfaces. The reliability of the dosing of standard solution was satisfactory and enables a spotting of well-defined absolute amounts in the picogram range and below for cobalt, for instance. Further, it was shown that a printing according to a given pattern in the micrometer range can easily be done with the aid of common computer software.

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GC/MS OF 2,4-DIETHYL-3-*N*-PROPYL-5-PENTANOLIDES

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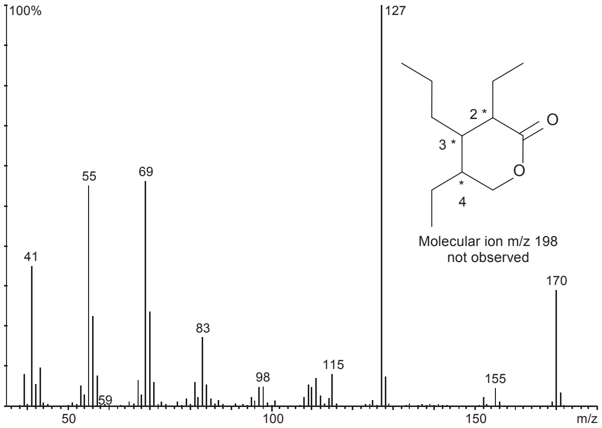
GC/MS nontarget screening for organic compounds of river waters provided comprehensive information on occurrence and distribution of contaminants along the Elbe and Odra rivers.

In water samples from both rivers a group of 4 substances showing nearly identical mass spectra was observed [1, 2]. Identified as the diastereomers of 2,4-diethyl-3-*n*-propyl-5-pentanolide, these lactones occurred in the river Rhine and industrial waste water, too [3]. 2,4-diethyl-3-*n*-propyl-5-pentanolides are formed as by-products of 2-ethylhexanol, an industrial large scale product, and one of most important alcohol-components for phthalate- and adipate- plasticizers.

The identification of the four isomeric lactones proceeded as follows: In the GC/MS analysis four compounds with nearly identical mass spectra were found, and therefore, considered as closely related isomers. The mass spectra did not match any in mass spectral data bases. Separation on a chiral GC column indicated at least three chiral centers in the molecule. GC/MS high resolution mass spectra resulted in atomic compositions of fragment ions, and the highest mass observable in the EI-spectra was m/z 170 ($C_{10}H_{18}O_2$). Ammonia-CI revealed a molecular weight of 198. Therefore, an elemental composition of $C_{12}H_{22}O_2$ ($C_{10}H_{18}O_2$ + C_2H_4) or $C_{11}H_{18}O_3$ ($C_{10}H_{18}O_2$ + CO) of the molecular ion was considered. The presence of a lactone carbonyl group could be deduced from a GC/FTIR analysis of river water extracts. A search in CA- and Beilstein-databases for $C_{12}H_{22}O_2$ resulted in a large number of hits, but just a few δ-lactones with tree chiral centers, and this, as well as the mass spectral fragmentation pattern made 2,4-diethyl-3-*n*-propyl-5-pentanolide the most promising candidate. This assignment was verified by the synthesis of the diastereomeric lactones from 2-ethyl-2-hexenal and butanal.



Although very similar, the mass spectra of the pentanolides are not identical. Two diastereomers show a fragment m/z 115 (~8 %) which is much smaller in the two others (~1 %). Formed by loss of a butenyl radical from the *McLafferty*-Ion, m/z 170, the difference in the intensities of the fragment m/z 115 has its origin in the different relative configuration of the stereogenic centers at C-3 and C-4 in the lactone ring. Therefore, two pairs of diastereomers can be distinguished by mass spectrometry.

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GC/FT-IR ANALYSIS OF DI-*ISO*-PROPYLNAPHTHALENES

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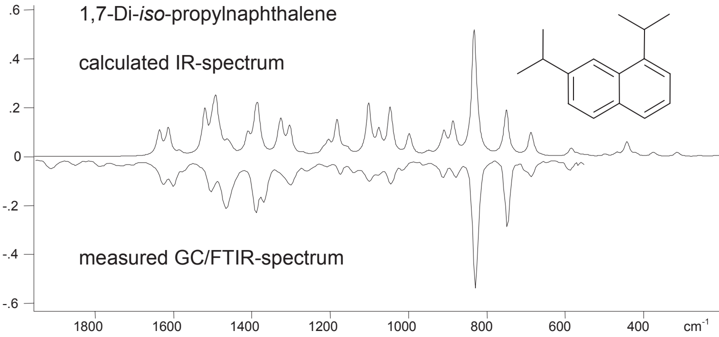
Di-*iso*-propylnaphthalenes (DIPN) are produced and in use as a mixture of isomers. DIPN have been shown to migrate from paper and packaging materials into foods [1, 2], and associated with tary off-flavours in drinking water [3]. DIPN are frequently observed pollutants of surface waters and aquatic sediments. We determined concentrations of 10 – 120 ng/L in Rhine river water between Bonn and Wesel, and up to 80 ng/g in Lippe river sediments for the sum of the isomers. Technical DIPN consists mainly of seven of the ten possible isomers (1,3-, 1,4-, 1,5-, 1,6-, 1,7-, 2,6-, 2,7-), and may contain minor amounts of the *ortho*- (1,2-, 2,3-) and *peri*- (1,8-) compounds. Gas chromatography on non- or medium-polar columns (SE 30, SE 52, SE 54, OV 17, OV 1701) resolves technical DIPN into 5 or 6 major and 1 minor peaks, and on carbowax-type stationary phases (INNOWAX, FFAP) into 7 major and 2 minor peaks. The mass spectra of different DIPN are virtually identical and do not allow to assign DIPN-isomers. IR-spectroscopy has been used to assign single DIPN by comparision with calculated IR-spectra [4-6].
To provide a basis for the isomer-specific analysis of DIPN in environmental samples, we determined linear retention indices of the components of technical DIPN on non-polar and polar GC-columns and aquired gas phase IR-spectra of the major DIPN-isomers by GC/FTIR-analysis.



IR-spectra of all DIPN-isomers were calculated using density functional therory (DFT) with Becke's three-parameter exchange functional [7] in combination with the Lee–Yang–Parr correlation functional [8] (B3LYP). A 6-311G(d,p) basis set gave excellent matches of theoretical and experimental spectra of 1,3-, 1,4-, 1,7-, and 2,6-DIPN after scaling of vibrational frequencies. However, for the 1,5-, 1,6-, and 2,7-isomers better fits to the experimental spectra were obtained after reoptimizing the geometry with a 6-311+G(d,p) basis set, and the spectra calculated finally allowed to assign the structures of 7 major DIPN-isomers to the corresponding GC-peaks.

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PHARMACEUTICALS, ENDOCRINE DISRUPTORS AND FAECAL STEROIDS IN TRANSITIONAL WATERS

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In recent years, it has been reported that many phamaceuticals, personal care products (PPCPs) and endocrine disruptors (EDCs) survive treatments in sewage plants. This has been demonstrated through research that compares concentrations in influent flows and those in effluent discharges. As a consequence, these families of compounds have been found at low levels (ng/L) in rivers and transitional waters (i.e. estuaries and coastal waters). However, the persistence, transformations, speciation, fate and toxicity of these compounds in aquatic environments remains poorly investigated.

Previous studies of PPCPs in aquatic environments have demonstrated that highly sensitive analytical methodologies (with strict quality assurance schemes) are required to assess their levels. Our approach in this research was to develop and upgrade current methods [1, 2] and to combine the determination of PPCPs, EDCs and also well used feacal steroid molecular organic markers of sewage pollution in coastal waters (e.g. coprostanol). The rationale behind this approach is that the PPCPs and EDCs are primarily derived from sewage outfalls and the faecal steroids afford an additional tracing mechanism. Our research has used SPE (OASIS® HLB, Waters) for the extraction of the water samples, followed by a single derivatisation step (MTBSTFA) and selected ion monitoring GC-MS for their determination. Preliminary results indicate few matrix interferences and both acceptable accuracy and precision throughout the selected calibration range (20-800 pg injected). The selected GC-MS conditions provide excellent resolution in less than 40 minutes. It is also highly sensitive with current limits of detection typically less than 10 ng/L (based on a concentration factor of 5000). The presence of some of the selected PPCPs, EDCs and feacal steroids has already been demonstrated in environmental samples. Further research (2005-2007) will be directed to refine/test the analytical protocols, introduce strict quality controls, and to assess both the spatial and temporal occurrence and transport/fates in estuarine environments. It is envisaged that this information will contribute to European Chemical Policies and the EU Water Framework Directive.

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METAL CONTENT IN BLOOD OF FREE RANGING HARBOR SEALS (*PHOCA VITULINA*) AND THEIR EFFECT ON IMMUNOLOGICAL FUNCTIONS

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Marine mammals as top predators are notably exposed to environmental contaminants. The accumulation of metals in tissues is already perceived. Toxicological studies of living animals are rarely due to limited choice of sample types and quantity. The aim of this investigation was to acquire the relationship between the metal content in blood and their immunological impact on seals. Immunotoxic pollutants my cause an imbalance of the immune system and were suggested to play a role in the incidence of infectious diseases.

Fresh whole blood samples from 28 harbour seals (*Phoca vitulina*) catched at the German and Danish Wadden Sea were analyzed.

The measurements of the total concentration of 22 essential and non-essential elements were performend by three different analytical methods: ICP-MS, TXRF and ICP-SF-MS.

In addition, immunological investigations were carried out using a lymphocyte transformation assay (LTT) according to MELISA® (memory lymphocyte immuno-stimulation assay) modification.

The T-lymphocyte response to metals in terms of hypersensitivities were determined for 13 animals. The sensitizing metals were Be, Al, Ti, Cr, Ni, Mo, Sn, and Pb. These elements were known allergens in humans but normally not measured in environmental monitoring programs. Seals with an Al-, Cr-, and Ni- sensibilisation also showed the highest concentration of these metals in blood. No age or gender differences in metal body burden were ascertained but significant geographical differences were determined.

Therefore high levels of metal concentrations in blood of seals developing metal-specific hypersensitivity support the suggestion of immunological dysfunction in seals feeding on fish from polluted coastal waters.

This results show the value of a combined biological and effect-monitoring tool to investigate metal pollution and their hazardous impact on marine mammals.

SPECIATION OF IODINE COMPOUNDS IN THE COSTAL/MARINE ATMOSPHERE: CONTRIBUTIONS TO UNDERSTAND NEW PARTICLE FORMATION FROM NATURAL PRECURSORS

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The study of the sources and formation pathways of new particles in the troposphere is presently a subject of considerable interest, prompted by the role of aerosols in global climate and their influence on heterogeneous processes. Uncertainties in the natural background source of atmospheric aerosol particles complicate estimates of the influence of anthropogenic aerosols. Therefore, one goal of current research activities is the identification and quantification of natural particle formation processes in the troposphere. Recent field and laboratory studies also point to coastal sites as a biogenic source region for new particle formation [1,2]. The current understanding is that volatile iodine precursors, such as diiodomethane or even molecular iodine are released by marine algae into the atmosphere, where they are rapidly photolyzed during daytime and form low volatile iodine oxides which finally self-nucleate [3,4]. However, still the characterization and identification of the precursors and products is analytically challenging and the detailed particle formation mechanisms remain unclear. This contribution will present and discuss current analytical concepts for the speciation of iodine compounds in the coastal/marine gas and particle phase as well as results from field measurements at a coastal research station in Mace Head, Ireland.

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APPLICATION OF 1-PHENYL-3-METHYL-4-STEAROYL-5-PYRAZOLONE DOPED MESOPOROUS SILICA AS A SORBENT FOR METAL DETERMINATION

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The metal extraction properties of 1-phenyl-3-methyl-4-stearoyl-5-pyrazolone (HPMSP) doped mesoporous silica prepared by a template-tailored sol-gel process were investigated in both batch and column methods. The metal sorption capacities of the modified sorbent determined by batch experiments were governed not only by the pH of metal solution but also the presence of salts in metal solution. The capacities of the modified silica at optimum conditions for the extraction of Cd(II), Pb(II) and Zn(II) were found to be 0.21, 0.12 and 0.32 mol/kg, respectively. A 2^3 factorial design served for the determination of principal parameters on the Cu(II) desorption efficiency of the sorbent reached the conclusion that the significant factors were the amount of Cu(II) and the concentration of HNO_3 as eluent. The Cu(II) sorption capacity of the modified silica determined by column process was found to be 0.0998 mol/kg. The potential application of the HPMSP doped mesoporous silica to the preconcentration of Cu(II) from aqueous solution was accomplished with the maximum preconcentration factor of 40. The study of metal adsorption-desorption cycles showed the reusability of the sorbent without considerable loss of adsorption capacity.

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Determination of trace elements in soil and plants in the Damascus basin of Syria by using instrumental neutron activation analysis

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Instrumental neutron activation analysis (INAA) methods have been used for the determination of some major, minor and trace elements such as (AS, Cr. Co, Ni, Zn, Sb, Sc, Ce, Ti, Fe, BA, Sr, Mn and V) in some kinds of plant leaves with their soil. Accuracy of measurements have v been estimated by triplicating the sample as well as the reference. Analysis results showed an increase in the concentration of the heavy and poisonous elements as a result of increasing the house, animal and industrial wastes.

The obtained accurate and reliable data on microgram quantities of some trace elements in plants and their soil will serve as the base line values, and will be helpful to monitor the changes in the trace elements content and the of plant leaves and their soil in Damascus basin, and observation of this basin contamination with the heavy and poisonous elements in the future.

Key Words: Instrumental Neutron Activation Analysis (INAA), trace elements, Plant leaves, Soil, Damascus basin.

EFFECT OF CISPLATIN ON PEAS (*PISUM SATIVUM L.*)

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Platinum complexes play an important role in the chemotherapy of various malignancies. The biological activity of the first platinum based cytostatic drug – cisplatin (*cis*-diamminedichloroplatinum(II)), which is still one of the most frequently used cytotoxic agent, was discovered in 1965 by Rosenborg during his studies on the effects of an electric current on bacterial growth. Since then hundreds of platinum(II) and platinum(IV) complexes have been synthesized and evaluated as anticancer agents over past 40 years. Although platinum based cytostatic drugs have been successfully used in the chemotherapy of cancer for more than 30 years, its biochemical mechanism of action is still unclear. The current accepted opinion about their mechanism of action is that the drugs induce their cytotoxic properties through binding to the nuclear DNA and subsequent interference with normal transcription, and/or DNA replication mechanisms. A huge number of scientist investigate influence of cisplatin on animal DNA, but it is less known about influence of cisplatin on plants, which could be treated by wastewaters from hospitals. Thus we aimed on investigation of effect of cisplatin on peas (*Pisum sativum* L.). We have conducted three different experiments: **Variant I**: peas kernels were germinated in the presence of cisplatin (0, 5, 40 and 160 µM) for 24 hours. After that, the kernels were transferred to vessel and cultivated for 14 days. **Variant II**: peas kernels were germinated and then were transferred to vessel, where has been added 200 ml of 0, 5, 40 and 160 µM cisplatin. **Variant III**: peas were germinated in the presence of wastewater contained cisplatin for 24 hours. After that, the kernels were transferred to vessel and cultivated for 14 days. We determined thiols and cisplatin content in the treated peas. We utilized adsorptive transfer stripping differential pulse voltammetry for determination of the total thiol content [1]. As for determination of cisplatin, we utilized differential pulse voltammetry using solid carbon electrodes and suggested biosensor [2]. The results obtained shows that cisplatin markedly influence thiol content in the treated peas.

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ELECTROCHEMICAL METHODS AS SUITABLE TOOL FOR DETERMINATION OF BIOLOGICALLY IMPORTANT THIOLS

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Sulfur exists in multiple stable oxidation states; hence it is a versatile component in biological systems. The most active and reduced form of sulfur in biomolecules is the thiol group (-SH), present in number of biologically active compounds such as the amino acid cysteine, the non-protein forming aminoacid homocysteine and glutathione, which is the most abundant non-protein molecule in mammalian cells. Thiol compounds have a huge number of biological activities, e.g. control of gene expression and receptor signalling, signal transduction and heavy metal detoxification. They could also serve as markers for many health troubles.

Electrochemical detection (ED) is an attractive alternative method for electroactive species detection, because of its inherent advantages of simplicity, ease of miniaturization, high sensitivity and relatively low cost. For these unique properties we have used electrochemical detection to determine biologically active compounds. We recently published a new approach for evaluation of LC-ED parameters. These evaluated parameters were used for the determination of cystein, reduced and oxidized glutathione, and phytochelatins2 [1]. In this work we present a comprehensive study of thiol behaviour using flow injection analysis/HPLC with electrochemical detection. This technique was consequently used for simultaneous determination of cysteine, cystine, N-acetylCysteine (NAcCysteine), homocysteine, reduced glutathione (GSH), oxidized glutathione (GSSG), desGlycinePhytochelatin (DesGly-PC) and phytochelatins (PC_2 and PC_5) in biological samples (maize plant tissues treated by cadmium and chlorinated organic pollutants).

The effect of different potentials of working electrodes, organic solvent contents in mobile phase, isocratic and gradient elution on simultaneous determination of thiol compounds (cysteine, cystine, NAcCysteine, homocysteine, GSH, GSSG, DesGly-PC and phytochelatins) were described and discussed [2]. These thiol compounds were well separated and detected at most suitable HPLC-ED conditions as follows – mobile phase: 80 mM trifluoroacetic acid and methanol with a gradient profile. Flow rate was 0.8 ml.min^{-1}, column and detector temperature 25 °C and electrode potential 900 mV. We were able to determine tens of femtomoles (3 S/N) of the thiols per injection (5 µl), except for PC_5 whose detection limit was 2.1 pmole. It clearly follows from the results that HPLC-ED technique can be used for sensitive analysis of thiols. As for analysis of treated maize, we found out that content of GSSG increased with increasing applied Cd(II)concentration and time of treatment.

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ELECTROTHERMAL COLLECTION OF HYDRIDE FORMING ELEMENTS ON A MOLYBDENUM-FOIL STRIP FOR DETECTION BY ATOMIC SPECTROMETRY METHODS

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Trapping behaviour of As, Bi, Sb and Se hydrides on the bare and modified molybdenum surface were investigated in a prototype of miniature electrothermal trapping/vaporization (ETV) device. It is based on a strip of the molybdenum foil and combined with miniature hydrogen diffusion flame for specific analyte detection in atomic absorption spectrometry system. Influence of trapping temperature, modification of the foil surface with noble metals – Ir, Pt and Rh, distance between the orifice of the injection capillary and the strip, argon carrier gas flow rate and composition of the gaseous phase (argon-hydrogen-oxygen) was investigated. Analytical figures of merit (LOD, LOQ) were assessed. Maximum trapping efficiency of Bi, Sb and As, Se was found on a bare molybdenum surface at temperatures of 550ºC, 750°C and 1200°C respectively. In contrary to As and Se, modification of the surface reduces trapping efficiency of Bi and Sb at higher amounts of modifiers (>30 μg) tested. Presence or absence of hydrogen in the gaseous phase during collection step does not play significant role in trapping Sb and Bi. Efficient trapping of As and Se is achieved only in hydrogen-rich atmosphere (>40 ml min^{-1} H_2). Some mutual interference effects of co-generated hydride forming elements were also studied and discussed.

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GLOBAL ASSESSMENT OF VOLATILE ORGANIC COMPOUNDS IN AMBIENT AIR

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Abstract: VOCs are an important group of air pollutants to study as they contribute to two of the most serious air quality problems. Firstly, they have been demonstrated to be active in the formation of photochemical smog and ground level ozone production. Secondly, several VOCs found in urban air are commonly accepted carcinogens (benzene, 1, 3-butadiene, formaldehyde etc) (Cetin et al., 2003; Dewulf et al., 2002; Chiu et al., 2005) Two of these compounds (benzene and 1,3-butadiene) account for 68% of the cancer risk from all vehicle related pollutants, whereas in comparison, particulate matter accounts for only 28% (USEPA, 1995). In view of the health and environmental hazards of VOCs, their investigation has always been a scientific topic although regular monitoring of VOCs got some momentum only in the recent past. Our effort is to make a snap-shot indication of the levels of VOCs in ambient air in various cities worldwide along with sampling technique, type of sorbent, method of extraction, duration of sampling etc. Similarly to criteria pollutants, many other VOCs need to be monitored regularly as well. Only few studies on the levels of volatile organic compounds present in troposphere have been done outside of the USA, Europe and Australia. Many more places are left uncovered in monitoring studies. Benzene, toluene, ethylbenzene and xylene (BTEX) are the compounds measured in most of the locations while measurement of compounds like MTBE, halogenated hydrocarbons or aldehydes and other compounds are reported only in some places. It's also clear from the study that thermal desorption and canister methods are gaining preference over solvent extraction method although some differences in results between canister and adsorbent tube are reported.

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Survey of mercury and methyl mercury in fish

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Total mercury and methyl mercury were measured in 400 samples of commercial fish. Combustion gold amalgamation method (mercury analyzer) was used for determination of total mercury. GC-ECD coupled with HR-Thermon-Hg column and solvent extraction (AOAC official method 988.11) was adopted for that of methyl mercury. The average recoveries of the samples for methyl mercury were in the range of 81~106%. The total mercury and methyl mercury found were in the range of [min-max (mean), unit: mg/kg]; 0.006-0.455(0.057) and 0.004~0.120(0.022) in 14 species of general fishes. In terms of predatory fish, the total mercury and methyl mercury were in the range of 0.014-1.565(0.318) and 0.006-0.901(0.165) in tuna, 0.020-2.315(0.563) and 0.012-0.897(0.212) in Marlines, 0.020-2.315(0.563) and 0.012-0.897(0.212) in canned tuna. The percentage of the methyl mercury in total mercury were 13.1~85.4(43.0) for general fishes, 19.7~105.2(55.0) for tuna, 18.4~91.7(41.5) for marlines, 38.3~93.8(49.2). In the regard of the intake of mercury, estimated weekly intake of total and methyl mercury due to general fishes, tuna, marlines, canned tuna are less than 1.5% and 2.4% of the Provisional Tolerable Weekly Intake (PTWI) and always below the PTWI, even in the worst case of 99th percentile intake.

PARTICLE SIZE-RESOLVED DETERMINATION OF THE ELEMENTAL COMPOSITION OF ATMOSPHERIC AEROSOLS IN A SUBTROPICAL COASTAL CITY, SALINA CRUZ, MEXICO, BY TOTAL-REFLECTION X-RAY FLUORESCENCE SPECTROMETRY

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Fine particulate matter influences cloud droplet formation, radiation (and, hence, climate), provides a medium for chemical transformations and is hazardous to human health. Key parameters for all these implications are particle size and chemical composition. Total reflection x-ray fluorescence analysis (TXFA) has been applied for multi-element analyses of aerosols [1,2]. In tropical and sub-tropical climates particulate matter removal (by rain), pollutant's dispersion and processing in clouds differ considerably from temperate climates. Many coastal areas are densely populated and often heavily polluted. We studied the variation of physical and chemical properties of aerosols at ground level during the wet season, June 2004, in the city of Salina Cruz, situated on the Pacific coast of the Isthmus of Tehuantepec (16.2°N, 95.2°W). The city, ca. 200 000 inhabitants, hosts the country's largest oil refinery. The site was in a backyard, 15 m a.s.l., close to road traffic sources and distanced 2-4 km from the refinery and 1.5 km from the coast (harbour).

For mass (gravimetry) and elemental analyses particles were collected by a Berner low-pressure round nozzle cascade impactor using 4 stages corresponding to 0.1-0.25, 0.25-1.0, 1.0-4.0 and 4-16 μm of aerodynamic particle size. Sampling times were 10-15 h and sampling flow 20 L min^{-1}. The impaction plates were modified such as a small part of it consisted of a plastic support (Persplex ®) for TXFA. By covering the plastic supports with a tape of which a central area of 8 mm by diameter had been punched out, only a small fraction of these was exposed (1-10 impaction spots). The total content of Si, Cl, K, Ca, Ti, V, Mn, Fe, Ni, Cu, Zn, Br and Pb in filter samples was determined by TXFA without any further sample pretreatment. Sc was added as an internal standard. Detection limits for individual impactor stages based on $\mu + 3\ \sigma$ of 5 field blanks corresponded to 15-100 ng m^{-3} for Cl, K and Ca, 1.5-20 ng m^{-3} for Ti, Fe, Ni, Cu, Br and Pb and 0.2-1 ng m^{-3} for V, Mn and Zn.

Advection to the site was determined by the diurnal cycle of land and sea breezes. Re-circulation of pollution transported off-shore previously was significant [3]. We present results on concentration levels and the influence of sources and meteorological conditions on these.

