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ISEAC 35

BOOK OF ABSTRACTS

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MESSAGE OF GREETING

The International Association of Environmental Analytical Chemistry (IAEAC) is a world-wide operating organization that aims at promoting and maintaining scientific excellence in analytical science as applied to different environmentally relevant research areas. Not only the traditional compartments soil, water, and air are included in its activities, but likewise fields such as process analysis, human health, or quality of food. In these efforts the IAEAC strongly interacts with relevant disciplines other than chemistry.

The realization of the *35th International Symposium on Environmental Analytical Chemistry* (ISEAC 35) is the result of a trustful collaboration of the Committee on Analytical Chemistry of the Polish Academy of Sciences (PAS), the Chemical Faculty of Gdańsk University of Technology (GUT), and the IAEAC. This is the 35th event of an impressive series of "flagship" symposia of the IAEAC. It started in 1971 in Halifax/Nova Scotia, Canada, marking the birth of our Association, and had its last edition in 2006 in Hamburg, Germany. The Symposium now being held in Gdańsk, Poland, another time underlines the IAEAC's idealistic goals, namely to provide platforms for scientists to exchange "cutting-edge" results relevant to our environment, at locations throughout the world to maximize the opportunities for researchers in the respective fields to participate. It is the first time in our more than 35-years-old history that a scientific institution in Poland is hosting one of our meetings.

I am extremely thankful to Prof. Namieśnik and his collaborators that they have agreed to set up such a platform together with the IAEAC. Through their tremendous engagement they have established an impressive frame for an international event comprising a quite promising scientific and social program at a famous place. It is now up to you, the participants, to fill this program with life, to exchange know-how and brand-new results, and by this means build bridges between your respective research institutions or even countries. Maybe that through this event you will be attracted by the goals of the IAEAC so that one day you decide to become a member.

On behalf of the IAEAC I wish all of you, organizers and participants, a successful and scientifically stimulating Symposium in the highly impressive City of Gdańsk.

D. Klockow
President, IAEAC

INVITED
LECTURES

INTEGRATED APPROCHES FOR DETERMINATION OF ENVIRONMENTAL AND HUMAN RISKS OF PERSISTENT TOXIC SUBSTANCES

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Organic substances that are persistent, bioaccumulative and posses toxic characteristics likely to cause adverse human health or environmental effects are called PBTs (Persistent, Bioaccumulative, Toxic substances) or more generally persistent toxic substance (PTS). In this context, "substance" means a single chemical species, or a number of chemical species which form a specific group by virtue of (a) having similar properties and being emitted together into the environment or (b) forming a mixture normally marketed as a single product. Depending on their mobility in the environment, PTS could be of local, regional or global concern.

Basic objective of the long-term research project INCHEMBIOL and approaches of the Centre RECETOX is complex approach to study of interactions among chemical compounds present in environmental compartments and their biological effects, study of the fate of mainly persistent chemical compounds in the environment, their effects on the environment and living organisms including human.

Fate in this concept consists of a summary of transport (from their input in the environment, transport within the environmental compartment, where they are discharged, transport among compartments and long-range transport in the environment) and transformation processes (abiotic and biotic transformations). It also includes study of distribution equilibriums, properties conditioning their environmental behaviour, study of the transformation processes and their products.

This complex approach is a part of long-term research activities of the centre RECETOX. It is based on exploration of the causality among chemical (presence of chemical compounds in the environment) and biological (mechanisms of effects on the living organisms) part of the problem of chemical contamination of the environment.

This complex approach requires interdisciplinary, team collaboration of specialists from number of natural sciences and is very demanding on equipment and financial sources.

Next to currently progressive specialized natural science disciplines studying basic chemical and biological processes on atomic and molecular level (such as structural chemistry, molecular biology etc.), the more complicated naturally existing components (such as atmosphere, geosphere, biosphere, real ecosystems etc.) are still studied very little and understanding of their structure and function is not sufficient.

Contamination of all environmental components produced from different human activities belongs among very topical problems of current society and the whole planet. This contamination has not only global consequences, such as global warming or increased levels of UV radiation in atmosphere, but direct negative and/or long-lasting (chronic) negative effects of contaminants on living organisms were also shown. It is often unclear to which extension are the processes in atmosphere consequences of anthropogenic activities and to which extension they are results of natural processes of the systems development.

The research plan concentrates on acquirement of new scientific information and experimental data concerned with problem of chemical contamination of the environment with persistent, toxic compounds (persistent, organic pollutants, heavy metals, organometallic compounds). It is necessary to distinguish this contamination from natural migration of the compounds in atmosphere, biosphere and geosphere, and also study its interactions within these environmental spheres.