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PESTICIDE RESIDUES IN WELLS AND BORES

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After tourism, agriculture is the second most important industry in terms of source of income in the Canary Islands. The excellent quality of the bananas, tomatoes, courgettes and other vegetable crops grown on the islands is well-known not only locally but also nationally and indeed internationally.

In recent years traditional farming has been supplemented by a considerable increase in covered greenhouse-style farming. Both systems commonly use fertilizers and pesticides to raise production levels, and their residues drain through the soil into well and resevoirs or, when the crops are grown in a coastal region, directly into the sea.

For the first time in Gran Canaria a study has been carried out of the possible presence of pesticide residues in wells and bores sourced from a water vein that may have been contaminated by pesticides used locally. Water from this same vain is otherwise mixed with water from a desalination plant for commercial purposes.

In summary, a study has been made of pesticide residues in bores and wells in the south-eastern area of the island of Gran Canaria (Barranco de Tirajana), where the principal crops grown are tomatoes, potatoes, various types of fruit tree and flowers. These crops have been treated with commercial pesticides whose active ingredients include, amongst others, Lindane, Aldrin, Dieldrin, etc.

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SEPARATION OF MOLECULAR TRACERS SORBED ON ATMOSPHERIC PARTICULATE MATTER BY FLASH CHROMATOGRAPHY.

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Flash chromatography is a medium-pressure separative technique developed by Still & al (1978) [1], which allows the separation and/or the purification of various samples.
It is an alternative to the gravity-fed chromatography sometimes too slow and inefficient. This method is carried out with a column filled with silica gel (stationary phase) crossed by a solvent (mobile phase), which eluates the sample according to his polarity. This solvent circulates under pressure in order to increase its flow, whereas in traditional chromatography, the solvent moves under the effect of the gravitational force. So the time necessary to the purification of the sample is considerably decreased and provides a better resolution.
Pre-packed columns in silica gel (very polar, normal phase) are used. The column is filled with an isocratic or gradient solvents, the polarity of eluent is thus very flexible in order to reach an optimal separation of the compounds. It allows the separation from a few mg to many tens or hundreds of gramms, according to the quantity of silica contained in the column.
The aim of our method is to separate the various compounds present in atmospheric aerosols samples, prior to their analysis with various analytical techniques (GC-MS, GC-FID, HPLC), in order increase the sensitivity and to reduce the background induced by the matrix effects if no purification is done.
A 4g silica gel column is crossed by eluent at a flow rate of 20 ml/min. To separate non-polar compounds (linear and branched alkanes), semi-polar (HAP and benzothiazole) and polar (methoxyphenols, carboxylic acids, levoglucosan and cholesterol), it is then necessary to increase the polarity of eluent, respectively: hexane, toluene/hexane, dimethylformamide. The use of different eluents for each class of compounds allows splitting the sample with good repeatability and satisfying yields (only the methoxyphenols are subject to lower rates because of losses during the stages of concentration/evaporation). Obtained results will be presented and discussed.

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POLYCYCLIC AROMATIC HYDROCARBONS ANALYSIS IN COMPLEX ENVIRONMENTAL MATRICES: COMPARISON OF METHODS INVOLVING HPLC/FLUORESCENCE DETECTION, GC/MS AND GC/MS/MS.

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Polycyclic aromatic hydrocarbons (PAHs) are an important group of organic micropollutants due to their widespread distribution in the environment (atmosphere, water, sediment, soil, sewage). They mainly arise from incomplete combustion or pyrolysis of organic matter, from industrial processes and from other human activities. It is well-known that some PAHs exhibit carcinogenic and mutagenic character and are listed by the US Environmental Protection Agency as priority pollutants. Moreover PAHs are rediscussed as potential synthetic estrogens. The majority of methods for the determination of PAHs involve high performance liquid chromatography coupled to programmable fluorescence detection (HPLC/PFD) or gas chromatography coupled to mass spectrometry operated in selected ion monitoring mode (GC/MS-SIM). Even if highly sensitive and specific, the former technique does not provide any unequivocal confirmation of identity and is often subject to matrix interferences. Thus MS detection is the preferred method in many environmental laboratories [1]. Although GC/MS in the SIM mode is necessary to provide adequate quantification at low levels, confidence in the confirmation of identity is reduced if one or more of the selected ions are affected by matrix interferences. Hence, improved analytical methodologies with adequate confirmation of identity and limits of quantification need to be available. The use of GC/ high resolution MS could be very efficient, but sector instruments are complex and expensive. Alternatively, hyphenated MS/MS with triple quadrupole or ion trap techniques can also be employed to achieve a high level of selectivity and low detection limits.

The aim of this study was to develop a method involving GC/MS/MS for the analysis of the 16 EPA priority PAHs and to compare its performance with methods using HPLC/PFD and GC/MS-SIM. The work particularly tried to explore the benefit provided by GC/MS/MS analysis when dealing with complex environmental matrices such as oil spill contaminated sediment or soil and sewage sludge. The MS/MS conditions in the single reaction monitoring mode, e.g. collision gas pressure and collision energy, were first optimized. Then the performance of the three above mentioned methods were compared in term of linearity range, repeatability and detection limits. Equivalent linearity ranges were observed with coefficient of correlation R^2 superior to 0.995. Identical relative standard deviations of about 5% were also obtained. Concerning the limits of detection (LODs), the three techniques gave similar results for PAHs with 2 to 4 rings. But for PAHs having 5 and 6 rings, HPLC/PFD proved to be the most sensitive methods while GC/MS/MS was the less efficient with tenfold superior LODs. For environmental case studies, samples were prepared by using a limited clean-up step. As example, the analysis of a sewage sludge from a petrochemical plant yields to the following comments. HPLC/PFD proved to be very inappropriate due to the complexity of the chromatograms obtained and to the numerous interfering compounds. By using GC/MS-SIM, for some PAHs, quantification was prohibited because of coeluted interfering compounds. The problem was solved with GC/MS/MS analysis by judiciously setting the collision energy, in order to "crack the matrix". In an other case, the third quadrupole acts as a filter, thus enabling the detection of trace of one PAH. The presence of this analyte could not have been revealed by the use of GC/MS-SIM.

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SIMULTANEOUS VOLTAMMETRIC DETECTION OF ORGANICS FROM WASTE WATER ON A COPPER OXIDE-COPPER ELECTRODE

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A copper oxides-copper electrode was tested in alkaline media for both individual and simultaneous anodic detection of thioacetamide and acetylsalicilyc acid using cyclic voltammetry (CV). These compounds were chosen as simulated pollutants for waste water resulting from drugs processing. Copper oxide electrode was obtained in-situ by five repeated scans in a potential range of –0.221 V to 1 V (first switch potential) and –1 V (second switch potential) vs SCE in 0.1 M NaOH as supporting electrolyte. Based upon the shape of the vomtammograms, which are different for each organic the potential range appropriate for the amperometric detection of both individual and simultaneous detection of these organics was selected. For the individual amperometric detection, a linear relationship between the amperometric responses of a copper electrode and the concentration of organic was obtained within the potential range of 0.2-0.6 V vs SCE. Under these potential range conditions, the calibration plot was established for the determination of acetlysalycilic acid within concentration range of 0.7-4.4 mM. The calibration plot for the thioacetamide determination within the potential ranges above-mentioned was established within the concentration range of 0.5- 3 mM. Also, for the simultaneous amperometric detection of the both organics using CV, the cumulative amperometric responses as sum of the individual amperometric signals were obtained. The presence of thioacetamide did not interfere the amperometric detection of acetylsalicylic acid in alkaline media. In this last case, the qualitative selective detection of thioacetamide on the copper oxides-copper electrode could be obtained in a potential range of –0.4-0.2 V vs SCE. Within the selected potential range, the correlation between the amperometric response of the copper oxides-copper electrode, as overall concentration of organics, and COD parameter corresponding organics concentration and determined by classical method was established.

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REMOVAL OF Cr (VI) FROM INDUSTRIAL WATER EFFLUENTS AND SURFACE WATERS USING ACTIVATED COMPOSITE MEMBRANES

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The problem of selective elimination of toxic metallic ions from the aqueous solutions has a great ecological and economical importance.

An experimental study for removal of Cr (VI) from industrial water effluents and surface waters using activated composite membranes (ACMs) is presented. The method is based on separation of Cr(VI) species in one ACMs separation unit cell. Methyltricaprylammonium chloride (Aliquat 336) was used as extractant in the activated membrane. Atomic Absorption Spectrometer (AAS) was utilized for measuring the concentrations of metal. In feed solutions, the concentration of metal was between 25 and 120 mg L^{-1} and the pH was greater than 3.00, to decrease the probability that Cr (VI) to be reduced at Cr (III). Metal standard solutions were obtained by dilution of 1000 mg L^{-1} chromium stock solutions prepared from potassium dichromate. In addition, the effects of the pH and the carrier concentration in membrane were discussed.

The results are presented like an efficiency of activated composite membranes such us: the membrane capacity (mole cm^{-2}) and the metal concentration in stripping solutions (mg L^{-1}).

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ANALYSIS OF TISSUES OF VERTEBRATES AND EARTHWORMS TREATED BY BROMADIOLONE

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Bromadiolone (3-(3-(4'-brom-1,1'-bifenyl-4-yl)-3-hydroxy-1-fenylpropyl)-4-hydroxy-coumarine) is commonly used rodenticide, which is commercially available as Lanirat. It acts as anticoagulant in very low concentration and its effect is cumulative. It's residues in nature can be cause of death of both house and wild animals and not only in direct, but in consequent consuming. The main organ damaged during deposition and metabolizing of these substance is liver.

In our work we developed a new way of bromadiolone detection based on use of high-performance liquid chromatography with electrochemical detection (HPLC-ED). Our method is quick, sensitive and allows us to determine a trace amount of bromadiolone in biological matrix. Moreover we are able to monitor the incidence of using of bromadiolone on non target fauna.

Our analysis by high-performance liquid chromatography was carried out on CoulochemIII analyser (ESA, Inc.). Hydrogenpaladium electrode, auxiliary carbon electrode and working glassy carbon electrode were placed in electrochemical cell of volume of 50 µl referent. We used acetate buffer (pH = 4.0):acetonitrile in ratio of 40/60 (*v*/*v*) as the most suitable mobile phase for determination of the compound of interest. Sample (5 µl) was injected.

Prior to analysis in flow system we have studied the basic electrochemical behaviour of bromadiolone by cyclic voltammetry on Autolab analyser (EcoChemie, Netherlands) connected with VA-Stand 663 (Metrohm, Schwitzerland). On the base of experimental results from cyclic voltammetry we designed optimal conditions for flow analysis of bromadiolone. From relation of signal height on applied potential we construed a hydrodynamical voltammogram. On its base we choose an optimal potential applied on electrodes (836 mV). Flow rate of mobile phase and the content of methanol influenced the electrochemical response significantly. We found out that our method is sensitive and allows us to determine tens of nanograms of bromadiolone per ml.

We utilized this optimized method to determine the amount of bromadiolone in real samples of tissues of animal which eaten bromadiolone in different forms. Earthworms (*Eisenia fetida*), were kept in presence of five granules of rodenticide Lanirat G in five litres of artificial soil (88 µg/l). These earthworms were used as a feed for field mice (*Microtus arvalis*). Other group of field mice was fed by defined amount of bromadiolone. Earthworms kept without rodenticide and field mice fed with non-treated earthworms or fed by usual feed for rodents served as a control. We analysed the content of bromadiolone in earthworms and in liver of these field mice.

Then we applied this method to determine the bromadiolone content in liver and stomach content of three hares (*Lepus europaeus*), which were found death in area where bromadiolone was applied. We found out that one them died by bromadiolone.

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DETERMINATION OF OXYGENATED POLYCYCLIC AROMATIC HYDROCARBONS BY LIQUID CHROMATOGRAPHY- TANDEM MASS SPECTROMETRY IN AEROSOL SAMPLES.

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An important group of semivolatile organic compounds are oxygenated polycyclic aromatic hydrocarbons (oxy- PAHs), which are formed in plants through incomplete combustion of organic matter such as fossil fuels and wood, and are directly emitted to the lower atmosphere as primary aerosols. Oxy- PAHs are also formed in the atmosphere by chemical or biological degradation of PAHs, which determines their abundance and mobility [1]. Many of them are known or suspected to be toxic, carcinogenic, mutagenic or allergenic [2].

The aim of this study is focused on the optimization of an analytical procedure for the separation and quantification of 17 oxy- PAHs.

Several analytical techniques have been employed for the determination of oxy- PAHs.

Measurements of oxy- PAHs have been reported using reversed-phase High Performance Liquid Chromatography (HPLC) with fluorescence detection. But many of these compounds, especially the quinones, cannot be detected with fluorescence. The online reduction of the oxy- PAHs to the corresponding hydroxy- PAHs was tested but gives a lower sensitivity.

For some oxy- PAHs, gas chromatography coupled to mass spectrometry (GC- MS) can be a useful analytical method [3]. However some of them are thermally labile or low volatile and consequently their detection is difficult.

For those substances, HPLC coupled to mass spectrometry (LC- MS) has been applied and with this method oxy- PAHs can be detected easily without the limitations which occurred in GC- MS and HPLC fluorescence after reduction.

For oxy- PAHs atmospheric pressure chemical (APCI) was found to be more sensitive than electrospray (ESI) ionization.

An LC- APCI- MS- MS method for the determination of selected oxygenated PAHs in aerosol sample was developed and optimized.

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IMPLEMENTATION OF A RADIOLOGICAL EARLY WARNING SYSTEM

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Abstract

In the framework of the radiological monitoring of the Algerian territory, we have implemented a radiological early warning system for the detection of any abnormal radiological situation and its spatiotemporal evolution.

This system is constituted of measurement stations and a processing central unit of data. A series of stations covering the north part of the country is installed at civil protection units for a continuous measurement of gamma radioactivity in air. The whole stations are connected through a reliable communication network to the central unit at Algiers laboratory. An appropriate treatment of the data will enable us to proceed to a radiological impact assessment of any abnormal increase of radioactivity on inhabitants of concerned areas and to start the protective actions related to the situation.

In normal conditions, the stations are called once a day by the central unit to collect recorded data in order to proceed to a computerized archive. In case of abnormal increase exceeding a prefixed level, an automatic call is sent to the central laboratory for an evaluation of the situation.

This represents the first step with the cover of the north band of Algeria facing European countries by thirteen radiological stations and the implementation of a central unit.

The second step will consider the extension of the network to cover the remaining part of the country and the development of tools to the decision making in case of radiological emergency.

EVALUATION OF DISSOLVED ORGANIC MATTER CONTRIBUTIONS TO SEAWATER ALKALINITY BY POTENTIOMETRIC TITRATIONS IN A CLOSED CELL

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Interest in seawater alkalinity measurements has increased over the past 10 years because of the need to measure the parameters of the CO_2 system with sufficient accuracy and precision to understand CO_2 dynamics in the global ocean (e.g. air–sea exchange, biological processes and ocean acidification). Currently, one of the most precise methods for oceanic alkalinity determination consists of a potentiometric titration with HCl to pH ~ 3.4 [1], followed by a non-linear least squares procedure for evaluating the titration data [2]. One complicating issue for estuarine and coastal waters is the extent to which dissolved organic acids may contribute to the measured alkalinity. Simulated titrations in which model organic ligands were initially 'added' to synthetic seawater samples [2] have indicated that their contribution to alkalinity was either negligible or small, and very much dependent on their deprotonation constants (K_a).

In this work, the potentiometric acid titration method developed for coastal seawater studies [2] was applied to the measurement of pH, total CO_2 and total alkalinity in fjord surface waters collected over the duration of a phytoplankton bloom. The first two measurements—combined with auxiliary measurements of boric, phosphate and silicate species—allowed estimation of all inorganic alkalinity components. The inorganic components were then subtracted from the measured alkalinity to produce an estimation of any organic species that might have consumed protons during the titration. Although these 'organic alkalinity' values were very small ($5–20 \pm 8$ $\mu mol\ l^{-1}$), they were found to correlate linearly with the total concentration of species with pK_a values of 9.1 ± 0.2. The latter were measured independently, after CO_2 stripping with N_2 gas, back-titration with CO_2-free NaOH, and nonlinear least squares fitting of the back-titration data. A second class of organic titratable species, with pK_a values of 4.0 ± 0.2, was also detected during the back-titration.

The results indicate that of the two main classes of organic acids that were present during the phytoplankton bloom, only the first class ($pK_a = 9.1 \pm 0.2$) contributed—if only partially—to the measured seawater alkalinity. The second class of acids ($pK_a = 4.0 \pm 0.2$), but not the first, seemed to be produced during the exponential growth of phytoplankton, which agrees with previous findings from a lab culture experiment [3]. Therefore, it would seem that the present technique is suitable for detecting terrestrial, but not marine-derived, organic acids in coastal waters.

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FLUOROPLASTIC CAPILLARIES FOR ON-LINE PRECONCENTRATION AND HPLC DETERMINATION OF POLYCYCLIC AROMATIC HYDROCARBONS.

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The presence of priority pollutants such as polycyclic aromatic hydrocarbons (PAHs) in the aquatic environment is an actual problem of analytical chemistry, because of the carcinogenicity, mutagenicity and toxicity of these compounds. While the instrumentation for the determination of these compounds has been improved dramatically during the past decade, simple, fast, efficient and reliable methods for preconcentration are still demanded in order to handle large numbers of samples at low cost.

Polytetrafluoroethylene (PTFE) capillary were proposed for preconcentration of PAHs (naphthalene, acenaphtene, anthracene, pyrene) and biphenyl within on-line approach. These compounds were preconcentrated on inner walls of capillary by pumping aqueous samples through it. Mass transfer rates of naphthalene, biphenyl, acenaphtene, anthracene and pyrene are limited by external diffusion. Experimental and calculated breakthrough curves were obtained. It was shown that dynamic breakthrough curves of sorption of these compounds on inner walls of capillary are well described by linear models of external diffusion sorption dynamics. Kinetic and thermodynamic parameters of sorption of naphthalene, biphenyl, acenaphtene, anthracene and pyrene on PTFE capillary were evaluated. Optimum conditions for preconcentration of these substances were calculated.

Desorption of analytes from PTFE capillary with water-acetonitrile mixtures was studied, optimum desorption conditions were found. There are no strong specific interactions between analytes and PTFE capillary, thus analytes are easy desorbed. After desorption the whole concentrate zone was cut with sample loop. “Heart-cutting” procedure was investigated, optimum conditions were determined. After desorption, analytes were separated and determined by HPLC with spectrophotometric detection using C_{18} silica gel column.

A novel on-line SPE-HPLC method for determination of hydrophobic organic substances in natural waters was developed. The procedure includes preconcentration of analytes on capillary from 20 ml of sample, desorption, “heart-cutting” of the whole concentrate zone with sample loop, HPLC separation and determination. Detection limits of SPE-HPLC method were established: 5 (biphenyl), 7 (anthracene), 8 (acenaphtene), 30 (pyrene), 40 (naphthalene) ng l^{-1}. It was shown that the application of capillary results in high selectivity of determination of these compounds. Several samples of natural and potable water spiked with mixture of PAHs were analysed using proposed technique.

DETERMINATION OF METHYLMERCURY IN SEDIMENTS BY HEADSPACE TRAP GAS CHROMATOGRAPHY AND ATOMIC FLUORESCENCE SPECTROMETRY AFTER AQUEOUS PHASE ETHYLATION

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Aqueous phase ethylation, pre-concentration on the Carbotrap or Tenax column and separation by GC with CV-AFS detection has become the most frequently used method for methylmercury determination in environmental samples [1]. Instead of collection onto Tenax column the ethylated species may be introduced directly to GC column by headspace (HS) injection which enables development of the automated method for methylmercury determination [2]. A new device developed by Perkin Elmer, TurboMatrix HS-40 Trap, which combines a headspace introduction system with trapping process that pre-concentrates analyte before injection into the GC, offers a possibility to combine these to approaches and to develop an automated method with lower detection limit. In this work TurboMatrix HS-40 Trap (filed with Tenax sorbent) coupled with GC and CV-AFS detector (TEKRAN) was tested for analysis of methylmercury in aquatic sediments and compared with HS injection system only. It was shown that combination of HS with Trap offered better performances for methylmercury determination than the HS only, regarding several aspects. The use of trap enabled use of higher thermostating temperature (up to 90 ^{o}C, comparing to HS where temperature was limited on 70 ^{o}C), due to possibility of elimination of water vapors from the gas phase during the drying step of the trap. Namely, during HS injection water vapors introduced to the GC may cause quenching during AFS detection and appearance of false peaks due to scattering of the excitation radiation. Trap system offered also better detection limit due to possibility of pre-concentration in several cycles, so a greater part of the analyt was introduced into GC. The optimization of instrumental parameters, as are thermostating and Trap temperatures, pressurization pressure and time of cycles will be presented. Method were developed and tested on sediments certified reference materials IAEA 405 and IAEA 433.

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CHARACTERIZATION OF PM2.5 PARTICLES ORIGINATING FROM A MODERN WASTE INCINERATION PLANT BY FACTOR ANALYSIS OF CHEMICAL DATA, MASS AND BLACK CARBON IN AMBIENT AEROSOL

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In the city of Borås, which is a medium sized city in the south-western part of Sweden, a new modern plant for electricity and heat generation has recently been installed and optimised with respect to internal parameters of efficiency and economy. The direct emissions of gaseous pollutants which are subject to restrictions are well below the allowed limits as stated by Swedish and European standards. The aim of the present work is to study the particle pollutants with emphasis on PM2.5 in the ambient air and to identify the specific contribution from the new incineration plant. Many different sources contribute to PM2.5 in urban air. Thus, the general problem is to characterise and identify the particle pollution, which can be attributed to gases and/or particles emitted by the waste incineration plant. For this reason aerosol samples, PM2.5, were collected and analyzed for concentrations of twenty elements by EDXRF. This was combined with the information on some gaseous species (SO_2 and NO_2) together with aerosol mass- and black carbon concentrations. All data were subjected to factor analysis in order to determine the characteristics of the different sources. Vehicle emissions, oil- and bio-mass fired stoves, industrial emissions and long range transported aerosols are believed to contribute to the observed data. Oil combustion was identified as one of the major sources to Ni and V in the urban air.

CELLULAR IMMUNITY OF NEWBORN HARBOR SEALS (*PHOCA VITULINA*) AND METAL-INDUCED IMMUNMODULATION

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The immune system of marine mammals and the influence of pollutants have not been adequately investigated and remain in the focus of interest. Each year, several harbor seal pups come ashore on the German Waddensea coast as natural behavior but also as result of weakness, potential illness, weather conditions, or human interferences. The immune function especially of newborn seals is not finally understood. During the early postnatal nursing period, immune defense mechanisms are not fully developed, and the immune function especially of newborns is not completely understood. Furthermore, the developing immune system is particularly susceptible to injury from chemical exposure during the perinatal period.

The goal of this study was to investigate alterations in lymphocyte function of harbor seals during the first months of life during their rehabilitation in the Seal Station Friedrichskoog, Germany, and to clarify the immunosuppressive and/or sensitizing influence of metals using a modified lymphocyte transformation test (LTT-MELISA®).

Firstly, we found a strong basal and mitogen-induced lymphocyte response in the newborns, which were often diseased. This indicates a well-developed cellular immunity. The proliferative response decreased in the following months during their rehabilitation in the station. Secondly, the study revealed two different impacts of metals on lymphocytes of newborns. Most of the metals showed an immunosuppressive effect; during their rehabilitation time of three months, the toxic metal effect on the lymphocytes decreased. At the same time, metal hypersensitivities were found in 2 of 15 pups. The sensitizing metals were molybdenum in both seals and, additionally, nickel in one seal.

This study suggests that lymphocytes of newborn seals are highly responsive to mitogens but particularly susceptible to the toxic effects of metals in. This effect appears to reverse as the seals become immunologically competent. Older seal pups (1 - 2 month) can develop metal-specific hypersensitivity reactions. This investigation shows the multiple influences of metals on lymphocytes and indicates the problem of animals living in polluted coastal areas, especially for young pups.

DETERMINATION OF SODIUM DIETHYLDITHIOCARBAMATE FROM WATER BY ANODIC VOLTAMMETRY AT BORON-DOPERD DIAMOND ELECTRODE

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The paper describes the direct electrochemical determination at a boron-doped electrode (BDDE) of diethyldithiocarbamate (as natrium salt, Na-DEDTC) by anodic voltammetry and chronoamperometry from aqueous solutions, used as simulated waste waters from pharmaceutical production or pesticides processing industry. Dithiocarbamates and alkyldithiocarbamates, have studied extensively over last decades in a response to their applications in many area [1] of chemistry, biology, pharmaceutical therapy, industry, or agricultural production. The most notable property is their strong metal-binding ability. Some other properties regard the toxicity and environmental aspects as well as the benefic interactions in various pharmaceutical formulations. The boron-doped diamond film is a very promising electrode material available now for electro-analysis and electrochemical detection [2], successfully tested for determination by electrooxidation of various sulfur-containing compounds. The great interest of a such electrode is due to its outstanding electrochemical features, especially wide potential window in aqueous solutions. The electrochemical study of anodic behaviour and oxidation of dithiocarbamates and alkyldithiocarbamates, e.g. diethyldithiocarbamates, imposed a reconsideration of some fundamental and practical aspects.The trace measurement of dithiocarbamate based pesticides by adsorptive stripping voltammetry and studies regarding electrochemical properties of alkyldithiocarbamates in aprotic media has been reported. An anodic determination of the water soluble natrium diethyldithiocarbamate by using a conductive diamond film electrode is not examined. Our paper correlated the useful features of BDDE with the anodic availability of the target analyze for amperometric determination in aqueous solutions. The working electrode used in this work was boron doped disc of 3mmm diameter, a Windsor product for analytical purpose mounted in a three electrode cell, having SCE (saturated calomel electrode) as reference.The electrochemical measurements were accomplished in neutral media(0.1M Na_2SO_4) and concentrations of analyte of 2.10^{-6} to 1.10^{-4}M with an Autolab PGstat20 Eco Chemie, as cyclic voltammogram (CV) in the potential range between 0 to 1.5 V vs. SCE and chronoamperometric (CA) data at a fixed potential and various concentrations of the analyte. The three anodic peaks were clearly manifested on the forward anodic branches of CVs, for scan rate of 0.001 to 0.1V s^{-1}, and attributed to the gradual oxidation, initiated by a first monoelectronic step, thiuram disulfide formation, followed by other successive electronic transfer and change in the hydrophobic character of the electrode. The linear plots of the anodic current peaks and the chronoamperometric currents vs. concentration were favourable evaluated (SD and recovery) for analytical determination of Na- DEDTC and the use of BDDE as amperometric sensor without fouling or degradation.

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SELECTIVE SEPATATION AND RECOVERY OF CADMIUM AND COBALT IONS BY SOLVENT EXTRACTION FROM ZINC PLANT RESIDUES

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Selective separation is essential for the environmental cleanup and can be used for economic recovery constituents [1, 2]. This paper is concerned with studies of selective separation and recovery of cadmium and cobalt ions from acidic solutions. Solvent extraction separation and recovery of Cd(II) and Co(II) from sulphate leach liquor was investigated using di-2-ethylhexyle phosphoric acid (D2EHPA) as an extractant, with tri-n-buthyl phosphate (TBP) as a phase modifier diluted in kerosene. Filter cakes from zinc plant residues were used as starting materials. Cadmium filter cake contains 6.43% Cd, 2.3% Ni, 40-45% Zn, 0.01% Fe and cobalt filter cake contains 1.43% Co, 10.6% Mn, 17.3% Zn 7.8% Ca. The distribution coefficients of Co(II) and Cd(II) between the organic phase containing the reagent and aqueous sulfate solution were determined under various experimental conditions with strict PH control. The experimental distribution data was treated graphically and numerically, to obtain the thermodynamic models describing the respective bi-phasic extraction reactions. The analysis of the equilibrium data indicated that the extraction of Cd(II) and Co(II) efficiency of 99.8% was achieved. The Cd-rich organic phase was scrubbed with $CdSO_4$ solution. The cobalt in the stripping solution was precipitated as oxalate solution. The total recovery of Cd and Co was about 97.3 and 94% respectively. Complete process flow sheet for the separation and recovery cadmium and cobalt were proposed.

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New challenging organic contaminant in high purity water; endocrine disrupters

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Endocrine Disrupters are organics that interfere with the proper functioning of hormones in humans and animals. These man-made and natural chemicals vary widely in structure and type. Exposition to these compounds may cause sterility or decreased fertility, birth defect, and metabolism disorders. The ubiquitous and increasing presence of such substances in the environment has prompted funding of large research programs to investigate the potential effect of hundreds of chemicals[1]. Regulations and norms will soon be applied to environmental testing laboratories to measure the levels of several classes of compounds, such as PCBs, dioxins, pesticides, tin derivatives, and plasticizers, in drinking water.

Since most of these chemicals are small organic molecules, they can be removed from water by the conventional technologies used to remove trace organic compounds, *i.e.* reverse osmosis, UV photooxidation and activated carbon. All activated carbons, however, do not adsorb small organic molecules with the same efficiency and a careful design is necessary.

A specific purification media was developed for use in a final point-of-use purifier[2]. GC-MS and LC-MS data on the selection of such a compound will be shown. This point-of-use purifier is installed at the outlet of water purification systems to deliver ED-free water. The study will show that this high purity water is suitable for the trace analysis of small organic molecules.

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Glycosylated Compounds in Seal Serum

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Glycosylation is one of the most extensive and complex posttranslational modification of proteins. It is an enzyme-guided process which imposes a recognitional role on the proteins. Glycosylation takes part e.g. in cell growth and development, tumor growth and metastasis and immune recognition/ response as well as microbial pathogenesis.

The glycoproteins comprised in the blood of seals were isolated by means of lectin affinity separation. Special attention is turned on the acute-phase-glycoproteins (APP) haptoglobin and serum amyloid A that were upregulated in plasma as a result of an acute phase reaction such as inflammation or stress. The aim is to obtain biomarker for monitoring the state of harbour seals health.

As analytical method for the enrichment of glycosylated compounds serial lectin affinity chromatography was developed. The lectin columns contained Concanavalin A (ConA), Wheat Germ Agglutinin (WGA) and *Ricinus communis* Agglutinin (RCA), which catch nearly all glycoproteins from the serum. The performance of the adsorbents was evaluated by means of investigations of immobilization characteristics as well as depicting adsorption isotherms [1]. The isolated compounds were identified by SDS-Page, protein-tests and matrix assisted laser desorption/ionization with time of flight detection. Detailed insight into the binding mechanisms of the glycoproteins to the lectins is given by interaction analysis employing the surface plasmon resonance (SPR) technique.

The biomolecules of interest can be easily and fast monitored, if the biospecific interaction analysis can be combined with mass spectrometric analysis. Then proteins can be affinity purified, and characterized in terms of their interactions, while the mass spectrometry provides structural identification of the biomolecules. This work provides a methodology to combine the SPR technology with MALDI analysis by examining the critical parameters like the threshold level of proteins and mild desorption conditions which maintain the biological function of the lectins and show good compatibility with the MALDI experiments.

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ELECTROCHEMICAL SENSOR FOR HEAVY METALS BASED ON CARBON PASTE ELECTRODE MODIFIED WITH GROUND COFFEE WASTE

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Carbon paste electrodes (CPE) modified with ground coffee waste were prepared and used as working electrodes in the electrochemical determination of lead(II) and other heavy metal ions in aqueous samples. The voltammetric responses of the modified CPE indicated that this electrode is a suitable substitute to mercury in anodic stripping voltammetry of some heavy metal species. The overall detection procedure involves preconcentration of the targeted metal ions on the electrode surface at open circuit, then cathodic electrolysis of the preconcentrated species in an acidic medium followed by a detection step using square wave anodic stripping voltammetry (SWASV). The best electrode contained 20% (w/w) of ground coffee waste and 80% (w/w) of carbon paste. The optimum operating conditions were 2-10 minute preconcentration period in metal ion solution, followed by a 60-second cathodic electrolysis of the preconcentrated species and SWASV detection in 0.1 M HCl. Under these conditions the voltammetric responses after a 5-minute preconcentration period were linear with respect to lead ion concentration in the range of 0.20-300 ppm. The detection limit for lead (II) was 0.02 ppm after a 20-min preconcentration period. Other heavy metal ions such as mercury(II), cadmium(II) and copper(II) were also detected using the prepared CPE modified with ground coffee waste.

ION SELECTIVE ELECTRODES FOR SOIL ANALYSIS

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Ion selective electrodes (ISEs) for the detection of heavy metals have been developed for environmental analysis of soil. Recent advances have extended the routinely-achievable limits of detection for ISE's to the nanomolar range [1]. This has opened up possibilities for their application to fields such as routine environmental analysis and early warning systems. The simple construction of ISE's, their straight-forward experimental procedure and low detection limits make the electrodes well-suited for environmental analysis.

In this paper, the development and use of ISEs for the detection of Pb^{2+} in a range of soil samples is described. The soil samples were collected from a series of abandoned mining sites and the surrounding community. Centuries of mining in the region has lead to pockets of high heavy metal concentration soil where maintaining vegetation cover has been nearly impossible [2]. As a consequence, dust-blows from these unvegetated areas are common and have led to concerns about human and animal safety as a result of heavy metal inhalation.

These problems have highlighted the need for high-frequency, real-time monitoring of metals in airborne dust at such sites. The long-term goal of this project is to develop an autonomous and portable sensor for the collection and analysis of airborne soil using ISEs. In this paper, the development of the sensors and their application to the soil samples is described. The Pb^{2+} ISEs were built using both solid- and liquid-contact methods and the suitability of each approach was assessed. In addition, soil digestion procedures were studied in order to optimize the metal extraction of the soil using techniques and solvents compatible with a portable device. The design of each electrode was chosen to address the requirements of portable devices such as minimization of the amount of sample and reagent consumed, sturdy construction, and a long lifetime. The sensors were used for the quantitative detection of Pb^{2+} in soil and future work will focus on the incorporation of the ISEs into a portable and autonomous device. This is part of a wider effort in our group to merge environmental and other analytical measurements with wireless communications infrastructure [3, 4].

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DETERMINATION OF ARSENIC IN URBAN AIR BY HYDRIDE-GENERATION ATOMIC ABSORPTION SPECTROMETRY

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Arsenic is widely distributed in the environment and may accumulate in soil, plants, animal tissues, and airborne particulate matter [1]. Arsenic is emitted into the atmosphere from both natural and anthropogenic sources and is present in the atmosphere in trace amounts. Its atmospheric concentration ranges from about 0.01 to 0.1 ng/m^3 in clean areas and up to 500 ng/m^3 in industrial environments. Arsenic is recognized as a cumulative poison and its determination in air is of great interest because a huge number of people are continuously exposure to this hazardous elements via urban air [2].

Airborne particulate matter from the atmosphere of the city of Isfahan was collected from a height of 1.5 m above the ground level. The exposed filters were leached with a mixture of nitric and sulfuric acid. The determination of arsenic concentration was performed by electrically quartz heated tube hydride-generation atomic absorption spectrometry. The determinations were carried out on a Shimadzu atomic absorption spectrometer, Model AA-670. Table 1 shows the atmospheric concentration of total arsenic in some samples collected in ordinary days and during an inversion in the atmosphere of the city of Isfahan.

Table 1: Atmospheric concentrations of arsenic in the urban air (ng/m3)

Sample	Concentration of As	Sample	Concentration of As
1	5.12	4	16.2
2	4.76	5	15.8
3	5.12	6	12.96

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DEVELOPMENT OF A PASSIVE SAMPLER FOR HYDROGEN SULFIDE AND FIELD VALIDATION IN A TROPICAL SITE

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Hydrogen sulfide, H_2S, is emitted to the atmosphere by urban, industrial and remote areas. Passive samplers have been used to monitor workplace exposure to vapors and gases for over 20 years. Recently these samplers have been applied to ambient air [1] and very few have been validated for tropical environment [2,3]. Advantages of its use include low cost, autonomy and possibility of spatial resolution for surveys.

The locally constructed passive sampler was based on diffusion in a static layer of air using the design which minimizes particle interference: polyethylene tube of 12mm diffusion length, with stainless steel net and Teflon membrane in front, and a 21mm diameter Whatman 40 filter impregnated for H_2S fixation. Alternatively a Palmer type sampler [5] have been tried with poor results. Several solutions for H_2S fixation were tested (2% $AgNO_3$ in HNO_3 0.1 mol L^{-1} and 20% ethanol; NaOH 1 mol L^{-1} and $Zn(OH)_2$ as zinc acetate in basic media) using constant H_2S atmosphere from a gravimetrically calibrated permeation tube. Best results were obtained for zinc oxide impregnation with H_2S extracted with ammonium molibidate followed by spectrophotometric determination at 580 nm.

Performance of the passive sampler was tested for different exposition periods as follows: in the laboratory, using Teflon chambers (120 x 30 cm) with concentration controlled by continuous H_2S monitor[6]; in two field sites, both downwind from the Camaçari Petrochemical Complex (Bahia, Brasil), during different times of the day and diverse meteorology conditions, in parallel with measurements of a continuous H_2S monitor [6].

Based on 6 samplers simultaneously exposed in chamber, precision was $\geq$ 97% and accuracy was within 91– 98 % as compared with the continuous monitor data. Field measurements lasted 7 weeks with simultaneous exposure of four H_2S passive samplers, totaling 28 samplers, in parallel with continuous H_2S monitoring, showing a strong and highly significant correlation ($y=0.830x + 0.236$, $R=0.9918$, $P=0.0001$) at atmospheric levels ranging from 0.97 – 3.20 µg m^{-3}. Exposed samplers were stable during one month when stored under refrigeration (4^oC) and for one week under room temperature. Passive sampler performance decreased when exposure time was $\leq$ 0.5 h, when other reduced sulfur compounds were present at concentrations above 30 µg m^{-3} and under air stagnation conditions (facial velocity = 0 m s^{-1}).

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NEW REAGENT SYSTEM FOR SPECTROPHOTOMETRIC DETERMINATION OFCERIUM IN ENVIRONMENTAL AND GEOLOGICAL SAMPLES

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A new, simple and highly sensitive method was developed for the determination of trace amount of cerium. The method involves bleaching of pinkish red colour of the dye, Rhodamine-B, by the action of iodine, which is released by the reaction between potassium iodide and cerium (IV) in acidic medium. The colour of the dye was measured at 555 nm. Beer's law was obeyed over the concentration range of 1.0 to 9.0 µg cerium (IV) in final volume of 25 ml (0.04 – 0.36 ppm). The molar absorptivity and Sandell's sensitivity were found to be 3.25X 10^5 l $mol^{-1}cm^{-1}$ and 0.0030 µg cm^{-2}, respectively. The reproducibility of the method was checked by seven replicate measurements, each containing 5.0 µg Ce(IV) per 25 ml of final solution, standard deviation and relative standard deviation were found to be ± 0.0059 and ±1.2%, respectively. The lower relative standard deviation value (±1.2%) and the range of error at 95% confidence level in terms of absorbance were ± 0.0054, indicating, good precision and accuracy of the method Some variables were studied in order to optimize the reaction conditions. The method developed has been successfully applied for the determination of cerium in silicate rocks, high purity rare earth oxides, soil, plant tissues and natural water samples.

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SELECTED CONGENERS OF POLYCHLORINATED BIPHENYLS IN ABIOTIC AND BIOTIC SAMPLES FROM THE ENVIRONMENT

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The resolution of individual PCB congeners in the sample makes high demands on both the isolation from the matrix and the instrumental implementation of trace and ultra-trace analysis. Moreover, real matrixes often contain other contaminants which may cause problems in quantification of target analytes. These problems are caused by possible coelutions on chromatograph columns. That is why we conduct our analysis by using the two-dimensional high resolution gas chromatography (HRGC) with micro-ECD detectors and optimized temperature program enabling to reach the high level of separation of individual analytes [1,2]. Under optimized conditions undesirable coelutions were identified on both columns using mixed standards and were taken into account at the analysis of real samples of sediments, water and animal tissues. We looked for indicator PCB congeners No. 28, 52, 118, 138, 153 and 180, minority PCB congeners No. 8, 18, 47, 49, 187, 189, 209 and some non-orthosubstituted congeners No. 77, 81, 126 and 169. All the monitored PCB congeners of different ratios and concentration were identified in the samples of sediments. The ratio of indicator and minority congeners corresponded with their representation in the technical mixtures of Delor 103 and 106. A significant contribution of monitored minority congeners to the total sum of PCBs was found in a lot of samples (max. 25 % of total sum of PCBs). There were rather low levels of the monitored PCB congeners found in the samples of water (on average 37 ng/L), except for the sample from Smradavka reservoir with the total amount of 151.5 ng/L of PCBs. We also analysed a lot of samples of the fat tissue from buzzards in order to assess the bioaccumulation of PCBs in the body of this bird of prey. The levels of indicator PCBs ranged from 0.25 to 2318 ng/g fat. But these results were rather trial. In our following research we would like to concentrate on the evaluation of some suitable method for the study of distribution of PCBs and some other chlorinated pollutants in the environment.

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EVALUATION OF AN OPTICAL BIOSENSOR FOR THE DRUG RESIDUE SCREENING OF ENVIRONMENTAL WATER SAMPLES

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The presence of residues of pharmaceuticals in the environment from their use in human and veterinary medicine as well as production effluents is of growing concern. Particular worries have been expressed over a potential influence of antibiotics residues on the development of antibiotic resistant strains of pathogenic bacteria in environmental compartments and their subsequent transmission to humans.

Current methods for the analysis of antibiotics in environmental samples are mostly based on chromatographic and mass spectrometric methods, in particular LC-MS/MS. These methods are precise, but often time consuming, and requiring sophisticated instrumentation as well as trained staff for operation and data evaluation. For a widespread monitoring of the presence of antibiotics in the environment techniques that allow simple and high-througput analysis would be favourable.

In the present work the potential of an optical biosensor for the screening of environmental samples for different antibiotics used in human and veterinary medicine, i.e. sulfonamides, streptomycin, chloramphenicol, tylosin, was evaluated. The used biosensor exploits the phenomenon of surface plasmon resonance (SPR) and is based on the immunochemical recognition of the target analytes. The selectivitiy and sensitivity of the approach was investigated for either direct injection of water samples as well as extracts obtained by solid-phase or liquid/liquid extraction. The method was applied to different types of environmental water samples.

Cd(II) PVC-Based Membrane Sensor Based on *N*'-[1-(2-furyl)methylidene]-2-furohydrazide

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The *N*'-[1-(2-furyl)methylidene]-2-furohydrazide was used as an excellent ionophore in construction of a Cd(II) PVC-based membrane sensor. This sensor shows very good selectivity and sensitivity towards cadmium ion over a wide variety of cations, including alkali, alkaline earth, transition and heavy metal ions[1,2]. The sensor revealed a great enhancement in selectivity coefficients for cadmium ions, in comparison to the previously reported cadmium sensors. The proposed sensor exhibits a Nernstian behavior (with slope of 29.4 ± 0.5 mV per decade) over a wide concentration range (1.0×10^{-6}–1.0×10^{-1}M) with a detection limit of 7.3×10^{-7}M. It shows relatively fast response time, in the whole concentration range (<10 s), and can be used for at least 9 weeks in a pH range of 2.8–8.6. The proposed sensor was successfully applied to the direct determination of cadmium ions in solution and as an indicator electrode in potentiometric titration of Cd(II) ions with EDTA.

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Novel PVC-Based Cobalt(II)-Selective Membrane Electrode Based on *N'*-[1-(2-thienyl)ethylidene]-2-furohydrazide

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In this work, a novel cobalt PVC-based membrane sensor based on *N'*-[1-(2-thienyl)ethylidene]-2-furohydrazide (NTEF) as a new ionophore is presented. The sensor displays a linear dynamic range between 1.0×10^{-6} and 1×10^{-1} M, with a near Nernstian slope of 29.6 ± 0.4 mV per decade and a detection limit of 4.2×10^{-7} M. The potentiometric response of the proposed electrode is independent of the pH of the solution in the pH range of 3.2 –8.4. The sensor possesses the advantages of short conditioning time, fast response time (<15 s) and good selectivity towards transition and heavy metal, some mono, di and trivalent cations[1,2]. The electrode can be used for at least 10 weeks without any considerable divergence in the potentials. It were successfully used as an indicator electrode in potentiometric titration of Co(II) ions with EDTA and direct determination of Co(II) in wastewater of the electroplating industry.

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Zinc(II) PVC-Based Membrane Sensor Based on 5,6-Benzo-4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8,8,8]hexacos-5-ene

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The 5,6-Benzo-4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8,8,8]hexacos-5-ene (BHDE) was used as an excellent ionophore in construction of a Zn(II) PVC-based membrane sensor. The best performance was obtained with a membrane composition of 30% poly(vinyl chloride), 64.5% nitrobenzen (NB), 2.5% BHDE and 3% sodium tetraphenyl borate (NaTPB). This sensor shows very good selectivity and sensitivity towards zinc ion over a wide variety of cations, including alkali, alkaline earth, transition and heavy metal ions[1,2]. The sensor revealed a great enhancement in selectivity coefficients for zinc ions, in comparison to the previously reported zinc sensors. The proposed sensor exhibits a Nernstian behavior (with slope of 29.1 ± 0.4 mV per decade) over a wide concentration range (1.0×10^{-6}–1.0×10^{-1} mol L^{-1}) with a detection limit of 6.3×10^{-7} mol L^{-1} (41.2 ng mL^{-1}). It shows relatively fast response time, in the whole concentration range (<10 s), and can be used for at least 10 weeks in a pH range of 2.8–7.3. The proposed sensor was successfully used in direct determination of zinc ions in wastewater of industrial zinc electroplating companies, and also as an indicator electrode in titration with EDTA.

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DISTRIBUTION OF METALS BETWEEN THE AEROSOL SIZE FRACTIONS IN WELDING FUMES

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There is a high risk of occupational health deterioration in many industries through inhalation exposure to toxic metals and metalloids. Nowadays, among these health damaging factors great attention is devoted to the toxic effects caused by welding fumes, which consists of airborne particles generated by welding and allied processes. In general, these particles, having less than 1 µm diameter, are respirable. However, most countries currently have exposure limits for welding fumes, and their specific components, that apply to the inhalable fraction of airborne particles [1]. Because of these facts, it is reasonable to collect both fractions and determine the metal distribution between them. These experiments could help the decision-makers in the reconsideration of the exposure limits.

The samples were taken in a welding plant, where different types of steels were welded with manual metal arc (MMA). Samples were collected with fix point and personal sampling techniques applying different sampling heads: The Institute of Occupational Medicine (IOM) sampler and conical inhalable sampler (CIS) for the inhalable aerosol fraction and the Higgins-Dewell (HD) cyclone for the respirable fraction. Fe, Mn, Cr and Ni concentration in the samples were determined after different sample preparation procedures (extraction, microwave assisted digestion) by different analytical techniques (spectrophotometry, inductively coupled plasma atomic emission spectrometry, inductively coupled plasma quadrupole mass spectrometry). Metal concentrations of the workplace air were calculated for the three samplers, and the results were compared to each other. Total metal concentrations in the respirable aerosol fraction were 57-98% of the concentrations in the inhalable fraction.

More detailed results will be presented at the Conference.

[1] ISO 10882:2001 Health and safety in welding and allied processes – Sampling of airborne particles and gases in the operator's breathing zone –

CHEMICAL CHARACTERIZATION OF PM10 FRACTIONS OF URBAN AEROSOL

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Airborne particulate matter has important health implications. The goal of this investigation was to give an overview about the metal and total organic/inorganic carbon (TOC/TIC) concentrations in the PM10 aerosol fraction in Budapest and to monitor monthly changes during the sampling period, whether there is a tendency in the seasonal change of the concentrations. The sampling took place in Budapest, Hungary between September 2004 and August 2005 in an area with heavy traffic. For the sampling, a high volume aerosol sampler equipped with a PM10 head was used. The samples were taken onto quartz fiber filters, which were previously pre-treated at 550 °C in order to eliminate organic contamination. Each month we collected two samples: one for 24 hours, an other for 96 hours. The air intake was 500 L/min.

To measure the metal concentrations two types of sample preparation were used: microwave assisted *aqua regia* digestion and water extraction by sonication.

The solutions were analyzed using a THERMO Finnigan ELEMENT2 sector field inductively coupled plasma mass spectrometer (SF-ICP-MS). The determined elements were: V, Cd, Zn, Cu, Ni, Sb, Cr, Pt, Pb, Be, B, Te, Tl, U, Mn, Fe, Co, Ga, Rb, Sr, Mo, Ag, Bi.

According to the data obtained from the *aqua regia* digestion the measured trace elements could be divided into four groups on the basis of their concentration:

1. Fe (1000-4000 ng/m^3)
2. Pb, Mn, Zn, Cu, Sn, Sb, Cr (10-60 ng/m^3)
3. V, Mo, Cd, Rb, Ni, Sr, Li (2-8 ng/m^3)
4. Co, Ga, Bi, Ag, Te, Tl, U, Pt (n.d.-0,4 ng/m^3)

In the water extract the classification among the concentration is the following:

1. Fe, Zn (50-85 ng/m^3)
2. Mn, Cu, Pb, Sb, Sr (2-15 ng/m^3)
3. V, Cr, Rb, Cd, Mo, Li, Ni (0.2-1.2 ng/m^3)
4. Ga, Co, Tl, Bi, U, Ag, Pt, Be, Te, Sn (n.d.-0,15 ng/m^3)

During this period, no proof of any seasonal change of trace element concentrations was found.On the analytical data a chemometric analysis was performed, and the data were compared with others obtained in several cities in Europe.For the TOC-TIC measurements a LECO Co. (USA) RC-412 type carbon analizator was used. The TOC ratio (30-50%) in the PM10 fraction showed a seasonal profile, increasing in the winter period because of the heating.

DETERMINATION OF CHLORINE DIOXIDE GENERATOR PERFORMANCES WITH SUPPRESSED ION CHROMATOGRAPHY APPLIED TO ON-LINE REDUCED AND PURGED EFFLUENTS.

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Chlorine dioxide is still considered one of the most viable alternatives to chlorine in the disinfection of surface waters containing a significant amount of THM precursors. Moreover, it is very effective in controlling taste, odour, iron, manganese, hydrogen sulphide and phenolic compounds. In spite of all these advantages, chlorine dioxide represents a potential source of risk for human health due to introduction of inorganic by-products such as chlorite and chlorate. Previous experimental surveys have proved that the latter as well as chlorine impurities are mainly generated by secondary reactions in ClO_2 reactors. The concentration of such contaminants may be reduced by optimizing residence time and fluidodynamics of reagents in chlorine dioxide generators. This task is made possible by carrying out repeated analyses of the generator effluent during the optimization procedure. The dosage of ClO_2 purity is often performed with differential iodometric titrations or selective colorimetric determinations of effluent aliquots collected discontinuously at the exit of the generator. However, this procedure is usually affected by a significant bias due to ClO_2 volatilization during sampling operations and chemical interferences in the following analyses.

In this research we have developed a different approach to collect and determine quantitatively the concentrations of chlorine dioxide and other inorganic chemicals (chlorite, chlorate, chlorine) at the exit of ClO_2 generators operating by mixing sodium chlorite with hydrochloric acid. A flow fraction of the produced effluent was drawn by a peristaltic pump and alkalinized (pH = 7.5 - 8.0) with Na_2CO_3 delivered by a HPLC pump. The concentration of ClO_2 in the resulting fluid was monitored by a chromatographic UV-VIS detector. The exit of the detector was alternatively connected to a purging system and to a reduction chamber by acting on a two-way valve. Residual chlorite, chlorate and chlorine were determined in aliquots of the purged effluent, while total chlorite (that is, $ClO_2 + ClO_2^-$) was dosed in the reduced eluent. Anionic by-products and chlorine were analysed by means of suppressed ion chromatography and DPD spectrophotometry, respectively. The effect of experimental conditions on method performances was evaluated.

POSSIBILITIES OF USING OF SOLID PHASE EXTRACTION (SPE) TO DETERMINATION OF FLUOXETINE IN WATER ENVIRONMENT

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The development medical care worldwide is one of the reasons for the increasing production of pharmaceutical products. Cheaper prices of medications, increases their accessibility for most people. Unfortunately, associated with this is a very important problem – accessibility to pharmaceuticals and their high volume production contributes to an increase of contamination in environment, including in aquatic ecosystems. The medicaments can enter aquatic ecosystems from municipal wastewater treatment plant or domestic septic systems, which often are not designed to remove them from the effluent. Knowledge regarding the environmental occurrence of pharmaceutical products is increasing, but information in the peer-reviewed literature regarding the fate and effects of most pharmaceuticals is limited. One of the reasons for this lack of data is that, until now, there have been few analytical methods capable of detecting these compounds at the low concentration, which might be expected in the environment [1].

In this work Fluoxetine (FLU) was determined. Fluoxetine is a widely prescribed drug, not only for depression but for a variety of other disorders (pain syndromes including diabetic neuropathy and fibrositis, panic disorders and nervous bulimia). FLU is extensively metabolized in humans, by demethylation in the liver, to its primary active metabolite norfluoxetine (NFLU). Drink water samples were spiked with the mixture of 0.6 ml of Fluoxetine and 0.24 ml of internal standard Maprotiline (100 µg/ml for each compound). The spiked samples were loaded on the SPE phases and tested in terms of their retention behaviour.

A high performance liquid chromatography - electrospray ionisation mass spectrometry and diode array detection techniques were employed for the analysis of Fluoxetine and Maprotiline. Analytes were separated using Discovery®RP Amide C16 (150 mm L x 3 mm I.D.) column working in isocractic mode. The mobile phase consisted of methanol-water mixture (60:40) acidified with 0.1% of trifluoroacetic acid. Analytes were detected using a DAD (at 226 nm) and MS (SIM m/z = 310 and 317) detectors.

This simple and universal method can be applied for the determination of Fluoxetine in different types of water samples like lake, river, drink and waste water.

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MONITORING OF POP AND RELATED COMPOUNDS BY PDMS-COATED STIR BARS IN AIR

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In recent years, there has been an increasing interest in developing new analytical tools for atmospheric monitoring of organic pollutants[1,2]. In general, sample preparation and conventional column chromatographic clean-up methods are labour-intensive and time-consuming. Therefore, it becomes necessary to develop sensitive, easy to handle methods, which allow an automation of the analytical process.

To establish a new sampling and assay technique, tests with Gerstel-Twister were carried out. Gerstel-Twister offer the possibility to analyse organic compounds from aqueous matrices and were used only as aqueous media passive samplers so far[3,4]. But it is also supposed that Gerstel-Twister are capable of atmospheric sampling. The operation principle of the sampling device Gerstel-Twister is based upon the Stir Bar Sorptive Extraction (SBSE), first introduced by Baltussen et al[5,6] and is similar to the Solid Phase Micro Extraction[7]. Commercially available Twister consists of glass covered magnetic stir bars, coated with a layer of polydimethylsiloxane to selectively enrich nonpolar compounds from aqueous matrices. The substances accumulated can be directly chromatographed after thermodesorption.

The employed thermodesorption unit (TDU, Gerstel) was connected to a programmed-temperature vaporisation injector (CIS 3, Gerstel) and coupled to a gas chromatograph (5890 SERIES II, Agilent Technologies) high-resolution mass spectrometer (MAT 95, Thermo Finnigan). The GC was equipped with a high-resolution column and a multipurpose autosampler (MPS 2, Gerstel). Twister can be conditioned in a special tube-conditioner (TC 1, Gerstel). Quantification was carried out by isotopic dilution method. ^{13}C-standards were placed on the respective stir bar with the help of an 1µl syringe before thermal desorption. The rapid TD-HRGC-HRMS method, combining some outstanding state-of-the-art techniques, made it possible to detect POP-chemicals adsorbed on Twister by atmospheric sampling. The established desorption conditions exhibited good repeatability and high analyte recoveries. Thermal desorption, chromatography and detection take directly place and no labour-intensive sample clean-up is required. Fast analysis, high sample throughput, no solvent consumption and a high sensitivity support further investigations in the field of air sampling.

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FAST AND RELIABLE DETERMINATION OF TRACE CONCENTRATIONS OF TI AND ZR IN SOIL SAMPLES

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The exact determination of the Ti/Zr ratio in soils is very important for the reliable study of the uniformity of parent geological material between soil horizons which is the basis for evaluating any change of soil properties during pedogenesis or caused by soil mangagement. Additionally, the identification of lithologic discontinuities or differences in parent materials is a prerequisite for distinguishing soil properties of pedological origin from those of geological origin. When uniformity of parent material of a profile is established, changes in chemical, physical and mineralogical properties of soils along profiles can be attributed to pedogenic processes, and quantitative pedological studies on soils may be conducted. Comparing the ratios of the concentration of two resistant minerals between horizons is the most common method of assessing the uniformity of parent material. If elements are present exclusively in certain resistant minerals, such as Ti in rutile and Zr in zircon, the ratios of the elemental concentrations can also be used for identifying lithological breaks.

For exact determination of the Ti/Zr ratio, both elements must be recovered quantitatively from the soil matrix which is difficult, in particular for Zr. Sample digestion can be carried out by fusion with either Na2B4O7, Na2CO3 or (NH4)2SO4. However, large amounts of reagents are needed and the system is prone to contamination. Additionally, due to the high salt content of the fusion solution, determination of Ti and Zr by ICP spectrometry is severely hampered. X-ray fluorescence, which can be used alternatively, suffers from matrix interferences and a lower sensitivity compared to ICP spectrometry.

We will present a method that allows both the fast and reliable determination of Ti and Zr in soil samples based on high-pressure microwave-assisted digestion and element-specific detection by ICP-OES down to 0.5 mg/kg for both Ti and Zr, respectively.

USE OF DECANOIC ACID REVERSED MICELLES-BASED COACERVATION FOR THE EXTRACTION OF PAHS FROM SURFACE WATER AND WASTEWATER SAMPLES.

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Sixteen PAHs are priority pollutants on both EPA and UE lists because of their mutagenic and/or carcinogenic effects. They are found in environmental water samples at concentrations of ng/L, due to their low solubility. Since they are considered toxic at this level, their presence in environmental waters needs to be monitored. With this purpose, several techniques for the extraction and pre-concentration of PAHs from water samples have been reported, mainly liquid-liquid extraction (LLE) and solid phase extraction (SPE) [1].

Coacervation of supramolecular assemblies constitutes an excellent strategy for solventless LLE. However, the number of coacervates used in analytical extraction procedures (mainly made from non-ionoic micelles, the “cloud point technique”) has been limited. So, research on new coacervation systems that permit different types of interactions with analytes under a variety of experimental conditions is of great interest [2].

In this work, the suitability of the water-induced coacervation of decanoic acid reversed micelles in tetrahydrofuran for the extraction of PAHs from environmental water samples is investigated. Liquid chromatography coupled to fluorescence was used for the separation and quantification of PAHs. Parameters affecting extraction efficiency and preconcentration factors were studied. The decanoic acid as well as the tetrahydrofuran percentages were the most influential parameters. High electrolyte concentrations or temperature and pH changes in a wide range did not affect PAHs recoveries, making the extraction procedure particularly robust. Because extraction efficiency and preconcentration factors in coacervated-extraction techniques do not depend on the volume of the sample, low volumes of water samples could be treated (40ml), which made the sample pretreatment simpler. The approach developed was applied to the determination of PAHs in different influent and effluent wastewater samples as well as in different kind of surface water samples, located all of them in the South of Spain.

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FERRATE(VI) FOR THE OXIDATION OF CYANIDE IN AQUEOUS SOLUTIONS : A GREEN CHEMICAL

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The increased level of industrialization/urbanization poses serious threat for the environment and of course the usual methods used for the waste water treatment is either, sometimes, ineffective or the chemicals used for the purposes are producing several hazardous by-products which, ultimately become burden for the environment. Hence, with the changed scenario it always worth concerning to innovate or to modify the existing technologies for waste treatment by using some alternative chemicals that can have good efficiency/selectivity and also possess more environmentally friendly. In this context the role of ferrate(VI), the higher oxidation state of iron showed very promising behavior as possess very high oxidative capacity (redox potentials of Fe(VI)/Fe(III) couple (E^0 (FeO_4^{2-}/Fe^{3+}) and E^0 ($FeO_4^{2-}/Fe(OH)_3$ are 2.20 and 0.72, respectively at pH 1 and 14) and the byproducts obtained followed by the reduction are not harmful for human being [1]. Hence, the application of Fe(VI) in various waste water treatment strategies are likely to play a key role in the next generation. Hence, in an attempt for greener remediation of environmental technologies we tried to apply Fe(VI) for the oxidation of cyanide in aqueous solutions.

Ferrate(VI) (as Potassium Ferrate salt, K_2FeO_4) was synthesized in the laboratory by the known wet method. Further, the purity of this Fe(VI) was optimized by UV/Visible analysis, as the molar absorption coefficient for Fe(VI) is 1150 M^{-1} cm^{-1} at 510 nm, and it was found to be *ca* 95% pure. The cyanide concentration was estimated by using cyanide active electrode (Orion Cyanide Electrode 9606, Ionplus annexed with Orion pH meter 720A, USA).

The experiments carried out by changing the cyanide concentration ($0.33x10^{-3}$ mol/L to $20x10^{-3}$ mol/L) with the Fe(VI) concentration ($1.0x10^{-3}$ mol/L) at constant pH~10.0 (phosphate buffer). It was observed that Fe(VI) can oxidize very rapidly the cyanide as only within 5 min of contact most of the cyanide is to be oxidized. Moreover, it was observed that upto the cyanide concentration of $10x10^{-3}$ mol/L, the amount of Fe(VI) remained in the solution increases and beyond that a constant value is to be obtained for bulk Fe(VI) concentration. Hence, we can assume that hereafter the cyanide is in excess in the solution. Taking, this as cyanide is in excess, we typically calculated the pseudo first order rate constant for the reduction of Fe(VI) and it was found to be $6.80x10^{-3}$ sec^{-1}. Similarly, the first order rate constants also calculated for the various concentrations of cyanide and it was observed that with the increase in cyanide concentrations, it increases and it attains a constant value at and beyond the cyanide concentration $10x10^{-3}$ mol/L.

Studies were further extended, by using the cyanide probe as to measure the cyanide concentration in the solution. Such studies enables that within *ca* 5 min of Fe(VI) contact, the cyanide concentration diminishes more than 90% while taking the initial cyanide concentration $1.6x10^{-3}$ mol/L and Fe(VI) concentration $1.0x10^{-3}$ mol/L at constant pH~10.0 (phosphate buffer). Hence, it can be concluded that the application of Fe(VI) is found to be promising in the oxidation of cyanide and also it can serve as a green chemical for cleaner environmental remediation.

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FLOW-INJECTION CHEMILUMINESCENCE DETERMINATION OF FORMALDEHYDE IN WATER

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Formaldehyde (HCHO) is an important air pollutant. It is the most abundant carbonyl compound in the atmosphere and plays an important role as a free radical source [1]. Formaldehyde is often found in indoor air at levels typically several times higher than in outdoor air as a result of emission from a variety of materials and products. As a suspected human carcinogen, formaldehyde is an important toxic compound [2]. Atmospheric deposition is a significant source of HCHO in aquatic systems, since concentrations in rainwater are expected to be up to three orders of magnitude higher than in surface water [3].

In this contribution, a modification of the Trautz-Schorigin reaction method into a flow-injection analysis (FIA) configuration is described. The sample (200 μL) is injected into a carrier stream (deionized water) that is merged with gallic acid, EDTA, hydrogen peroxide solution and directly in a chemiluminescent detector with potassium hydroxide solution. The FIA system was optimized by both one-variable-at-a-time method and a modified simplex method. The both ways of optimization led to the similar optimal values.

A calibration graph is linear in the concentration range 4×10^{-8} - 1×10^{-5} M HCHO. The detection limit of formaldehyde for S/N=3 is 4×10^{-8} M. The relative standard deviations for 15 repeated measurements of 1×10^{-6} mol l^{-1} and 5×10^{-6} mol l^{-1} HCHO are 4.32 and 3.33 %, respectively. Acetone, formic acid, acetic acid, nitrite and nitrate do not interfere. The effect of acetaldehyde due to its low concentrations in rainwater can be considered negligible. Interference of sulphite at common aqueous concentrations is also insignificant. Interference of metal ions are eliminated by the addition of Na_2EDTA.

The method was applied to the determination of formaldehyde in urban rainwater. A comparison of results found by proposed method with those obtained by fluorimetric reference method provided a good agreement. Detailed results will be presented.

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TRIHALOMETHANE FORMATION KINETICS BY CHLORINATION OF RAW WATER

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The chlorination efficiency, THM speciation, and THM formation potential was determined in the river water of Cluj-Napoca, Romania. With regard to THM formation, raw water resources, under typical treatment conditions (total chlorine residual 0.5–0.9 mg/L), the total THM formation was always below EU and USEPA drinking water standards. The speciation of bromo-THMs in river water is due to the bromide level. Based on chlorine exposure estimations, it was concluded that the current chlorination practice for waters is sufficient for inactivation of bacterial contaminants.

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Poster contributions series B

B 1 Alka, Oh H Kwon, Kyu M. Choi, Dept. of Electronics & Information Communication Engineering, Kwandong University, Kangwondo (Korea)

Preparation and characterization of small sized particle PZT powders: a sol-gel modified approach

B2 Esteban Alonso, Irene Aparicio, Manuel Callejón, Salud Garcia-Rodriguez, David Olano, Juan Luis Santos, Dept. of Analytical Chemistry, University of Seville, Seville (Spain)

Monitoring and occurrence of selected pharmaceuticals in southern Spain municipal wastewater treatment plants

B 3 Nikolai V. Alov, Dept. of Analytical Chemistry, M.V. Lomonosov Moscow State University, Moscow (Russia)

XRF determination of heavy metals and their distribution in roadside soil

B 4 Israel Jimenez-Zapata, Mathieu Bauer, Nicolas H. Bings José A.C. Broekaert, Institute for Inorganic and Applied Chemistry, University of Hamburg, Hamburg (Germany)

Progress in the use of cold vapour techniques for the plasma atomic emission spectrometric determination of mercury

B 5 Francesca Bettazzi, Serena Laschi, Marco Mascini, Università degli Studi di Firenze, Firenze (Italy)

One-shot screen-printed thylakoid membrane-based biosensor for the detection of photosynthetic inhibitors in discrete samples

B 6 Nicolas Bukowiecki, Gerald Falkenberg, Peter Lienemann, Christoph N. Zwicki, Matthias Hill, Robert Gehrig, Ferenc Hegedüs, Markus Furger, Ernest Weingartner, Urs Baltensperger, Daniel Grolimund, Markus Willimann, André Scheidegger, Steven S. Cliff, Empa, Materials Science and Technology, Dübendorf (Switzerland)

RDI-SR-XRF: Detection of trace elements in ambient air at low concentration levels with high temporal resolution

B 7 Peter Beaven, José A.C. Broekaert, Elisa Daneva, Andreas Prange, Daniel Proefrock, GKSS Research Centre, Institute for Coastal Research/Marine Bioanalytical chemistry, Geesthacht (Germany)

Capillary Liquid Chromatography – Mass Spectrometry: a powerful combination for arsenic speciation in marine algae

B 8 Ch. D. Rasheed, Nabil A. Fakhre, Dept. of Chemistry, College of Education, University of Salhalddin, Erbil (Iraq)

Extraction-spectrophotometric determination of nitrate in polluted water and soil samples using diazo-coupling reaction

B 9 Laura Achene, Emanuele Ferretti, Alessandro Frugis, Luca Lucentini, Massimo Ottavini, Istituto Superiore di Sanità, Rome (Italy)

Simultaneous determination of several cyanotoxins in water destined to human consumption by using liquid chromatography – mass spectrometry

B 11 Stephan Franke, Christiane Meyer, Götz Neurath, Michael Specht, Institute for Organic Chemistry, University of Hamburg, Hamburg (Germany)

Identification of dioxypyramidon in Elbe river water

B 12 Stephan Franke, Nicolas Heinzel, Michael Specht, Institute for Organic Chemistry, University of Hamburg, Hamburg (Germany)

Thiosterols in Odra river sediment

B 13 Benedict C. Gbaruko, Paschal N. Gabruko, Hongtao Yu, Matthew Anyanwu N., Dept. of Industrial Chemistry, Abia State University Ututu, (Nigeria)

Nanotechnology, fibres and occupational health hazards

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B 61 Thorsten Hoffmann, Christopher Reinnig, Mathias Schott, Jörg Warnke, Institute for Inorganic and Analytical Chemistry, Johannes-Gutenberg-University of Mainz, Mainz (Germany)

Online measurement of peroxides from the ß-pinene/ozone reaction by atmospheric pressure chemical ionization – mass spectrometry

PREPARATION AND CHARACTERIZATION OF SMALL SIZED PZT POWDERS : A SOL-GEL MODIFIED APPROACH

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Current research basically diverted towards an increase in the operational output with the minimization of the materials used, which ultimately scaled down the dimensions of ceramic electronic components. In this direction the nano-technology pave the revolutionary changes in particular the electronic industries. The applications of nano-sized particles or nano-sized materials are hence, playing a significant role for various purposes. The PZT (lead, zirconium, titanium) based ceramics which, are reported to be ferroelectric materials have their important applications in the areas of surface acoustic waves (SAW), filters, infrared detectors, actuators, ferroelectric random acess memory, speakers, electronic switches etc. Moreover, these PZT materials possess the large electromechanical coupling factor, large spontaneous polarization, low dielectric loss and low internal stress etc. Hence, keeping in view the unique properties of pzt piezoelectric ceramics we also tried to synthesize indigenously the small sized PZT ceramic powder in the laboratory by using the modified sol-gel approach.

A propyl alcohol based sol-gel method was used as to replace the 2-methoxyethanol with 1,1,1 tris (hydroxymethyl) ethane for preparation of pzt piezoelectric ceramic[1]. The preparation process includes the excess of lead as to compensate the loss of lead during sintering. Precursor of lead, zirconium and titanium corresponding to 0.5 mol were used. The powder obtained by this sol-gel process were calcined at 900 ^{0}C and followed by the sintering at 1100 ^{0}C for about 2 hrs as to reach a pyrochlore-free crystal phase. The characterization of synthesized material was carried by the XRD analysis and the surface morphology were determined by high resolution scanning electron microscopy(SEM). Particle size distribution was measured by using laser particle size analyzer. Further, the prepared small sized pzt thin films are likely to be used in various applications of speakers as an attempt to 'miniaturization' with the enhanced practical efficiency.

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MONITORING AND OCCURRENCE OF SELECTED PHARMACEUTICALS IN SOUTHERN SPAIN MUNICIPAL WASTEWATER TREATMENT PLANTS

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The presence of pharmaceutical compounds in the environment is becoming a new environmental problem as these compounds have been detected in the aquatic environment not only in rivers, streams and surface water but also in drinking water [1-2]. Tons of drugs produced per year are being applied in human and veterinary medicine. After their use, pharmaceuticals used in veterinary applications can end up being dispersed in field or landfills and enter into the aquatic environment through rain events. In the case of pharmaceuticals used in human applications they enter into the sewer system through the urine and faeces and finally are discharged to wastewater treatment plants (WWTPs). Because of that, effluents from wastewater treatment plants can be considered one of the most important sources of pharmaceuticals in the environment.

In this paper, the efficiency of elimination of pharmaceuticals in conventional WWTPs has been evaluated over a year-period. Conventional wastewater treatments are not specifically designed to remove pharmaceuticals so their elimination depends on their ability to adsorb to solid particles and to biodegrade. The WWTPs studied were located in Seville (Spain) and were based on activated sludges. Pharmaceutical compounds monitored were four anti-inflammatory drugs (diclofenac, ibuprofen, ketoprofen and naproxen), an antiepileptic drug (carbamazepine) and a nervous stimulant (caffeine). Pharmaceuticals selected have some characteristic property that allows evaluating the work of the WWTPs by evaluating their removal rate.
Pharmaceuticals were determined by high-performance liquid chromatography (HPLC) with diode array and fluorescence detectors after solid phase extraction in Oasis HLB cartridges [3]. HPLC separations were carried out on a RP-18 column (125mm x 4 mm i.d., 5 µm) using gradient elution with methanol, acetonitrile and 50 mM potassium dihydrogen phosphate solution at a flow rate of 1 ml/min. The removal rates in the WWTPs evaluated were ranged from 12-16% for carmamazepine to 76-89% for ibuprofen. K_{ow} (K_{ow}: octanol-water partition coefficient), k_a (acid base constant) and k_d (sludge-water coefficient) values of each compound were used to understand the different removal efficiencies of each compound. Operational parameters of the WWTPs evaluated were used to understand the different removal efficiencies from one WWTP to another. Correlation coefficients between Total Suspended Solids (TSS), Chemical Oxygen Demand (COD) and pharmaceutical concentrations were also calculated finding that, at a confidence level $P = 0.05$ or 95 %, there were significant correlations between the three variables ($r > 0.80$).

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XRF DETERMINATION OF HEAVY METALS AND THEIR DISTRIBUTION IN ROADSIDE SOIL

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The application of X-ray fluorescence analysis (XRF) for the determination of heavy metals and their distribution in soil is very promising. XRF has a number of advantages such as simultaneous multielement analysis, large set of elements and wide range of element contents being determined, good reproducibility of the results, possibility of standardless analysis and low labour investment (simple sample preparation, automatic measurement, express analysis).

In this work the high efficiency of standardless multielement XRF for the determination of heavy metals in soil was demonstrated. We have analysed soil samples from the various regions of Moscow by a sequential WDXRF spectrometer SRS 3000 (Bruker AXS, Germany) and a precalibrated analytical program Semiquant 3000 based on the use of fundamental parameters (fluorescence yield, mass absorption coefficient, etc.) for the element content calculation.

It was established that the chemical composition of soil in Moscow essentially depends on the sampling region and the variety of pollution source (factory, highway, etc.). It was found that the contents of a number of elements are significantly greater or lower than in the standards of temperate climatic zones of Russia. The anthropogenic effect results in the considerable difference of chemical compositions of soil in Moscow and soddy podzolic soil characteristic of the near Moscow area.

X-ray fluorescence monitoring of heavy metal (Fe, Mn, Ti, and Pb) pollution of Moscow soil near highways with heavy traffic was fulfilled. The average Fe, Mn and Ti contents in roadside soil were found to exceed the usual background level by 2–5-fold, maximum Pb content – by 10–15-fold. Heavy metals enter roadside soil mainly as a result of transport work. When engine barrels and other inner parts are abraded, iron enters air and soil; the combustion of ethylated fuel is the main source of lead. Iron, manganese, titanium and other elements enter roadside soil as a result of tire abrasion. The lateral distribution of Fe, Mn, Ti and Pb contents in soil near the highways was studied. It was shown that the behaviour of lateral pollutant distribution in roadside soil has no specific exponential shape. It has local extremuma and depends on the metal nature and the roadside terrain topography.

PROGRESS IN THE USE OF COLD VAPOR TECHNIQUES FOR THE PLASMA ATOMIC EMISSION SPECTROMETRIC DETERMINATION OF MERCURY

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The cold vapor generation has been shown to be the technique “par excellence” for a sensitive determination of mercury in environmental samples. The present investigations focus on the development of a miniaturized plasma source for the detection of volatile metal species as well as on a new device enabling the generation of cold vapor as sampling technique for inductively coupled plasma optical emission spectrometry.

A microwave 2.45GHz Ar Microstrip plasma working at a power input of only 40 W is generated on a sapphire wafer substrate and evaluated for emission spectrometric determination of mercury using the cold vapor technique. The mercury contained in a liquid sample is reduced to the elemental state by mixing the liquid flow in a T-shaped tube with a solution of $SnCl_2$ and the generated vapor is carried to the microplasma after passing a gas-liquid separator. A miniaturization of the whole system has been achieved by using a dispersive CCD-spectrometer having a focal length of only 23 mm for atomic emission line detection.

The determination of mercury by inductively coupled plasma optical emission spectrometry with conventional pneumatic nebulizers is hampered by poor limits of detection being far above the german authorized limit for drinking water (1 $\mu g.L^{-1}$). A modified cross-flow nebulizer fitted with two tips for liquid introduction enables the on-line generation of mercury vapor, when the sample and $SnCl_2$ solutions are nebulized simultaneously and mixed during the aerosol generation. A jacketed spray chamber cooled at 1°C was used to perform a partial desolvation of the aerosol. This easy nebulizer set-up was found to allow an improvement of the limits of detection for mercury by more than one order of magnitude.

ONE–SHOT SCREEN-PRINTED THYLAKOID MEMBRANE-BASED BIOSENSOR FOR THE DETECTION OF PHOTOSYNTHETIC INHIBITORS IN DISCRETE SAMPLES

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Screen-printing technology offers the possibility to produce sensors in a large number and at low cost. Thus due to their intrinsic characteristics and reproducibility, screen printed electrodes can be used in the development of disposable electrochemical devices.

In the presented work, carbon based screen-printed electrodes (SPCEs) have been used to develop a one-shot-measure biosensor for the detection of photosynthetic inhibitors in discrete samples. The measurement was based on the electrochemical evaluation of the activity of photosystem II (PSII), a protein complex present in the photosynthetic organisms and involved in the photosynthesis. The biosensor was prepared by the modification of the working electrode, using thylakoid membranes extracted from spinach leaves. The modified sensors were then used as one-shot system to measure the presence of PSII activity inhibitors in discrete standard solutions. The coupling of the developed biosensor with a custom-made cell allowed to perform tests using only 50 µL of total solution volume within 10 min as measurement time. Inhibition curves were recorded for some photosynthetic inhibitors in a concentration range of 10^{-6}-10^{-8} M. Reproducibility (RSD%) of 10% was found and calculated LODs were in the nanomolar range.

Measurements on real samples have been also performed, comparing the results with those obtained using a fluorescence-based commercial instrument for the analysis of photosynthetic inhibitors.

RDI-SR-XRF: DETECTION OF TRACE ELEMENTS IN AMBIENT AIR AT LOW CONCENTRATION LEVELS WITH HIGH TEMPORAL RESOLUTION

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Excessive load of the ambient air with fine particles (PM10, particulate matter with a diameter smaller than 10 μm) is one of the most pressing issues of air pollution control. Knowing the elemental composition of air samples, especially with high time resolution, is highly important in this context and will allow for a more profound source contribution of the complex ambient air mix. Air quality monitoring by means of filter based sample collection is a major approach that is followed worldwide. Filter analysis is generally reaching its limit by the minimum quantity of material that has to be collected for subsequent analysis by a common analytical technique.

Recently, an innovative SR-XRF application originally developed in the US has been optimized and adapted for the specific requirements at HASYLAB (Hamburg) and SLS (Switzerland) [1]. It is used as powerful tool for the size-segregated high time resolution elemental analysis of ambient air samples. A three-stage rotating drum impactor (RDI, [2]) collects ambient aerosol in 3 size ranges (0.1-1 μm, 1-2.5 μm and 2.5-10 μm) with a time resolution of 1 hour by particle impaction and deposition on a thin Mylar substrate film (thickness 1.8 μm). For the SR-XRF measurements, the Mylar films are transferred from the RDI sampling wheels to slitted aluminum wheels that are used as sample holders. The wheels are placed on a goniometer, which enables the wheels to turn step by step. According to the selected Z region of interest, a monoenergetic X-ray primary microbeam (7 – 20 keV primary energy) is used. The count accumulation interval per individual sample spot is usually 15 s. Absolute calibration of the measured XRF spectral data is performed using stock solutions with known element concentrations that are pipetted on a Mylar blank and analyzed under identical SR-XRF conditions. The detection limits achieved with our SR-XRF experiments is in the range of pg/m^3 ambient air, with only 15-s counting time per step for a 1-h RDI sample. This represents a strikingly higher sensitivity compared to laboratory based XRF methods. The average uncertainty for the determined absolute elemental concentrations (ng/m^3 air) is ± 10 %.

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LIQUID CHROMATOGRAPHY - MASS SPECTROMETRY: A POWERFUL COMBINATION FOR ARSENIC SPECIATION IN MARINE ALGAE

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Capillary HPLC on-line hyphenated with both elemental and molecular mass spectrometry has been used for arsenic speciation in brown and red marine algae. Different species were separated by anion-exchange capillary HPLC - inductively coupled plasma mass spectrometry (cHPLC-ICP-MS) after water-methanol liquid/liquid extraction. They were identified by on-line anion-exchange capillary HPLC - electrospray ionization tandem mass spectrometry (cHPLC-ESI-MS/MS). Methylated arsenic species and arseno-riboses (arsenosugars) were determined by monitoring their product ions. Another compound, arsenobetaine shown to be together with arsenosugars the most abundant forms of As in the both seaweed samples. They were determinate without any additional sample pre-treatment after extraction and without the need for a synthesized standard of natural occurring arseno-riboses. Variation of the distribution of As among the different species in the red and brown algae is presented. Although the main species found in the algae extract are arseno-riboses and arsenobetaine, a small trace of dimethylarsinic acid was determined by the both analytical techniques, i.e. cHPLC-ICP-MS and cHPLC-ESI-MS/MS. Four more, so far unknown compounds were observed in the anion exchanged cHPLC-ICP-MS chromatograms of the algae extracts and have been further investigated by cHPLC-ESI-MS/MS. Structural and sequence information for identification of the unknown peaks in the samples was obtained with tandem mass spectrometry approach. The results indicated a presence of As forms (metabolites) conjugated with thiol groups of glutathione (GSH) and glutathione derived peptides or proteins, so called phytochelatins (PCs). Oligomers of two, three sub-units, respectively PC_2 and PC_3, with internal oxidation of SH groups, have been monitored in the algae extracts as well as potential As-PC_2, iso-PC_2-As, As-PC_3 and iso-PC_3-As complexes. The complementary application of cHPLC-ICP-MS and cHPLC-ESI-MS/MS provides a powerful tool for analyzing arsenic metabolites in complex biological samples, such as marine algae.

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Extraction-Spectrophotometric Determination of Nitrate in Polluted Water and Soil Samples using Diazo-Coupling Reaction

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Abstract

A simple and sensitive spectrophotometric method was described for the determination of nitrate. The method is based on the reaction of nitrite with 3-amino-5-methyl isoxazole to form a diazonium ion, which is coupled with resorcinol in an alkaline medium to form the azo dye, with a maximum absorption at 354 nm. Nitrate is determined by it's reduction to nitrite using amalgamated cadmium column. Beer's law is obeyed over the range of 0.04-6 μg/ml, with a detection limit of 0.02μg/ml. The molar absorptivity, Sandell index are 2.482 x 10^4 L/mol.Cm and 0.00249 μg/ml respectively . The effect of 35 cations and anions were studied. The method was applied for determination of nitrate in polluted water and soil samples, the results were compaired with the standard method, NEDA. The prepared azo dye was extracted into 1:1 (v/v) mixture of isoamyl alcohol-isobutyl methyl ketone. Nitrate was determined over the range of 0.005-2 μg/ml with a detection limit of 0.003 μg/ml and molar absorptivity 6.486 x 10^4 L/mol. cm.

Nitrate is generally more stable, nearly inert in the ground-water environment, and can travel significant distances from the source[1]. The World Health Organization (WHO) report states that nitrate concentration in surface water have been increased substantially, especially in the last 30 years, the main factors responsible for the trend being the increased use of artificial fertilizers, change in land use, disposal of wastes from intensive animal farming, increasing industrialization, urbanization, and other development activities [2]. Determination of nitrate in trace concentrations is of great interest in connection with problems of water pollution, sanitation and allied areas relating of public health [3]. Nitrate determination is based on direct spectrophotometric methods, or a measurement after derivatization, usually as reduction to nitrite [4]. In the present work an extraction-spectrophotometric determination of nitrate in polluted water and soil samples was proposed based upon diazo-coupling reaction.

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SIMULTANEOUS DETERMINATION OF SEVERAL CYANOTOXINS IN WATER DESTINED TO HUMAN CONSUMPTION BY USING LIQUID CHROMATOGRAPHY - MASS SPECTROMETRY.

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Cyanobacteria (blue-green algae) are commonly observed in water bodies used for drinking water supplies and represent a public safety hazard due to the capability of many species to produce metabolites lethally toxic to livestock and humans.

Cyanotoxins are most frequently hepatotoxic or neurotoxic. Hepatotoxins are the most abundant and consist of cyclic heptapeptides, namely microcystins [1,2], cyclic pentapeptides nodularins [3] and cylindrospermospin, having a tricyclic guanidine moiety combined with hydroxymethyluracil [4,5]. Among the neurotoxins found in cyanobacteria anatoxin-a, a low molecular weight bicyclic secondary amine, is a potent depolarising neuromuscular blocking agent [6].

The monitoring of drinking water supplies for the presence of cyanotoxins is of pivotal importance for the assessment of environmental and health risks.

We developed a multiple ion monitoring (MIM) LC-MS method able to provide simultaneous detection and unambiguous identification of intracellular and extracellular cyanotoxins (anatoxin-a, nodularin, microcystin-LA, microcystin-LF, microcystin-LR, , microcystin-RR, microcystin-YR, and cylindrospermopsin) in samples of water destined to human consumption.

The analytes were simply extracted from filtrated cyanobacterial cells or from water samples following cell lises by using an optimized SPE procedure.

The analytes were chromatographed on an SGE (250 × 4.6 mm) SS Wakosil II C18RS column, by using mixture of acetonitrile-water cointaining 0.01% of formic acid as mobile phase, and ionised in a TurboIonSpray (TIS) interface operating in the positive ion mode.

The developed MIM LC-MS method achieved a rapid and simultaneous screening of the entire range of toxins in freshwater and tap water samples collected in Italy and Sri-Lanka.

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IDENTIFICATION OF DIOXYPYRAMIDON IN ELBE RIVER WATER

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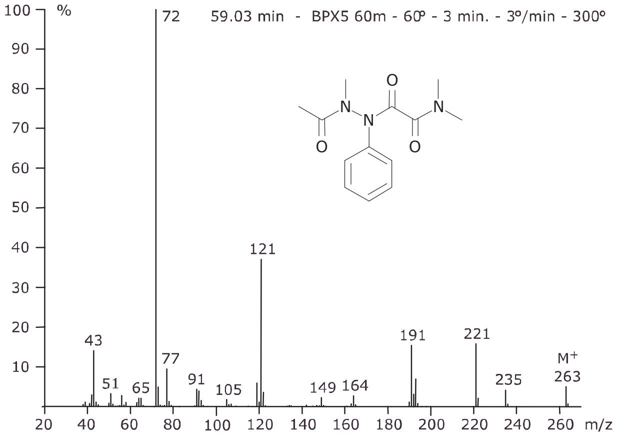
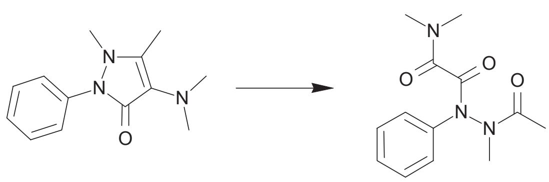
Recently, dioxypyramidon (AMDOPH) was shown to be present in high concentration in various water treatment plant and surface water samples from Berlin (e.g. wells of an artificial groundwater replenishment plant ~3 µg/L [1], stream or lake samples ~0.13 µg/L [2]).
Dioxypyramidon (1-acetyl-1-methyl-2-dimethyloxamoyl-2-phenylhydrazide, AMDOPH) known since 1929 as the product of oxidation of 4-dimethylamino-1,5-dimethyl-2-phenyl-3(1*H*)-pyrazolone (pyramidon, aminophenazone) with hydrogen peroxide is a water-soluble compound (76.9 g/L at 20 °C, 482 g/L at 37 °C) [3] that was observed during the 1990s throughout the Elbe river downstream from Pardubice (Tschechia) and in groundwater from the Elbe river glacial valley near Hamburg. In addition, we found the compound in industrial waste water from a chemical plant in Pardubice and in a tributary of the Odra river [4].
GC/MS analysis of solid phase (SPE) and dichloromethan extracts of water samples resulted in a mass spectrum not present in mass spectral data bases. GC/MS accurate mass measurements at 10 000 resolution allowed to determine elemental compositions of molecular ($C_{13}H_{17}N_3O_3$) and fragment ions (m/z 235 $C_{12}H_{17}N_3O_2$, 221 $C_{11}H_{15}N_3O_2$, 193 $C_{10}H_{15}N_3O$, 191 $C_{10}H_{11}N_2O_2$, 121 $C_7H_9N_2$, 77 C_6H_5, 72 C_3H_6NO). With this information a Beilstein search led to dioxypyramidon [5], and the identity of mass spectrum and retention time was verified by synthesis.





Photosensitized oxidation of pyramidon with singlet oxygen gave dioxypyramidon in high yield and purity.
Ames-tests (S. typhimurium, TA 100, TA 98, TA 102 with and without S9) gave no hints of a mutagenic potential for dioxypyramidon.

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THIOSTEROLS IN ODRA RIVER SEDIMENT

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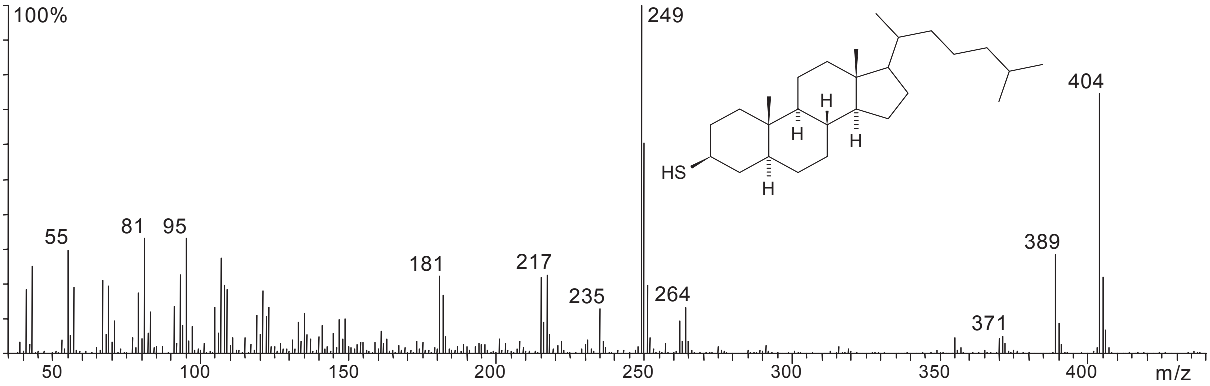
The International Odra River Project was initiated after the Odra flood in summer 1997. GC/MS nontarget screening provided comprehensive information on the occurrence and distribution of organic compounds in the Odra river system [1].

Odra river sediment from a polluted site contained a major component with an unknown mass spectrum. The isotopic pattern of the molecular ion showed the presence of sulfur in the molecule. In addition, two minor components with homologuous mass spectra were detected. Search for mass spectral similarity (SISCOM) [2] pointed to a steroidal carbon skeleton as the common structural feature of the compounds.



Mass spectral key fragments of saturated 3-steranols are the ring C and D cleavage products. The replacement of oxygen with sulfur in the thio-analogues causes characteristic mass-shifts of the corresponding frament ions confirming the steroidal carbon skeleton of the compounds. Steradienes, also present in the sediment allowed to use GC retention characteristics to assign the alkyl chain structure of the thiosterols.

Thiosterols, steranes with a 3β-sulfhydryl group were detected in subaquatic river sediment. 3β-Sterane thiols have been found only once in polluted mediterranian marine sediments before [3]. A sulfur-rich, anoxic environment possibly provides the conditions to transform ordinary zoo- and phythosterols into thiosterols.

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Nanotechnology, Fibers and Occupational Health Hazards

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The emerging field of nanotechnology is revolutionalizing many areas of science, showing a lot of promise at improving health, cleaning up the environment, enhancing production and productivity and reducing our energy dependence on oil, among many others. Nanotechnology has not only extended the use of current materials, but is facilitating the introduction of new materials and devices with intricate and closely engineered structures. As these materials experience massive patronage in nanotechnology, there is consequent rise in their presence in consumer and industrial products. Nanometer- diameter particles have been shown to be more toxic than large particles on a mass basis because of a combination of many factors. However, knowledge about the potential environmental and public health effects of these materials is still limited. This paper reviews the many applications of fibers in nanotechnology, their potential entry points into the human body, their likely pathways and bioactivity and their known and potential occupational health hazards

ISOLATION OF HAPTOGLOBIN FROM HARBOUR SEALS

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Marine mammals such as harbour seals (*Phoca vitulina*) may serve as indicators of the status of the North Sea ecosystem, which is influenced by pollutants and increasing commercial use. To monitor the health status of individual marine mammals, different immune system parameters are evaluated as potential biochemical indicators. In humans and animals the acute phase response as a defence to inflammation and stress leads to increased plasma level of acute phase proteins such as the glycoprotein haptoglobin.[1]

To investigate the potential of haptoglobin as biochemical indicator of anthropogenic influence (i.e. stress) in harbour seals, an analytical strategy for the isolation of seal haptoglobin and the determination of its yet unknown structure is shown. Special attention is paid to the glycosylation pattern of seal Hp, also with regard to possible disease specific modifications of the carbohydrate moiety. [2, 3]

The strategy for the isolation of haptoglobin includes the following steps: prefractionation of plasma samples by ammonium sulfate precipitation, isolation of haptoglobin by affinity chromatography and final purification by size exclusion gel chromatography. [4] The hereby used steps were optimised on easily accessible canine blood samples and transferred to plasma samples from wild living seals as well as from seals kept in captivity.

Preliminary results of *De novo* sequencing of the isolated seal haptoglobin by mass spectrometry are shown after development of important steps for structure determination with commercially available human haptoglobin.

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EMISSION OF MONOTERPENES FROM PICEA ABIES (L) KARST UNDER NORMAL AND ELEVATED CO_2 ATMOSPHERE

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Monoterpenes belong to the group of biogenic volatile compounds [1], originating as metabolites in some plants, mainly trees, and in particular conifers [2]. Although the concentration of monoterpenes in the atmosphere varies from a few ppb (v/v) down to a few ppt (v/v) the production of these types of terpenes is significant [3] and influences the chemistry of the atmosphere in a fundamental fashion [4]. The total production of terpenes is several times larger than total production of NMHCs emitted from anthropogenic sources. They play an important role in tropospheric chemistry, especially as precursors in production of ozone and atmospheric aerosols.

This contribution describes the study of emission of monoterpenes (α-pinene, β-pinene, *S*-limonene, camphene) by Picea Abies (L) Karst in normal and elevated CO_2 atmosphere. The study was performed at the Experimental environmental station at Bílý Kříž, Czech Republic in two spheres with normal (350 ppm) and elevated (700 ppm) concentration of CO_2.

The new method [5] was applied to the determination of monoterpenes in air. The method is based on the terpenes preconcentration from air into a thin film of n-heptane in the cylindrical wet effluent diffussion denuder (air flow rate of 0.5 l/min, liquid flow rate of 400 µl/min). Denuder concentrate with collected monoterpenes is taken away at the bottom of the denuder into small vial over 6 minutes periods. The concentrate was analyzed by the GC-LVI/MS [6].

Dependence of monoterpenes emission on temperature, humidity and light intensity (i.e., FAR) were measured in parallel in both spheres. The emission of monoterpenes (α-pinene, β-pinene, camphene, S-limonene) by Picea Abies (L) Karst in sphere with elevated CO_2 concentration is about 3-5 times smaller than emission of monoterpenes in sphere with normal CO_2 concentration. Detailed results will be presented.

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DESIGN OF A HIGHLY EFFICIENT TRIPODAL AMINOPHENOLATE CHELATOR FOR TRIVALENT GALLIUM AND IRON

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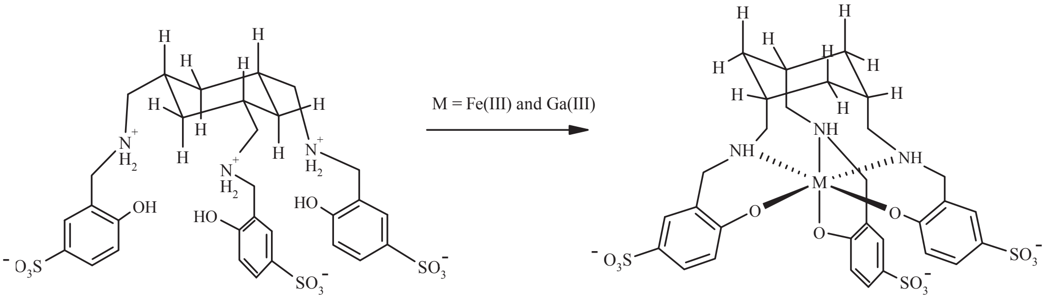
There is a considerable clinical need for the design of new chelators that can be used to reduce metal ions overload diseases and the health effects associated with it. For such a chelator, one needs to consider several factors: (i) strong chelating ability (ii) water solubility and (iii) neutral complex formation. Considering these facts a water-soluble tripodal amine phenols, c*is,cis*-1,3,5-tris{(2-hydroxybenzyl)aminomethyl}cyclohexane (H_6TMACHSALS) bearing three equivalent side-arms each contained two donor sites (an amine N-atom and a phenol O-atom) has been synthesized by Schiff base condensation of *cis,cis*-1,3,5-triaminomethylcyclohexane (TMACH) [1] with three equivalent of sodium-5-sulfosalicylaldehyde, followed by reduction with $NaBH_4$ and characterized through elemental analysis and various spectral (UV-VIS, IR, ^{1}H and ^{13}C NMR) data. The peaks at 0.71, 1.72 and 1.82 ppm in ^{1}H NMR (D_2O, 300 MHz) spectrum of ligand indicate that the three coordinating arms are appended through the equatorial positions. Further the optimized geometry and its spectroscopic data were calculated through quantum mechanical treatment and compared with the experimental data.



H_6TMACHSALS M(TMACHSALS)

The complexation behavior of the ligand with Ga(III) and Fe(III) have been investigated in an aqueous medium of 0.1 M KCl ionic strength and 25±1°C by potentiometric and spectrophotometric method. Complexes of the types MLH and ML have been observed and their formation constants were calculated. Iron(III) formed strong complexes than Ga(III) and their solution structures have been probed by spectroscopic and NMR studies, and the results from molecular modeling calculations. The ligand coordinates through three phenolate-O-atoms and three amine-N-atoms, where the three appended arms involves a ring-flip into energetically disfavor axial conformer giving distorted octahedral geometry. On comparing to *cis*,*cis*-1,3,5-tris((2-hydroxy-5-sulfobenzyl)amino)cyclohexane (H_6TACS) [2], which shows slow complexation kinetics and weaker binding, H_6TMACHSAL, formed strong complexes due to the presence of an additional methylene groups in each pendant arms.

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Multiple pesticides screening and quantitation using GC-Triple Quadrupole Mass Spectrometer

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Currently, GC with single quadruple mass spectrometry has been commonly used for various pesticides analysis. However, due to the complexity of sample matrix and increasing expectation to detect and quantitate low residues pesticides in environment or food, it has been an increase challenge to analyze or detect this pesticide in accuracy using GC single quadrupole system. The requirements for rapid and sensitive multiple pesticides residue analysis method has pushing the performance of GC single quadrupole mass spectrometer to its limit. GC tandem quadrupole mass spectrometry system with its function of Multiple Reactions Monitoring (MRM) has been found to be an excellent alternative technology to complement the limitation of GC single quadrupole in this area of application. [1]

The aims of this experiment were to show the capabilities of GC triple quadrupole mass spectrometry system in screening & quantitation of 200 pesticides in a single GC separation analysis. The results were also shown the capability & important of deconvolution software in reducing work of the data mining and library matching for compound identification.

The 200 pesticides were separated using DB-5 MS GC column in 30min. The range of LOQ was 8 to 50 ppb. The calibration was performed between 4 -10 ppb to 40-100 ppb depends and a good linearity (above $r^2 = 0.99$) were obtained. The accuracy, in term of quantitation of all pesticides was between 92% and 108%.

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UTILIZING OF ELECTROCHEMICAL TECHNIQUES FOR DETERMINATION OF SALICYLATES

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Salicylates, in the form of willow bark, were used as an analgesic during the time of Hippocrates, and their antipyretic effects have been recognized for more than 200 years. Acetylsalicylic acid (AcSA), or aspirin, was introduced in the late 1890s and has been used to treat a variety of inflammatory conditions. There have been also demonstrated aspirin therapeutic benefit in a variety of cardiovascular diseases but the mechanism of its action is still unclear. Besides that, salicylic acid (SA) is one of such compounds, which has been shown to play an important signalling role in the activation of various plant defence responses following pathogen attack. These responses include the induction of local and systemic disease resistance, the potentiation of host cell death, and the containment of pathogen spread. The mechanisms through which SA mediates these effects are varied and can involve alterations in the activity or synthesis of certain enzymes, increased defence gene expression, potentiation of several defence responses, and/or the generation of free radicals

The aim of this work was to study the electrochemical behaviour of salicylic acid on the surface of carbon paste electrode (CPE) by square wave voltammetry (SWV). The optimized technique with detection limit 1.3 ng/ml was utilized to determine SA in a pharmaceutical drug. Moreover, salicylates have been analysed by flow injection analysis using graphite porous electrodes. The most suitable potentials for determination of SA and ASA were 1.2 V and 1.0 V vs. H_2/Pd, respectively. After that, we aimed on indirect determination of AcSA by SWV CPE. AcSA did not give any SWV signal on the surface of CPE, but it is common knowledge that it could be hydrolyzed on salicylic acid. The method for indirect determination of acetylsalicylic acid has been optimized and utilized for analysis of real samples. On the base of the obtained results we used carbon microelectrode for determination of SA in different willow species (*Salix laponum*, *S. planifolia*, *S. foetida*, *S. foetida x hastata*, *S. x "Aegma Brno"*, *S. purpurea cv. Nana*, *S. reinii*, *S. repens*, *S. x erythrotoflexuosa*, *S. caterii*, *S. fragilis*, *S. triandra* a *S. viminalis*). We determined that the average content of SA in branches was 750 µg/g FW and in barks 560 µg/g FW. Thus branches contained more SA than barks. The highest content of SA was observed in a bark of *S. laponum* (2986 µg/g FW) and in branches of *S. purpurea cv. Nana* (2095 µg/g FW) and *S. planifolia* (2168 µg/g FW). We also found out that the content of SA in the hybrid (*S. cv. Aegma Brno*) cultivated in city of Brno was very low (85 µg/g FW). Moreover, we utilized the technique for determination of SA in maize plant, which were attacked by pathogen. The determination of salicylic acid by square wave voltammetry on carbon electrodes is selective, sensitive and low-cost way how we could study this compound in different biological samples. The results obtained could be used for suggestion of a biosensor used for investigation of hypersensitive response of plants.

Acknowledgement: *The work on this project was supported by grants: GACR 525/04/P132 and MSMT 06030.*

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APPLICATION OF ASE-GC-IDMS TECHNIQUE FOR THE DETERMINATION OF ORGANIC COMPOUNDS IN ENVIRONMENTAL SAMPLES

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The main trend in quantitative analysis of environmental samples is possibility to fast and labour less determination of analytes with high accuracy and precision [1]. Environmental samples have usually very complicated matrix and an isolation step in analytical procedure is needed.

Accelerated solvent extraction (ASE) is an extraction technique, in which liquid solvent is used as an extraction solvent under elevated temperatures and pressures. The entire extraction process is fully automated and performed in minutes for fast and easy extraction with low solvent consumption. Therefore, ASE has been developing as a substitute for the classical extraction techniques [2].

Isotope dilution mass spectrometry (IDMS) is a definitive technique; it does not depend on sample recovery, generates results with high precision, and can be tested for bias. The use of IDMS for organic analytes is based on adding a known amount of an isotopically labeled version of the analyte to the sample as an internal standard, equilibrating the labeled analyte with the endogenous analyte, processing the sample, and then measuring the ratio of unlabeled-to-labeled analyte by using gas chromatography-mass spectrometry (GC-MS) [3].

Combining ASE technique during isolation of analytes, GC for separation of analytes and IDMS for quantitation analytical chemists can have powerful tool for determination of organic compounds in environmental samples.

The results of application of ASE-GC-IDMS technique for determination of PCBs in sediment and soil samples and TBT in sediment samples are presented.

Results were a part of CCQM exercises concerning determination of PCBs in sediment samples (CCQM-K25) [4] and TBT in sediment (CCQM-P18) [5].

The ASE-GC-IDMS technique is efficient, precise and suitable for the analysis of PCBs and TBT in environmental samples.

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MOBILITY OF POLLUTANTS AND THEIR TOXICITY ON THE BASIS OF STUDIES OF SEDIMENTS FROM LAKE TURAWSKIE

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Lake sediments contain thousands of substances of natural and anthropogenic origin. Taking into account that a great number of them are toxic, the presence of some of them may have negative influence on aquatic ecosystem. That's why, it's very important to obtain a reliable information about the toxicity of the described environmental element, namely – the lake's sediments.

Chemical analysis provides only part of the knowledge necessary to evaluate and assess toxic potential compounds for wildlife and humans. This is due to different bioavailability of forms in which pollutants exist in the environment and their different biological activities. Besides, the complex interactions between different environmental chemicals are not completely understood and considered. The parallel use of selective biotests provides the more complete information about the potential ecotoxicological effects.

The impoundment Lake Turawskie was indicated to the preliminary project financed by the Province Environment Protection Fund in Opole. The aim of this project was to assess the ecological state of this lake. Lake Turawskie is an artificial reservoir on the Mala Panew River. The sources of pollutions for Mala Panew River waters are industrial wastes (mainly from metallurgical plants), agricultural activity and municipal waste waters.

This paper reports on the toxicity assessment and the bioavailability of metals in sediments samples collected at different depth from bores made in bottom of Lake Turawskie. The toxicity of aqueous elutriates was measured applying the acute toxicity test - Microtox® (Strategic Diagnostics Inc., USA). The inhibition of bioluminescence of freeze-dried *Vibrio fischeri* bacteria after 30 min was used as endpoint. The ecotoxicological data set was compiled with results of metal content analyses. The total contents of metals were determined by AAS and ICP-AES techniques, while Hg and As were determined by CV-AAS and HG-AES, respectively. Assuming that only water-soluble forms of metals are bioavailable, the speciation of metals was investigated using a sequential extraction technique [1,2]. An attempt was also made to search for a correlation between results of toxicity assays and the content of metals present in the bioavailable fractions.

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Pb, Sr, Nd and C isotopic evidence for sources of atmospheric heavy metals and their deposition in the urban environment of Strasbourg-kehl

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The topography and the meteorological conditions of the plain of the Rhine valley are particularly unfavourable for the ventilation and the dispersion of pollutants. Therefore the urban communities of Strasbourg and Kehl still suffer from significant air pollution. The major sources of pollution are waste incinerators, chemical industries, power stations, steel-works and road transport.

During the last three decades, the emissions of heavy metals in the atmosphere caused much attention due to their toxicity for human beings as well for the environment. The monitoring and tracing of the major sources of the heavy metals associated with aerosols, and in particular lead, was carried out successfully with help of Pb isotopes.

The tracing of the anthropogenic sources of atmospheric lead is made by the collection of the aerosols directly on filters or indirectly by sampling rain and snow. [1, 2] but lichens or tree barks have been successfully used in order to study air pollution and to determine the sources of atmospheric Pb [3, 4, 5, 6].

In our study we collected barks (as biomonitors) as well as aerosols trapped in particle collectors. The samples were analysed using specific tracers like the isotopes of Pb, Nd, Sr, C, and the rare earth elements.

This analytical approach is due to the combination of different isotope systems novel in the field of environmental research and enables us to identify not only the various sources of the pollutants but also their redistribution in the urban environment.

The first results are very promising and indicate that the combination of the analyses of the various isotopic systems in the tree barks allow us to make a clear and significant distinction of various sources in an urban environment.

The Pb isotope data of aerosols collected on filters indicate that more the quantity of particulate matter PM (43µg/m3) is important more these particulates have an industrial anthropogenic isotopic signature (206Pb/207Pb ~1.155) while when the quantity of particulate matter PM is low (10µg/m3) the Pb isotopic composition is closer to the natural signature (206Pb/207Pb ~1.184).

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BLACKISH SURFACE DEPOSITS ON HIGHWAY ROADSIDES

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A blackish, sandy material (‘blackish deposit’, BD) accumulates on roadsides of highways, and may few years after road opening reach several centimeters of depth. Apparently, suspended solids from infiltrating road runoff constitute part of BD, while aerial depositions of local dust and debris constitute the rest. Blackish deposits are assumed to play a key-role for near-road control of contaminant dissipation. In this study of four Danish highways, the similarity of BD’s from different locations was pronounced, as was their divergence from now-buried original surface (OS) materials. Compared to OS-materials, BD-materials contain more organic matter (4-8% versus around 1 % in OS), have a high and less-variable content of clay and oxides, and a slightly lower bulk weight and pH. Similar clay mineralogy suggests both BD and OS to be of local origin. As expected, the border between BD and OS is also a border between different levels of soil contamination: Zn up to 330 mg/kg in BD versus 19-63 mg/kg in OS, Pb up to 210 mg/kg versus 5-33 mg/kg, Cr up to 250 mg/kg versus 3-10 mg/kg, Cd up to twice as high in BD as in OS, Br and As markedly higher in BD than OS, heavy mineral oils up to 680 mg/kg versus 16-24 mg/kg, and sum of PAH up to 1.4 mg/kg versus <0.05-0.72 mg/kg. Thus, the continuous deposition of organic matter, calcite, oxides and clay suggest BD to be able to accumulate – in addition to particle-bound - dissolved contaminants from infiltrating road runoff.

ACID-INDUCED CLOUD-POINT EXTRACTION WITH SODIUM DODECYLSULFATE FOR THE PRECONCENTRATION AND QUICK FLUORIMETRIC DETERMINATION OF SOME POLYCYCLIC AROMATIC HYDROCARBONS IN AQUEOUS MEDIA

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Polynuclear aromatic hydrocarbons (PAHs) are well-known environmental pollutants, which may be formed during the combustion of carbonaceous materials at high temperature. Owing to their mutagenic and carcinogenic potential, they have been determined in several matrices, particularly waters, soils, and sediments. Due to their high hydrophobicity PAHs concentration in nature water is low, and the determination of PAHs requires a preconcentration step, For these purpose the acid-induced cloud-point extraction (CPE) was applied [*испанцы*]. CPE based on the separation of a homogeneous aqueous micellar solution into two isotropic liquid phases has become increasingly attractive, since it allows one to combine extraction, preconcentration and removal of PAHs adsorbed on the soil colloids into one step. CPE has been used for preconcentration of ten representatives of polycyclic aromatic hydrocarbons (benz[a]pyren, chrysene, pyren, acenaphthene, anthracene, benz[a]anthracene, dibenz[a,h]anthracene, phenanthrene, fluorene, fluoranthene and some pyrene derivatives) for the following fluorescence determination. On the two-phase separation process and extraction percentages of PAHs have systematically been examined the following variabilities: surfactant type and concentration, HCl concentration, electrolyte presence (sodium chloride, sulfate and sulfite), the centrifugation rate and time over the range [2]. The extraction percentages and limits of detection have been obtained for all PAHs after CPE ranged from 67 to 93% and 10^{-7} to 10^{-12}, respectively. Pyrene was used as a fluorescent probe to monitor the micropolarity of the surfactant-rich phase compared with SDS micelles and this allows one to conclude that water content in micellar phase after CPE was reduced. The spectral, metrological and analytical characteristics of the fluorimetric determination of PAH and pyrene derivatives after the acid-based CPE with sodium dodecylsulfate were examined. The determination of benz[*a*]pyrene in water was examined as an example.

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Determination of Lycopene in watermelon by High Performance Liquid Chromatography Method

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In this work, the determination of lycopene in watermelon by high-performance liquid chromatography (HPLC) method was described. Samples were extracted in Erlenmeyer flasks with hexane–ethanol–acetone (50:25:25). After extraction, 15 mL of water were added to separated the solution into poler and nonpolar layers. Lycopene was concentrated in the upper nonpolar phase while other components and polor pigments were contained in the lower polar phase[1,2]. The lycopene phase was analyzed using isocratic HPLC with a C-18 column and methanol–THF- water (67:27:6) mobile phase. Lycopene eluted as chromatographically pure peak.

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ON SITE LEAD-MONITORING USING A PORTABLE ELECTROANALYTICAL DEVICE TO DIAGNOSE CORRODED PIPES IN DRINKING WATER DISTRIBUTION SYSTEM.

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Lead is one of the most ubiquitous heavy metal encountered in everyday life. Its toxic effects to human health, even if present at trace levels, is unquestionable and also well-known by everybody. Accordingly stronger regulations are set. Thus, the maximum admissible concentration of lead in drinking water will be decreased from 25 µg/L to 10 µg/L in 2013, as stipulated in the European Directive (98/83/CE). Rather high levels of lead in drinking tap water, exceeding sometimes regulation threshold, are generated by oxidative corrosion of lead pipes or soldered fittings. This problem is particularly worrying in France, where 10 millions of habitations are still equipped with supply lead pipes. Moreover, until 1995, lead-containing materials were installed in the distribution system of cities like Marseille or Paris. Consequently, in addition to regulations obedience, increasing pressure on water companies came up from growing concern of the general population. The determination of lead in potable water is almost exclusively performed using standard spectroscopic techniques such as inductively coupled plasma atomic emission spectroscopy (ICP-AES) or mass spectrometry (ICP-MS). Electroanalytical techniques [1], such as anodic stripping voltammetry (ASV), represent a highly attractive alternate because of their unique features: high sensitivity, limitation of sample perturbation due to sampling and storage, compact and portable instrumentation. Additional advantages in regard to the present study were the rapidity of the analysis and the capability of building detailed spatial data banks at low cost.

The aim of this work was to evaluate if an easily affordable portable electroanalytical device could be a useful tool for on-site lead-monitoring for distribution systems screenings. The electroanalytical method involved square wave ASV with a mercury-electroplated-iridium working electrode. The measures were performed at pH 4.5, in acetate media. A linear response was obtained between 5 to 100 µg/L with coefficient of correlation, R^2 of 0.9969. Relative standard deviations of repeatability and reproducibility were about 5 and 13%, respectively. Detection and quantification limits as low as 2 and 7 µg/L were achieved. These analytical thresholds demonstrated the suitability of the method for compliance monitoring purpose. The accuracy of the analysis was estimated by analyzing standards and water certified samples. Bias in the results due to sample matrices were examined by analyzing fortified or naturally contaminated water samples, such as sea and surface waters as well as industrial wastewaters. The method was then applied to monitor lead concentrations at several points in the drinking water distribution systems of Marseille and suburbs municipalities. To validate the on-site application of the method, lead concentrations measured by ASV were compared to those determined by ICP-AES. Noteworthy, the use of field screening method could enable subsequent targeted sampling to better locate the point of the distribution system, which must be incriminated as responsible of lead contamination.

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DETERMINATION OF ^{90}SR IN A WATER COLUMN ALONG THE ALGERIAN COAST

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In the framework of the radiological survey project of the marine environment along the Algerian coast, and in collaboration with the IAEA, where Algeria is a member of the regional project RAF/7/004, on oceanographer campaign was organized by the IAEA, jointly with COMENA and ISMAL from 08 to 23 August 2001, on board of the M.S. BENYAHIA Research vessel of ISMAL.

The aim of the oceanographer campaign is to have new data of a more scientific interest related to the already obtained, by collecting deep seawater using more accurate equipments, mainly provided by IAEA , COMENA and ISMAL .

Three stations, at the centre, east and west of the coast were taken. At each station, five seawater samples were collected along a water column from the surface to a maximum depth of 2000m, preconcentrated on board in order to extract 90Sr at the laboratory.

In this work preconcentrated samples were submitted to radiochemical separation to extract 90Sr at traces level using a selective resine of crown ether.

The results obtained at station 02 (Alger) and station 03 (Ténés) show that the 90Sr concentration ranges from the limits of detection (1.0 mBq/l to 9.7 mBq/l) .

Profile of 90Sr along the water column was also determined and compared to that of 137Cs.

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POST- COLUMN DERIVATISATION OF NITRO- POLYCYCLIC AROMATIC HYDROCARBONS TO AMINO- POLYCYCLIC AROMATIC HYDROCARBONS FOR THEIR ANALYSIS BY HPLC FLUORESCENCE. APPLICATION TO ATMOSPHERIC AEROSOLS.

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Nitrated polycyclic aromatic hydrocarbons (nitro- PAHs) are of particular interest to the environmental analytical community because of the extraordinary mutagenic and carcinogenic activities, even at low concentration levels [1]. The main source for nitro- PAHs in the atmosphere are direct emissions from combustion processes such as automobile exhaust emission or nitration of PAHs through atmospheric reactions [2].

The complexity of atmospheric environmental samples and the low concentration levels of nitro- PAHs require a sensitive and selective analytical method.

The aim of this study is focused on the optimization of an analytical procedure for the separation and quantification of 15 nitro- PAHs, present in aerosol samples, by liquid chromatography coupled to fluorescence detection. Indeed, the use of fluorescence detection gives a very simple, specific and sensitive alternative to GC- NIMS. However, this method require on line reduction of the nitro- PAHs to the corresponding amino- PAHs since generally, nitro- PAHs exhibit only very weak fluorescence signals [3].

The principles factors affecting the efficiency of this reduction such as the flow rate (from 0.5 to 1.5 mL.min^{-1}), the temperature (from 20 to 100°C), the position (after or before the analytical column) and the packing (5 % Pt- Al_2O_3 or Zn- Al_2O_3) of the catalytic column have been studied and optimised.

Results obtained from these diverse experiments were presented, discussed and compared with other methods.

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Meteo - diffusive Characterization of the Algiers's nuclear research reactor

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Abstract

In the framework of the environmental impact studies of the nuclear research reactor of Algiers, we will present in this paper the works related to transfer of atmospheric releases of the installation in normal operation and which consisted on the assessment of spatial distribution of yearly average values of atmospheric dilution factor. The aim of these works is characterization of the site in terms of diffusivity, which is basic for the radiological impact evaluation of the reactor.

The meteorological statistics result from the National Office of Meteorology and concerns 15 years of hourly records. In agreement with the nature and shape of these data, a Gaussian type model with wind directional sectors was used. Values of wind speed at release height were estimated from measurement values at 10 m from ground. For the assessment of vertical dispersion coefficient, we used formulas of Briggs related to a sampling time of one hour.

Areas of maximum impact were delimited and points of highest concentration within these zones were identified.

DETERMINATION OF OZONE PRECURSOR HYDROCARBONS AND OTHER POLLUTANTS EMITTED BY HEAVY-DUTY ENGINES USING BIODIESEL

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In urban areas, motor vehicles represent one of the main sources of CO, PM, NOx and hydrocarbon emissions. These emissions tend to be either unburned or partially oxidized fuel components, and several, such as benzene and 1,3-butadiene, are known carcinogens [1,2]. Others are involved in atmospheric reactions, the so-called ozone precursors. The European Commission, through the Ozone directive [3] obliges the member states not only to monitor and reduce atmospheric ozone, but also its photochemically reactive precursors in the air. The investigation of ozone precursors and regulated pollutants in vehicle emissions, together with efforts to develop improved vehicle emission and fuel quality standards are important to reduce air pollution and to reach a sustainable development in the future.

In the present work, a EURO 3 heavy-duty engine was fueled with different types of biodiesel (rapeseed, soy methyl esters, etc) and emission tests were performed in the *Vehicle Emission Laboratory* (VELA) of the EC Joint Research Centre. The emission tests were carried out following the European Transient Cycle (ETC) on a dynamic engine test bench equipped with a suitable brake and a conventional full flow dilution system based on the CVS (Constant Volume Sampling) concept and equipped with a secondary dilution tunnel. Regulated emissions (HC, CO, NOx and particulates) were measured according to the legislative measuring procedures. For the hydrocarbon speciation, engine exhaust samples were collected in Tedlar™ bags and subsequently transferred to a multilayer adsorbent trap, followed by thermodesorption/injection and 2D-GC/FID analysis [4].

The results were expressed in grams of pollutant per kWh. The hydrocarbon speciation allowed the calculation of the potential of ozone formation for each fuel. It was found that biofuels can be efficient in reducing the emissions for heavy-duty engines when compared to the use of fossil diesel. Using pure rapeseed oil methyl ester, the CO emissions were reduced to 46%, HC emissions to 44% and PM to 38%.

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DISTRIBUTION OF NATURAL RADIOACTIVITY, ^{137}Cs, ^{90}Sr AND PLUTONIUM ISOTOPES IN A WATER COLUMN AND SEDIMENT CORE ALONG THE ALGERIAN COAST

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Abstract

Concentrations of natural (^{40}K, ^{210}Pb, uranium and thorium series) and artificial radioelements were determined in seawater samples and sediment cores collected from different stations along the Algerian coast. Seawater samples were collected from the surface to a maximum depth of 2000m, the sediment cores were sampled from a depth of around 1500m. This work was carried out in August 2001, in the framework of the regional project RAF/7/004, by the accomplishment of an oceanographic campaign organized by the IAEA in collaboration with COMENA and ISMAL, on board of the research vessel M.S. Benyahia of ISMAL. In addition to the record of the CTD parameters (T°C and S) done at each station, seawater samples were treated and preconcentrated on board, those of sediment cores were divided into different layers, in order to undergo analyses in the radiological impact studies laboratory of Algiers. Concentration results were obtained for ^{137}Cs, ^{90}Sr and plutonium isotopes in seawater, and also for natural and artificial radionuclides in sediments. Different profiles of ^{137}Cs, ^{239,240}Pu and ^{210}Pb concentrations against depth were presented to show artificial radioactivity distribution in the water column and sediment core.

Concentrations of ^{210}Pb in the sediment core were also used to determine sedimentation rate, estimate the radioactive inventory and possibly identify the ^{137}Cs peak.

Key words: ^{137}Cs, ^{90}Sr, ^{239,240}Pu, ^{210}Pb, contamination , marine environment , sedimentation rate, nuclear fallout, inventory.

TRACE ELEMENT CHARACTERIZATION BY INAA OF A RICE FLOUR PROPOSED AS A REFERENCE MATERIAL AND A NEW BLACK RICE CULTIVAR

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Rice (Oryza sativa L.) is the main foodstuff for more than half of the global population, especially in the developing countries [1]. The analytical characterization for trace element contents of the different rice varieties provides a significant support to nutrition information. For this purpose, the availability of suitable reference materials, certified for both essential and toxic elements, is of prominent importance [2], along with the acquisition of new data.

A rice flour, derived from a rice grown in a polluted field in Japan, has been reprocessed and assessed at IRMM (Institute for Reference Materials and Methods) in Geel (B), to be proposed as a Reference Material (CRM IRMM 804) for trace element contents in rice [3].

Our laboratory has participated to the characterization of this material by using Instrumental Neutron Activation Analysis (INAA). Furthermore, we have investigated the trace element contents in the grains of a new black rice variety, cultivated near Pavia in fields fed with Ticino river waters. This cultivar – called *Venere (Venus)* - which derives from an experimental line obtained by IRRI (International Rice Research Institute), has been developed by the Italian firm SA.PI.SE, registered in Italy in 1997 and successively in the EU.

The levels of As, Cd, Co, Cr, Cu, Fe, Mn, Sb, Se, Th and Zn have been reported for both matrices.

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VALIDATION OF CAPILLARY GAS-CHROMATOGRAPHIC METHOD FOR DETERMINATION OF TOXIC COMPOUNDS IN AIR

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In experimental work, firstly, the sampling from working place air containing volatile organic compounds (adhesive) was carried out in accordance with the standard. Then, the separation was performed by capillary gas-chromatography (HP 5890 A) equipment with a column packed by Ultra 1 (crosslinked methyl siloxane), nitrogen and FID were used as carrier gas and detector, and in addition controlled temperature program was applied. The volume injected to the column was 2 μl in every case. The compounds were identified by the retention time using standard solutions for comparison.

The experimental conditions were the followings:

Capillary gas-chromatograph:	HP 5890A
Column type:	Ultra 1
Column length:	50 m
Column diameter:	0,3 mm
Thickness of layer	0,52 μm
Column pressure:	15 psi
PC Software:	EAK 96,
Injector:	split/ splitless
Injector temperature:	50 °C
Detector:	FID
Detector temperature:	50 °C
Eluens:	Nitogen
Injected amount:	2 μl.

From the results, the mean characteristics of the analytical method were evaluated namely specificity, linearity, accuracy, precision, repeatability, reproducibility, range, stability, detection limit (DL) and quantification limit (QL).

In the investigated range, the linearity was ascertained for each component and the accuracy was proved within the indicated range for the following components: benzene (3.3 – 2197 μg/cm^3), butyl-acetate (19.43 – 2207 μg/cm^3), isopropyl-alcohol (72.02 – 3925 μg/cm^3), methanol (89.15 – 3965 μg/cm^3), mesitylen (21.17 – 4325 μg/cm^3), o-xylene (867.4 – 2200 μg/cm^3), styrene (893.0 – 2265 μg/cm^3), toluene (22.64 – 2167 μg/cm^3), and p-xylene (37.88 – 4360 μg/cm^3). The values of RSD are between 1.0 and 16.1 %, the smallest value was obtained for toluene and the highest one for isopropyl-alcohol.

The applied gas-chromatographic process can be considered as a validated method for benzene, butyl-acetate, mesitylene, toluene and p-xylene.

DETERMINATION OF METALS OF THE PLATINUM GROUP ELEMENTS IN RUNOFF WATER SAMPLES BY ICP-MS

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Since the introduction of the catalytic automobile exhaust gas converters in the 1970s in the USA and in the mid 1980s in Europe, autocatalytic converters containing platinum group elements (PGEs) have been employed successfully in the treatment of pollutants in exhaust gases from motor vehicles [1]. The use of catalytic converters is enormously beneficial to the environment. Along with the beneficial aspects of the technology, a disadvantage was a widespread distribution of fine particulate matter, or dust, containing PGEs. The dust originated from abrasion and deterioration of the bulk catalysts. Thus, PGEs have been deposited along roadways, on vegetation and soil surfaces adjacent to roadways, and in streams, rivers and waterways either directly or as runoff [2].

Runoff from roads contains a wide range of compounds. Many contaminants are present as a result of their emission from a number of sources associated with motor vehicles (e.g. exhaust emission). Compounds present on road surfaces and in runoff include, among other things, PGE at low concentrations. Their road transport source is principally the emission from the vehicle catalysts. The PGE content in stormwater generated in motorways is a function of a number of factors the principal influences being amount of vehicle per day, rainfall composition, road surface composition, gutter dust accumulation and chemistry (Road transport effects on a aquatic ecosystems). The concentration of PGE in run-off samples is usually about tens ng/l or even lower.

Platinum and palladium are known as the very potent sensitizers with a high incidence of allergic reactions [3], they can also enter the food chain [4]. Information about PGE species is required in order to determine how they are distributed in the environment and the possible health effects [1]. Therefore, to check the contamination level of environmental by PGE, the determination of these metals in environmental samples at ng/g (ng/ml) concentration level is required.

In the studies used one of the most suitable analytical methods for the metals of the platinum group elements determination at such a low concentration level which are mass spectrometry with the ICP ionisation (ICP-MS). The development of a procedure is described with the ultimate goal to direct determine platinum group metals at nanogram concentration levels in run-off samples. The preliminary results demonstrate the potential of this ICP-MS method for the precise and accurate determination of PGE.

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Application of Capillary-LC hyphenated to Element and Molecule Specific Detection Techniques for Protein Analysis

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The recent outstanding progress in both instrumental and methodological developments namely the possibility to combine proteomic standard techniques such as gel electrophoresis[1] or nano- and capillary-HPLC[2,3] with ICP-MS via state of the art interface technology opens the versatile field of bio-analytics and life-science for the analytical spectrochemistry.

Especially the complementary utilisation of ICP-MS for a selective and sensitive detection, quantification and pre-selection of bio-molecules via (hetero)element tags before their ESI or MALDI-MS based identification represents a promising approach within the scope of bio-analysis in environmental and life-science.

This contribution will focus on the development of a methodology which included the complementary application of capillary LC hyphenated to collision-cell ICP-MS and molecule specific mass spectrometry (ESI-MS/MS, MALDI-TOF-MS) for the investigation of protein species derived from seal samples (*Phoca vitulina L.*), which might be suited as biomarkers for their health status.

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MEASUREMENT OF ELECTROCHEMICAL OXIDABILITY OF WASTEWATERS BASED ON VOLTAMMETRIC DETERMINATION BY USING A BORON DOPED DIAMOND ELECTRODE

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The paper proposes a new characteristic and direct accessible parameter for oxidable organic and inorganic load of waste waters, so called amperometric oxidability level (AOL) as a substitute of the usual chemical oxygen demand (COD). The COD is a conventional parameter which converts the oxidation of organic compounds (usually responsible for contamination of industrial waste water) by chemical oxidizing compounds, e.g., dichromate, in a number of oxygen equivalents. This parameter does not reflect a real oxygen demand but conventionally defines the availability of contaminants for a strong chemical oxidation. The chemical method is time consuming, demands large effort and has a subjective reproducibility governed upon operator abilities. Also, this method is unsuitable for on line quantification and monitoring. Electrochemical methods were explored in the past decade to obtain an equated COD as electrochemical oxygen demand (EOD).The feasibility of an easy working method has been hampered by limited anodic windows and stability or fouling of the usual electrode materials. The BDDE solves these problems optimally. This conductive diamond film electrode offers certain valuable characteristics: low and stable voltammetric and amperometric background currents, wide working potential window in aqueous electrolyte solutions and high overpotential for oxygen and hydrogen evolution, low adsorption of polar molecules, enhanced signal-to-background ratios and very promising properties in electroanalytical applications, extreme electrochemical stability, high resistance to deactivation by fouling, lack of sensitiveness to dissolved oxygen and long-term response stability. The persistence in equating oxidability as oxygen demand involve some complications and time consumption disadvantage and can be substituted by an immediately detected amperometric current , or a series of chronoamperometric (CA) responses. The CA data succeeds a preliminary cyclic voltammogram obtained in an extended anodic range, between starting and high oxygen evolution potential. Thus, some progressive amperometric oxidability levels could be delimited. They were associated with the sensitivity (high current, detectable current, low detection limits, susceptibility to oxidation (to low, moderate and high potential), and defined succession of the waves or current peaks from the voltammograms, prior to oxygen evolution, and the corresponding electrode potential. An overall amperometric oxidation level could be selected under conditions of maximum resultant current, or several successive sum-levels which can characterize the sum of oxidable organic and inorganic species contents in the explored potential range. The final AOLs data are obtained by a series of chronoamperograms registered continuously at selected successive potential levels. By using aqueous solutions with various ratios of oxidable organic and inorganic components, the concept of AOL was verified in practical conditions at a BDDE by preliminary cyclic voltammetry and chronoamperometry. The simulated wastewaters contained several target analytes, e. g. natrium diethyldithiocarbamate, sodium urate and sodium nitrite. Linear dependencies between anodic current, AOLs, at several fixed potentials (low, moderate and high) and individual load and additivity in overall load (correlated with COD) were obtained.

ENVIRONMENTAL PROBLEMS OF MOSCOW CITY AND POSSIBILITIES OF THE MONITORING SYSTEMS OF ATMOSPHERIC POLLUTION AND INDUSTRIAL EMISSIONS

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Environment problems and problems of environmental safety remain most important problems in the majority of Russia regions. For now air pollution which is caused by the industrial and motor transport releases, natural and sewages, industrial ground, waste products have reached very high value.

Especially dangerous situation is on industrially-urbanized territories where the main part of the country population lives. Last years motor transport was the main pollution source for the large cities. At the same time the essential emission levels are brought by the industrial enterprises, objects of power, building industry. The environmental situation here is also declined because of the more frequent technogenic failures; the value of the noise level, electromagnetic radiations intensity and other harmful factors has increased.

The report is devoted to the basic environmental problems of Moscow and to the environmental monitoring system including stationary posts of observation, mobile and remote tools for the pollution control. Also there are laboratory methods of the analysis and the used equipment in the report.

There are concrete examples of pollution research in the local city territories. The special attention is given to the control of emissions of the industrial enterprises of a various structure, among them there are examples of enterprises built by firms from the CE (France, Italy, Germany, etc.).

The main attention in the report is devoted to the creation of effective systems for monitoring of dangerous and potentially dangerous manufactures and their pollution release, it is still remains an actual problem in Russia. This situation demands the further developing both the general methodological approaches, and corresponding hardware - methodical and information-analytical tools.

It is necessary to create legislatively lists of the persistent organic pollutants which have to be controlled permanently (from the Kioto protocol and others). In particular, this list for air pollution should include: the total value of the weighed substances, the weighed substances in the size less than 10 microns, heavy metals, aromatic hydrocarbons, etc. In emissions of the industrial enterprises connected to high-temperature processes (the power, metallurgy, burning of waste products, etc.), such pollutants should be included: the gaseous pollution, the weighed substances, carbon dioxide, fluorides, chlorides, heavy metals, dioxins. And at last, the further development of normative-legal base of the control, social - environmental risk estimation, the environment damage measuring become more and more important.

HIGH CONCENTRATIONS OF PARTICLE-BORN POLYAROMATIC COMPOUNDS IN KRAKOW (POLAND) FROM HOME HEATING BY COAL BURNING

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The European Commission has proposed a target limit value of 1 ng/m^3 annual mean concentration of benzo[a]pyrene (used as a marker for the carcinogenic risk of polycyclic aromatic hydrocarbons) as part of the 4th Air Quality Daughter Directive [1]. Episodes of high ambient benzo[a]pyrene concentrations (up to 200 times higher than the EU target value) occur regularly during winter in the region of Krakow (PL). The combination of coal combustion, traffic exhaust and atmospheric conditions with thermal inversion is believed to cause these pollution events. Particulate matter samples have been taken at four different air monitoring stations in Krakow (traffic site, industrial site, urban background site and domestic coal heating district) and compared to samples from the Zakopane sub-urban mountain site with dominating domestic coal heating and to samples from the major sources of emissions (traffic, power stations, industry, etc). In total more than 200 samples were collected and chemically analysed for a high number of organic and inorganic compounds. PM samples were analysed for determination of content of soot, of organic carbon (OC) vaporizing at 900 ^oC and of polyaromatic compounds (15 PAH and 18 azaarenes) using GC-MS technique. Elements (three of them cited in 2004/107/EC, namely As, Cd and Ni and other 25) as well as some ions (Na^+, Mg^{2+}, NH_4^+, Cl^-, SO_4^2- and NO_3^-) were investigated using proton induced x-ray emission (PIXE), ion chromatography (IC), automated colorimetry (AC), and atomic absorption spectrophotometry (AAS).

High concentrations of PAC were found on the sampled PM, particularly for benzo(a)pyrene. The highest values were recorded at the domestic coal heating district, which is in accordance with results on emissions from coal fired small stoves, which reveal extremely high PAH (4-6 rings) concentrations of on the particles compared to e.g. traffic emissions [2]. The chemical fingerprint (organic and inorganic chemical composition) of the five sites displays similar profiles which indicate that one source (possible coal burning) is dominating in this region.

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ECOTOXICITY OF WASTE MATERIAL FROM THE METALLURGICAL INDUSTRY IN POLAND

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The increasing amount of industrial and municipal wastes, and their illegal or improper storage, cause a serious hazard for aquatic ecosystems and for human health. In Poland, ninety percent of the total amount of industrial wastes originate from the metallurgical industry. One of the old industrial waste lagoons is located close to the bank of the Mała Panew river, near its mouth to Lake Turawskie. For many years, toxic substances present in the slags, were eluted by rain water and then transported by river water, either dissolved or adsorbed on suspended matter, directly into Lake Turawskie.

A preliminary screening evaluation of the hazard caused by the slag dump for the ecosystem of Lake Turawskie, was performed with a biotest battery composed of the acute toxicity test with luminescent bacteria *Vibrio fischeri* (Microtox ®) and the "direct contact" chronic toxicity test with the ostracod crustacean *Heterocypris incongruens* (Ostracodtoxkit F).

The Ostracodtoxkit F microbiotest was carried out directly on the waste material, according to the Standard Operational Procedure. Microtox tests were performed on aqueous elutriates prepared by shaking waste material with aerated distilled water (1:4, v:v) for 24 hours. After centrifugation and filtration (using fiberglass prefilters; pore size: 0.45 µm), the pH of the elutriates was adjusted to 6.0 – 8.0 pH. Tests were carried out according to the Basic Test Protocol of the Microtox with four concentrations and one control in each test and measurement of the inhibition of bioluminescence of freeze-dried *Vibrio fischeri* bacteria after 30 min. Internal quality control tests using zinc sulphate ($ZnSO_4 \cdot 7H_2O$) were run periodically during the study. The data were used to calculate the mean % mortality and growth inhibition of the ostracods, and the EC_{20} (NOEC) and EC_{50} for the bacterial bioluminescence assay.

All the samples examined were found very toxic to the two types of test organisms, pointing to the serious hazard of the metallurgical wastes discharged into the Mala Panew river. NOEC values for the Microtox were even below 1%. The results obtained with the Ostracodtoxkit F generally confirmed the toxicity levels detected with the Microtox.

Additionally, chemical analyses were performed. The aim of these analyses was an attempt to identify chemical substances responsible for the observed toxicity effects.

The chromatograms obtained using LE-GC-MS technique indicated a very complex composition of examined dichloromethane extracts but precluded their unequivocal identification. Further analyses with using the HPLC-DAD and HPLC-MS techniques confirmed the presence of high-molecular polycyclic organic compounds with polar character.

MICROWAVE ASSISTED SAMPLE PREPARATION FOR TRACE ELEMENTS DETERMINATION BY STRIPPING VOLTAMMETRY

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Anodic stripping voltammetry is very useful alternative method for trace elements determination in various environmental samples of biological origin. It offers low detection limits, accuracy and/or precision for many trace elements being in focus of environmental analysts. The important part of the entire analytical procedure is the sample preparation step, in which analyte must be transferred into solution without any contamination and/or losses. Voltammetry is a method, which is extremely sensitive to the quality of the digestion process. Residual electro-active organic substances are potential interferences for subsequent instrumental measurement. High-pressure microwave digestion procedure seems to be a suitable method for sample preparation prior to voltammetric analysis. Using the system Multiwave 3000 (A.Paar, Austria), the sample preparation method was developed, which enables digestion of biological samples both of plant and animal origin. Using a mixture of hydrochloric acid, nitric acid and hydrogen peroxide a digestion procedure was set up, including final evaporation of the digestion mixture. After re-dissolving of the residue in 0.02mol/L nitric acid, determinations were performed using the Metrohm 757 (Switzerland) voltammetric analyser. The acetic buffer (pH = 4.6) was used as supporting electrolyte. Certified reference materials have been used as biological samples, namely: BCR-62 Olive leaves (BCR, Belgium), BCR-063R Skim milk powder (BCR, Belgium), BCR-186 Pig kidney (BCR, Belgium), BCR-422 Cod Muscle (BCR, Belgium), NIST-1577a Bovine liver (NIST, USA), NIST-8414 Bovine Muscle (NIST, USA), and A-11 Milk (IAEA, Austria). Determination of cadmium, copper, lead and zinc led to satisfactory agreement between the certified and found concentrations. No statistically significant differences have been found. The digestion procedure is rather universal and enables the determination of the above given trace elements with required accuracy and precision.

CONTINUOUS DETERMINATION OF PAHs IN URBAN ATMOSPHERE BY CAPILLARY GAS CHROMATOGRAPHY

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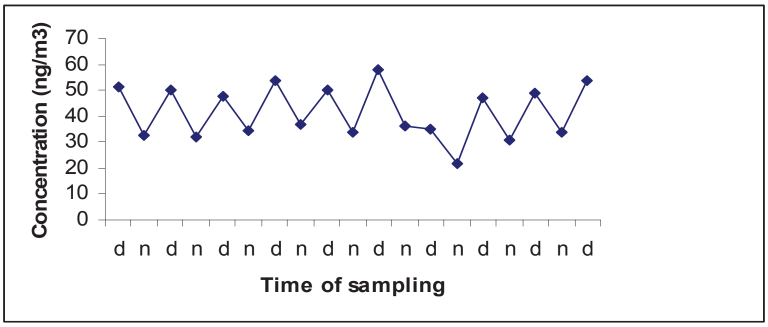
Polycyclic aromatic hydrocarbons (PAHs) are products of incomplete combustion of carbonaceous material at high temperature[1]. PAHs are ubiquitous in the lower atmosphere and generated from both natural and anthropogenic sources. Human exposure to PAHs can occur through several environmental pathways due to their numerous sources. However the occurrence of PAHs in urban air has caused particular concern because of the continuous nature of the exposure and the size of population at risk. Polycyclic aromatic hydrocarbons in the atmosphere are known to be predominantly associated with particular matter [2].

In this work, airborne particulate matter from the atmosphere of the city of Isfahan was collected on ultra-pure quartz fiber filter (Whatman QM-A) using a high volume air sampler. Sampling flow rate was 1 m^3 min^{-1} and performed in days and at nights. 1 m^3 min^{-1} respectively. The exposed filters were extracted by soxhlet procedure with dichloromethane. The determinations were carried out on a Varian gas chromatograph, Model CP-3800. The system was equipped with a FID detector and a temperature programming was used for successive separation. Figure 1 shows the day and night variation in concentrations of PAHs in the atmosphere of the city of Isfahan.

Figure 1: Day and night variation in atmospheric concentrations of PAHs.



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INTERCALIBRATION OF ATMOSPHERIC METHANOL AND ETHANOL BY TWO DIFFERENT ANALYTICAL METHODS IN A TROPICAL ENVIRONMENT

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Brazil utilizes ethanol as vehicle fuel, mainly in mixtures of 22 % with gasoline. Methanol is emitted by plant leaves and by biomass burning, either naturally or manmade. Several chemical industrial activities emit methanol into the atmosphere, particularly petrochemical. The presence of these alcohols in the atmosphere increases the concentration of its oxidation products (aldehydes and carboxylic acids) and the oxidation capacity of the troposphere, thus photochemical smog and acid rain.

Two independent analytical methods which have been used for air measurements in different areas of Brazil have been intercalibrated. The first [1] was based on 40-50 min cryogenic sampling in borosilicate glass tubes at -55 ^{o}C after O_3 removal on MnO_2 screen and determination with HPLC separation, followed by post-column enzymatic derivatization and electrochemical detection of the H_2O_2 formed. Detection limit of method in in µg m^{-3} was 4.7 for methanol and 20.8 for ethanol. The second method [2] was based on instantaneous grab sampling in evacuated glass flasks and determination by CG/ED of the corresponding alkylnitrite after derivatization with NO_2 in gaseous phase. Detection limit of method in µg m^{-3} was 5.2 for methanol (as methylnitrite) and 5.3 (as ethylnitrite).

Intercalibration for methanol was conducted in laboratory by generation of constant atmosphere ranging from 18 - 67 µg m^{-3}. Within this concentration range, the two methods proved to be significantly correlated ($y=0.5706x + 18.923$, $R= 0.8078$; $P= 0.02793$). This study took place in Salvador City, Bahia, where methanol levels are normally below 4.7 µg m^{-3}, thus preventing intercalibration in the field. Intercalibration for ethanol was conducted in the field, in a wind tunnel type street, where concentrations ranged from 37.7 – 545 µg m^{-3}. The two methods correlated well for this concentration range($y= 1.5769x -25.813$, $R = 0.8981$, $P = 0,000098$). Systematic differences at lower concentrations were attributed to decrease on cryosampling efficiency at these levels or to the difference in time windows of the two sampling methods, where average of 2 to 3 instantaneous gaseous samples grabbed in flasks is compared with measured value of continuous cryosampling over a 40-50 min period .

These intercalibration results enable comparisons of different studies undertaken in diverse areas of Brazil such as great urban centers [2, 3] and remote areas (i.e. Amazon forest) [4] and with data of other parts of the world [3].

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MICROFLUIDIC SENSOR FOR THE CHEMILUMINESCENCE OPTICAL DETECTION OF POLLUTANTS USING MAGNETIC BEADS

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Taking into account the large amount of water samples which have to be analysed, the development of fast and inexpensive tests is very important. There is a need for rapid field-based bioassays for herbicide monitoring in water. Herbicides can be highly toxic for human and animal health, and increase in the application of herbicides in agriculture during recent decades has resulted in the herbicide pollution of both soil and water.

A method of detecting herbicides is proposed; many herbicides act by binding to Photosystem II (PS II), a multiunit chlorophyll–protein complex which plays a vital role in photosynthesis, located in the thylakoid membrane of algae, cyanobacteria and higher plants. The inhibition of PS II causes a reduced photoinduced production of hydrogen peroxide (H_2O_2), which can be measured by a chemiluminescence reaction with luminol and the enzyme horseradish peroxidase (HRP).

The production of H_2O_2 by thylakoid membranes was investigated, and H_2O_2 was detected under illumination with concentrations increasing in a time- and light intensity-dependent manner. The presence of specific herbicides in water samples reduces the H_2O_2 measured, in a concentration-dependent manner. The integration of the above reactions, which were initially performed in cuvette assays, has been achieved by designing a microfluidic device. The sensing device proposed combines the production and detection of hydrogen peroxide in a single flow assay by combining all the individual steps in a compact device that utilises magnetic beads.

To address issues of reagent stability and re-generatability both HRP and thylakoids have been covalently coupled on superparamagnetic beads, using different chemistries. This allows for the 2-step detection to take place in the same assay, as the beads with thylakoids and the beads with HRP are magnetically entrapped in separate areas of the channel, at different times, allowing a sample flowing in the channel to first react with the thylakoids, while then the produced H_2O_2 reacts with the pre-mixed luminol and the immobilised HRP to produce a light signal, detected by an Avalanche photodiode.

ECOTOXICOLOGICAL EVALUATION OF POLYURETHANE FOAMS

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Polyurethanes (PUR) that belong to a large group of polyesteramides are most common waste occurring in abiotic components of the environment such as water and soil. PUR are also used in the manufacture of expanded plastics, i.e. foam-like materials formed in a reaction between diisocyanates, polyhydroxy compounds and water. The possible migration of polymer degradation products of the environment has to be monitored since additional major pollutants that can be formed may endanger some of the components of the environment. Foams filled with special filling agents that ensure good biodegradability were selected for verification. Flexible BIO-PUR foams were prepared using commercially available products based on cellulose and starch derivatives without any additional modifications: acetylated starch AMISOL HS, acetylated cellulose, hydroxyethyl cellulose sodium salt of carboxymethyl cellulose [AS, AC, HEC, CMC]. Polyurethane foams were evaluated in respect to their ecotoxicity. Ecotoxicity was evaluated by using alternative toxicity tests such as DAPHTOXKIT FTM MAGMA, ROTOXKIT F, ALGALTOXKIT FTM, THAMNOTOXKIT FTM. THAMNOTOXKIT FTM is crustacean toxicity screening test for freshwater. This alternative toxicity test was better than the other alternative toxicity tests.

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DETERMINATION OF ACIDIC HERBICIDES IN SOIL FROM THE VICINITY OF PESTICIDE DEPOT.

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Acidic herbicides (phenoxyacids, selected phenols, etc) are widely used in agriculture and forestry; they are also applied to clean-up sport areas, railways, highways, cemeteries and also seaweed and other vegetation in marshy areas, water bodies and drainage ditches [1].

Only a small part of herbicide formulation reaches targets; the remaining part either undergoes some chemical changes or cycles in the environment [2] and can have harmful effects on humans and other non-target organisms. In Poland some used pesticides are stored in pesticide depots, which can be sources of pollution of surface and ground water and soil. Therefore acidic herbicides should be monitored at low concentrations in agricultural soil and other environmental samples, which are usually very complex. They are generally determined by gas chromatography after appropriate sample preparation based on isolation of acidic herbicides of interest, removal of interfering substances, and transfer of analytes to a solvent compatible with GC. Most acidic herbicides must be converted to derivatives before GC analysis.

In this work selected acidic herbicides were isolate from soil, using environmentally friendly and effective extraction procedure - *Accelerated Solvent Extraction* (ASE) with water as a solvent. Water was exchanged for organic solvent with the use of solid phase extraction (SPE) and then herbicides of interest determined in the concentrate produced by gas chromatography coupled with mass spectrometry. Before GC analysis the analytes were converted to less polar and more volatile methyl derivatives, by means of methyl iodide in the presence of trimethylphenylammonium hydroxide (TMPH). Chromatographic separation was performed in a capillary column coated with 50 % phenyl – 50 % methyl polysiloxane as a stationary phase (30 m x 0.25 mm i.d.; d_f 0.25 μm) (Rtx – 50MS). Using a mass spectrometer (in SIM mode) detection limits for whole procedure were: 3 ng/g soil for MCPP, MCPA and 2.6 for 2,4-D; 2 ng/g soil for 2,4,5-T and 21; 21 and 25 ng/g soil for PCP, dinoterb and dinoseb, respectively.

With the procedure developed, selected acidic herbicides were determined in soil from the neighbourhood of pesticides depot in Skorzewo (community Kościerzyna, Pomorskie voivodship). In the samples collected MCPA, 2,4-D and 2,4,5-T were found in rather large concentrations: 56 μg/g, 1,6 μg/g and 5,4 μg/g, respectively. In these samples many other pesticides were also identified, eg.: lindane, chlorpropham, 2-methoxybenzenoacetic acid, 4,6-dinitro-*o*-cresol. The procedure was also used to determine herbicides in soil from cultivated fields. The samples were collected ca one months after application. Their content was below the detection limits of the procedure.

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Novel Fe(III) Ion-Selective Membrane Electrode Based on 4-Amino-6-methyl-3-methylmercapto-1,2,4-triazin-5-one

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In this work, a novel Fe(III) PVC-based membrane sensor based on 4-Amino-6-methyl-3-methylmercapto-1,2,4-triazin-5-one (AMMTO) as a new ionophore is presented. The sensor displays a linear dynamic range between 1.0×10^{-6} and 1×10^{-1} M, with a near Nernstian slope of 19.4 ± 0.5 mV per decade and a detection limit of 6.8×10^{-7} M. The best performance was obtained with a membrane composition of 30% poly(vinyl chloride), 65.5% nitrophenyl octyl ether, 2% sodium tetraphenyl borate and 2.5% AMMTO. The potentiometric response of the proposed electrode is independent of the pH of the solution in the pH range of 2.2–4.8. The sensor possesses the advantages of short conditioning time, fast response time (<10 s), and especially, very good selectivity towards transition and heavy metal, and some mono, di and trivalent cations[1,2]. The electrode can be used for at least 9 weeks without any considerable divergence in the potentials. It was successfully used as an indicator electrode in potentiometric titration of Fe(III) ions with EDTA and the direct determination of Fe(III) in different water samples.

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Highly Selective and Sensitive Chromium(III) Membrane Sensors Based on 4-Amino-3-hydrazino-6-methyl-1,2,4-triazin-5-one as a New Neutral Ionophore

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A poly vinyl chloride membrane sensor for chromium(III) ions was prepared based on 4-Amino-3-hydrazino-6-methyl-1,2,4-triazin-5-one as a membrane carrier. The sensor has a linear dynamic range of 1.0×10^{-6} -1.0×10^{-1} M, with a Nernstian slope of 19.7 ± 0.3 mV decade^{-1}, and a detection limit of 5.8×10^{-7} M. It has a fast response time of <10 s and can be used for at least 3 months without any considerable divergences in its potentials. The proposed sensor revealed comparatively good selectivity with respect to most alkali, alkaline earth, some transition and heavy metal ions[1,2] and could be used in a pH range of 2.7-6.6. It was successfully used as an indicator electrode in potentiometric titration of Cr(III) with EDTA and also to the determination of Cr(III) in wastewaters of chromium electroplating

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METHODS FOR COMPREHENSIVE EVALUATION OF THE ENVIRONMENTAL EFFECT OF RADIOLOGICALLY HAZARDOUS OBJECTS

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Comprehensive research of environmental effects of radiologically hazardous objects is aimed at studying the influence of both radiological and non-radiological factors (such as chemical pollution agents, heavy metals, etc.).

A method for taking and analysis of environmental samples in the vicinity of a radiologically hazardous object to determine the content of radioactive nuclides and heavy metals was developed, which has been employed since 1961.

The present paper presents the results of studies of soil, surface water, bottom sediments, and snow samples taken in order to determine:

- radiation parameters (total alpha and beta activity levels, specific activity of natural and man-produced radioactive nuclides);
- content of heavy metals.

Radiometric and spectrometric analysis methods involving radiochemical methods of isotope separation were used to determine radiological parameters of environment samples. High-sensitivity radiometric and spectrometric measurement devices using radiochemical methods of concentration and separation of isotopes were used to measure radiological parameters of environment samples. Gamma radiation sources were measured using an HP-Ge detector with a relative efficiency of 100%, while beta and alpha radiation sources were measured using a TRI-CARB 2550 TR/AB liquid scintillation analyser. The obtained results are relevant as background level values for the region under study [1].

The content of heavy metals in water and snow samples was determined using the Inductively Coupled Plasma with Mass Spectrometry (ICP-MS) method at a VG PlasmaQuad apparatus (UK). Samples of soils and bottom sediments were analysed using the X-Ray Fluorescence (XRF) spectrometry method at a PW-2400 sequential wavelength spectrometer (the Netherlands). The obtained results were evaluated in comparison with the existing maximum permissible concentration values. Possible polluting elements were determined based on the heavy metal content in the samples, and distributed into the classes of chemical hazard. The obtained results are suggested to be taken for background level values for the area under study.

According to the evaluated level of radioactive nuclide and chemical pollution hazard, and taking into account the hazard class of heavy metals contained in the samples, the observation area of the radiologically hazardous object was classified as 'clean'.

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DETERMINATION OF PLATINUM IN HUMAN URINE BY SECTOR FIELD INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY (SF-ICP-MS)

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The platinum group metals (PGMs) used in automotive catalysts are partly emitted into the air during driving and can enter the human respiratory system. Although, its extent is relatively small, the increasing use of catalysts makes the problem increasingly actual. Previously, we have analyzed urine of 100 adults each from Budapest and Vienna. The results were compared to others published in the literature, and showed that the concentration was in the same order of magnitude (1-10 ng/g creatinine). At that time, we could not use a sector field ICP-mass spectrometer, so the determination of Pd and Rh was not possible due to spectral interferences. In order to avoid these interferences, in this study, electrothermal vaporization was used to evaporate the interfering elements before atomization of PGMs. The ashing as well as the evaporation temperature of the interfering elements were optimized. Using this pre-treatment, the organic matter, Cd, Pb, Zn, and Cu could be removed before atomization. On the other hand, Sr could not be eliminated. The determination limits were calculated for Pt, Pd, and Rh, and were 0.1, 5, and 10 ng/L, respectively. The developed method was used for determination of PGMs in the urine samples of tram drivers in both cities. Thirty-eight subjects were investigated in Vienna and 34 subjects in Budapest. Three samples were taken from the Viennese drivers (before, during and after shift), from the Budapestian ones two (before and after shift). The concentration of PGMs was determined using the above-mentioned method. The results for Pt were compared to those from our previous study. The comparison showed that the concentration median has increased by a factor of four. Between the cities, the Budapestian values were about the twice of those from Vienna. There was not any significant relationship between the data corresponding to the sampling time. The determination limit of the method was very close to the measured results. Thus, a further development of the method is necessary. On the basis of the very recent publications in the literature, the complexation and scavenging of the PGMs could be the possible way.

APPLICATION OF ICP-MS AS A TOOL FOR ENVIRONMENTAL MONITORING

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A key requirement in the field of environmental monitoring is the measurement of elements at trace and ultratrace concentrations in a variety of materials, including waters, soils, and biota.

This presentation outlines some key application areas, including the analysis of drinking water, river water and other natural waters, along with the analysis of more challenging materials, such as seawater and digests of soils. Major sample preparation and analysis details are presented in each case. For more challenging samples, major benefits are provided by the use of collision cell technology for the removal of polyatomic interferences formed from the major matrix constituents of the sample. These benefits are highlighted.

In addition, a developing area of interest for environmental scientists is the determination of the concentrations of specific species of particular elements present in a sample, rather than just the total concentration of an element. This is particularly important when assessing the environmental impact of a contaminated sample. Most speciation determinations are performed by combining a separation technique, such as liquid or gas chromatography with the sensitive, element specific detection of ICP-MS. Technological solutions for performing such analyses are presented along with topical example applications.

SUPPORTED LIQUID MEMBRANE EXTRACTION PROBE (SLM EP) FOR STUDY OF HEAVY METALS SPECIATION IN ENVIRONMENTAL MATRICES

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The study of trace metal speciation is an important aspect to gain information about bioavailability and toxicity of the metal. Determination of trace metals in environmental and biological samples is difficult due to the matrix effect and low concentrations. Speciation studies are even more complicated. Separation and preconcentration is necessary to enhance final determination.

The use of liquid/liquid extraction has shown some problems, mainly due to the emulsion formation which lead to bad separation of immiscible solvent and the use of a high quantity of solvents. The membranes have been used for extraction of liquid or gas from donor solution to acceptor solution. Extraction systems can be from aqueous to aqueous, aqueous to organic or organic to organic media. For reproducible results the optimization of the extraction has to be carried out; pH, salinity and extraction time are the main parameters which have to be optimized.

The new miniaturised supported liquid membrane probe was designed and developed. It is made from glass tube (dimensions: 13mm i.d., 16mm o.d. and 92mm length). In this configuration, one end of a glass tube is closed with the porous Millipore fiber filter sealed with PTFE tape and soaked in organic solvent. The inside of this probe serves as the acceptor phase container. The probe is then immersed in a glass vial containing the stirred sample.

Compared to traditional SLM configurations, this has many advantages. It is the simplest configuration to be reported to our knowledge, inexpensive since no pumps are needed, possible to perform many probe extractions simultaneously which is an important aspect in routine environmental analysis and drug screening process. Since the sample is stirred, it allows the same sample to be extracted many times thus, giving higher extraction efficiency. This means that only small sample volumes are needed. Depending on the matrix of the sample, the SLM probe can be used many times. It is also very easy to regenerate. The SLM probe extraction gives also the advantage of reducing the amount of solvent.

A developed system has been used for extraction and preconcentration of hexavalent chromium and uranium from aqueous environmental samples [1], manganese extraction from aqueous and biological samples [2] and organotin and organolead from aqueous environmental samples [3].

The analysis of heavy metals gave the recovery ranged between 43 and 68 % for manganese in biological fluids (water, milk and blood serum) and between 2 and 10 % for chromium (VI) in urine sample.

The extraction of organolead and organotin compounds from aqueous to organic phase, lead to good recoveries ranged between 50 and 91% with efficiency coefficient ranged between 5 and 8 % for both type of organometallics.

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ANALYSIS OF NATURAL ORGANIC MATTER MOLECULES BY MEANS OF ELECTROSPRAY IONIZATION-HIGH RESOLUTION MASS SPECTROMETRY

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Although the potential of electrospray ionization-mass spectrometry to analyze highly polar organic compounds has long been known its potential to analyze natural organic matter (NOM) from the environment has been recognized only a few years ago [1]. Fulvic acids are an important, but only operationally defined class of NOM, that is isolated by a traditional XAD enrichment procedure.

We have used size exclusion chromatography to fractionate fulvic acid isolates and SEC-MS analysis of fulvic acid isolates [2] has outlined a systematic pattern in the signal intensities with a periodicity of 2 and 14 amu. However, each integer mass in such mass spectra of fulvic acids, and even more so of NOM, is occupied by several ions. Thus, high resolution mass spectrometry is required to separate these isobaric ions. A first separation of the major ions can be obtained by time-of-flight MS and we have used a Q-TOF mass spectrometer with a mass resolution of about 10'000 to obtain structure information on individual fulvic acid molecules [3]. It was shown that carboxylate groups dominate the functional groups of fulvic acids and that only a few hydroxy groups are present. ESI-high resolution-mass spectrometry has shown that fulvic acids are no mixture of molecularly uncharacterized components but are well defined in terms of their elemental composition and structure. The information provided by Q-TOF-MS was sufficient to elaborate structure proposals for a number of individual fulvic acid molecules [3].

A full resolution of fulvic acid molecules requires the use of Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR-MS) with a mass resolution exceeding 100'000. Using this technique exact mass data of thousands of molecular species in fulvic acid isolats can be determined and more than a thousand of molecular formulas of individual molecular species could be calculated [4]. Our investigation shows that differences in the elemental composition of the molecules forming one isolate are highly systematic and that identical sets of molecules can be found in isolates of different origin [4]. Fulvic acids appear to be a well defined and independent class of organic compounds.

Using electrospray ionization-high resolution mass spectrometry it is now possible to study the reactivity of large numbers of individual molecular species of fulvic acids, in the environment as well as in water treatment processes [5]. We now also have a powerful tool in hand to tackle the questions related to the formation of fulvic acids and other natural organic matter.

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ELECTRIC FOCUSING PRECONCENTRATION DEVICE FOR ELEMENT COMPOSITION MONITORING OF AIR AEROSOLS BY ATOMIC EMISSION SPECTROSCOPY

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The role of aerosols in climate and atmospheric chemistry is very important. Aerosols can substantially affect human and animal health. Therefore, characterization of aerosols is of great importance. An electric focusing pre-concentration combined with in-time monitoring by atomic emission spectroscopy is the promising way for determination of elemental aerosol particulate composition, and consequently in regulatory, epidemiological and toxicological applications, in detection of primary and secondary aerosol sources. Based on calculations new theoretical models of electric focusing devices were proposed for pre-concentration of aerosol particulate and for specific separation of particle size fractions. One of these perspective designs was optimized for in-line connection to microwave induced argon plasma in order to create stable argon plasma conditions for accommodation of air aerosol preconcentrate and for excitation of atomic emission radiation achieving very sensitive detection of elemental composition. Preliminary results of experiments with dry aerosols, based on simple inorganic salts and produced artificially in a laboratory made generator, are presented. Technical and analytical figures of merit of the optimized apparatus are also shown.

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STABILITY OF AMPHIPHILIC AND HYDROPHOBIC POLLUTANTS IN ANIONIC MICELLE-BASED COACERVATES

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Preservation of water samples from their collection to their analysis in the laboratories is an important issue in chemical analysis. Ineffective conservation leads to losses and incorrect results. Traditionally, chemical addition and temperature control during sample storage have been used, but these procedures are not recommended for long periods of time [1]. In the last years stabilization of analytes on SPE cartridges has been successfully proved, reducing the effort of transport and storage of large volumes of water samples [2].

Supramolecular assemblies (e.g. micelles, vesicles, etc) have a high potential in analytical extraction processes [3], both in liquid-liquid (coacervates) and solid-phase (hemimicelles y admicelles) extractions, because of the number of interactions they can establish with analytes. Since they have been known to efficiently extract a variety of pollutants from environmental water and solid matrices, their ability to stabilize the extracted analytes should be investigated in order to use them advantageously in monitoring campaigns. Recently, hemimicelles and admicelles have been known to effectively stabilize some pollutants [4]; in this work the ability of coacervates for this purpose was assessed.

Anionic micelles of sodium dodecanesulfonic acid (SDSA) undergo coacervation in an acid medium [5]. The coacervates yielded efficiently extract amphiphilic and hydrophobic compounds, so their capacity to stabilize them before sample analysis was investigated. Benzalkonium surfactants (BAS) homologues and PAHs were the analytes selected for this study. The preservation of the target compounds in the coacervate was investigated under three temperature conditions (room temperature, 4ºC and -20ºC). Quantitative recoveries were achieved during at least three months at the different conditions tested. No influence of the water matrix (tap, river or waste water) on the stabilization of BAS and PAHs was observed. So, coacervates is an interesting strategy for the simultaneous extraction, preconcentration and stabilization of analytes.

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INCREASED BIOLOGICAL PHOSPHATE ELIMINATION BY MEMBRANE BIOREACTOR- MECHANISM CLEARING-UP VIA PHOSPHORUS FRACTION-

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The Eutrophication of waters by a too high concentration of phosphorus and other nutrients is a global problem. In order to prevent the Eutrophication of waters with the over-foaming development of the algae, it is one of the important tasks in the waste water purification to remove the inorganic nutrients. The increased biological phosphorus elimination finds their wide application in the local waste water purification.

The advantages of the Membrane simulation process activated sludge process are upward gradient of the TS content in the biological reactor, thereby reduction of the necessary volume with same sludge load or reduction of surplus sludge production during same volume and reduced sludge load and the final clarification are saved [1].

It is based on temporal or local change in anaerobic and aerobes conditions. Under the processing species in the activated sludge enrich themselves, the phosphate in high quantity as polyphosphate more intracellular to store can. Under departure of surplus sludge thus has an increased phosphorus freight that should be scaled down.

For this purpose the mechanism clearing-up of the bio- phosphorus process was accomplished by cracking method with and without precipitant after Witt. Deviating from the original method the separation of the water phase took place from the sludge phase in the first step. Thus an accurate separation between solved and individual-bound phosphorus is possible. This step is particularly important with the investigation of dredging from anaerobic reaction ranges, i.e. a high portion of the dissolved phosphorus is present [2].

The basic precipitations partner of the phosphate, calcium, iron and aluminium is not to be regarded as primary measured variables of the bio phosphorus. The original connection of the phosphate takes place via biological procedures, in the form of phosphates, NaOH NRP represents by the parameter. This phosphate species proves as a reversibly bound p-parliamentary group, which shows as responsible for the characteristic dynamics of the process. The biological phosphorus back solutions overlaid by physical chemistry counter actions on anaerobic process conditions, particularly in the form of calcium phosphate precipitation and by adsorption processes. Iron precipitation to without iron precipitation clearly increased, at aluminium and iron bound phosphate quantities become to observe in a comparison, Without iron precipitation the biologically bound p-portion with 8.6% became (AN) and 20.4 % (AF) more highly than the physical chemistry bound p-portion. With the iron precipitation the physical chemistry bound become p-portion with 22% (AN) and 29% (AF) more than the biologically bound phosphorus portion takes part. The dissolved portion was measured with or without iron precipitation by same quantity i.e. the iron precipitation did not affect the dissolved portion.

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Hyphenated techniques in phytoremediation research

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Hyphenated techniques are needful tool in analytical chemistry. The most important area of applying coupled techniques is speciation analysis of trace elements especially in food, human and plant tissues. According to IUPAC definition speciation of an individual element refers to its occurrence in or distribution among different species. Speciation analysis is the analytical activity of identifying and quantifying one or more chemical species of an element present in the sample [1]. Trace element speciation analysis requires a method that would be both species selective and extremely sensitive since the species of interest accounts for a small fraction of the total trace element concentration.

For biological tissues liquid chromatography is usually used as separation technique because metals and metalloids are present in non volatile complexes and cannot be volatilized for gas chromatography. The analytical challenges concern the use of separation techniques in the liquid phase, such as HPLC with ICP-MS detection in combination with the use of molecular specific techniques, such as ES MS/MS [2].

Plants growing in contaminated environment acquire a wide range of adaptive strategies. The most prominent mechanism is the synthesis of phytochelatins PC_s. These peptides are synthesized from glutathione in the presence of heavy metals and are responsible for metal transport from cytoplasm to vacuole. The primary method for PC_s determination is liquid chromatography with post column derivatization by Ellman's reagent, but lack of standards and reference material makes analysis very hard. This is why coupled technique HPLC – ES – MS/MS was applied in these research. Using this technique allowed us to separate and identify phytochelatins and homophytochelatins in plant tissues incubated with Cd and Pb.

To identify metal complexes SEC – ICP-MS was applied. SEC-ICP-MS coupling instrumentation allows studies on metal biomolecule associations and on the mechanisms of biological action of metals in plants. The advantages of SEC are high tolerance to sample matrix, good compatibility of the mobile phase with ICP-MS ionization conditions and possibility of estimation of molecular mass of element species.

In our research we examined two types of plants: pea *Pisum sativum* and lupin *Lupin luteus*. Seedlings were cultivated in hydroponics conditions with Hoagland solution. Seven-day-old seedlings were exposed to Pb and Cd ions – 0,5mM Pb; 0,1mM Cd and 0,1mM Pb+0,1mM Cd. $Pb(NO_3)_2$ and $CdCl_2$ were added to culture medium. Plants were grown under controlled condition. After 4 days of incubation plants were sampled, divided to roots, shoots and leaves, washed in bidistilled water, frozen in liquid nitrogen and prepared for analysis.

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SPECIATION OF CHROMIUM IN WASTE WATER

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Chromium occurs in oxidation states, $Cr_{(III)}$ and $Cr_{(VI)}$ in environmental systems. Both forms of Cr enter the environment from various sources i.e. tanning, electroplating, chrome plating, dyes, paints, pigments, mordents, rubber, plastic, ceramic, textile, leather, tannery, welding, smelter works, steel and alloy plants, etc. The trivalent form of Cr exhibits very low toxicity whereas $Cr_{(VI)}$ is toxic and it can cause cancer if it is inhaled [1]. A simple, rapid and selective spectrophotometric method for the speciation of $Cr_{(VI)}$ and total Cr in wastewater is described. The method is based on color reaction of $Cr_{(VI)}$ with the organic reagent: N-hydroxy-N,N`-diphenylbenzamidine (HODPBA) in strongly HCl solution, and subsequent extraction of the complex into chloroform. The determination of total Cr is carried out by prior oxidation of $Cr_{(III)}$ with $Ce_{(IV)}$. The value of apparent molar absorptivity of the complex in the terms of Cr is (7.20) x 10^4 l $mol^{-1}cm^{-1}$ at $\lambda_{max,}$ 400 nm. The limit of detection (LOD) and limit of quantitative (LOQ) determination of the method are 8 and 25 μg L^{-1} Cr, respectively. The calibration curve is linear 25 - 700 μg L^{-1} Cr with value of slope, intercept and correlation-coefficient of $1.37x10^{-3}$, $-1.82x10^{-5}$ and +0.999, respectively. The optimization of analytical variables, composition of the complex and effect of diverse ions in the determination of $Cr_{(VI)}$ are described. The method has been applied for the quantification of $Cr_{(VI)}$ and total Cr in the industrial waste water. The validity of the present method has been checked by the graphite furnace-atomic absorption spectrophotometric (GF-AAS) method.

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ONLINE MEASUREMENT OF PEROXIDES FROM THE β-PINENE / OZONE REACTION BY ATMOSPHERIC PRESSURE CHEMICAL IONIZATION - MASS SPECTROMETRY

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Atmospheric aerosols affect climate and health. In the fine mode particles consist mostly of secondary constituents. The formation of secondary aerosols in the atmosphere takes place when volatile compounds react to low volatile substances. These substances can condensate on existing particles or they may even generate new particles.

An important source of secondary organic aerosols (SOA) is the ozonolysis of terpenes emitted by plants. Latest studies predict that a major fraction of SOA from terpene ozonolysis consists of organic peroxides and hydroperoxides. Due to their reactivity organic peroxides may have negative effects on human health. Nevertheless, a direct proof of the formation of organic peroxides in the particle phase during ozonolysis has been missing. Since there is little knowledge and understanding of the contribution, the reaction and the degradation pathways of peroxides in SOA, it is important to study these compounds in the particle phase.

For this reason chamber experiments were carried out to investigate the reaction of β-pinene with ozone. Particles formed in this reaction were studied in real time using an online-APCI-ion source coupled to an ion trap mass spectrometer. Before ionization the gas phase was removed by a denuder (activated carbon). Among well known oxidation products peroxides could be identified in the particle phase, showing a loss of m/z 34 (H_2O_2) in their MS/MS-spectra.

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