The basic objective of the research plan is characterization of fate and negative effects of chemical compounds in real ecosystems by interconnection of a few scientific disciplines studying:

(i) chemical compounds in the environment - fate - transport and transformation, distribution in and among compartments; their determination in different abiotic and biotic environmental components,

(ii) abiotic processes in the environment - differentiation and migration of the compounds in the atmosphere and geosphere - geology, geochemistry, paleontology and climatology

(iii) effects of chemical compounds on living organisms - biochemical toxicology, genotoxicology, ecotoxicology, ecological epidemiology;

(iv) ecologic and human risks combining knowledge of more disciplines for quantification of existing risks

Basic Directions of the Project Solution

- Studying properties of chemical compounds found in biotic and abiotic compartments of the environment, their transport and interactions with the environment, transformations and effects of these compounds and their transformation products on living organisms - defining of properties responsible for increased or modified mobility of the compounds in different matrixes
- Study of the significance of bioavailibility of chemical compounds in different matrixes, model processes affecting bioavailability and consequences for exposure models in different types of real ecosystems.
- Development and applications of methods for determination and chemical speciation of elements in environmental samples using separation techniques along with atomic spectroscopy detection and further speciation of spatial distribution of the elements in solid, namely geologic matter using modern unique methodologies "laser assisted spectroscopy".
- Study of interactions among individual components of the ecosystem with emphasis on little-studied processes of interchange between snow and atmosphere and possibilities of chemical and photochemical changes in ice.
- Development of biosensors based on available biocatalyzators and their use for monitoring of contamination of environmental components and for decontamination technologies (bioremediations).
- Experimental and theoretic study of redox and adsorption properties of low- and medium molecular biologically and environmentally important compounds to obtain new scientific information on the phenomenological and molecular level about behavior, reactivity and transformation processes connected with electron transport, with the possibility to be used in optimization of degradation and analytical processes.
- Development, modification and validation of analytical approaches for studying presence, concentration and changes of studied chemical compounds in the environment.
- Differentiation and migration of chemical compounds in different geotectonic regimes, influence of seat rock on chemical compounds migration and ecosystem development.
- Model study of geochemical properties of compounds concentrated on long-term predictions of their development and potential risk changes, identification and determination of importance of geochemical and geological processes controlling distribution of chemical compounds in the environment.
- Bioindication of stress factors in ecosystems of younger Tertiary and Quaternary period, their interactions in transition to recent antropogenically modified ecosystems.

- Role of climatic conditions during transport of chemical compounds in natural environment and in evaluation of current and potential environmental risks in real ecosystems.
- Study of biological effects of model chemical compounds at different levels of the biological systems from different types of environment (aquatic, soil..) and application of new knowledge for development of new tests, study of mechanisms of the toxic effects.
- Genotoxicity of model chemical pollutants and study of possibilities of its characterization in real environmental pollutant mixtures.
- Study of contaminant ecotoxicology in aquatic and terrestrial ecosystems - relationships among different types of anthropogenic contamination (eutrofization, organic and organometallic compounds) and complex biological effects on different hierarchical levels (individuals, populations, model communities and ecosystems) - bioindication of the chemical stress in real ecosystems.
- Retrospective and prospective bioindication of stress changes on the level of real ecosystems, study of effects of multiple stress factors, study of adaptation capacity and resistance of the real systems, development and optimalization of the bioindication methodologies, above all so called "early risk indicators".
- Model evaluation of effects of chemical mixtures in different-focused testing systems, study of potential synergistic and/or antagonistic interactions.
- Typology of model recent ecosystems from the point of view of definition natural conditions (geological, geochemical, geobotanical, climatic, evolutional etc. factors) and determination of the sensitivity to potential impact of anthropogenic influences, comparative case studies based on real data from contamination of such systems.
- Evaluation of the ecological risks in real ecosystems focused on investigating the impact of multicomponental exposure, development of model exposure scenarios and their evaluation, model evaluation of primary and secondary risks and uncertainty analysis.
- Analytical research focused on multivariate analysis of environmental data and population human data with the use of environmental pollutants fate modeling, influence of the rock background, evaluation of stress changes on the ecosystem level, biodiversity analysis, definition of the reference states and analysis of human risks related to chemical stressors influence.
- Modeling in the area of ecological and human risks and development of information systems, algoritmization of stochastic and deterministic approaches, development of analytical SW tools.

Research plan

Project INCHEMBIOL proposes to contribute to following research directions:

- Fate of chemical compounds in the environment (sources, physical chemical and environmental-chemical properties, distribution in abiotic and biotic environmental compartments, levels of contamination of environmental components and living organisms, abiotic and biotic transformations) as the basic source of information for evaluation of possible exposure of humans and living organisms;
- Study of the impacts of chemical compounds on the living organisms (on all levels of organization - cell, organism, population and ecosystem);
- Evaluation of ecological and human risks in relation to different types of stressors under real ecosystem conditions.

Experimental design

This long-term project which will be realised during the period 2005-2011 in the following basic parts:

1. Experimental (laboratory) study:
    1A. Chemical compounds properties

1B. Biological effects of chemical compounds, the mechanisms of action

Partial principal studies will be realized in compliance with the research plan:

- Effects of defined priority compounds
- Toxic effects of chiral compounds
- Ecotoxicology of mixtures and effects of different environmental matrices
- Ecotoxicology of environmental processes (transformation, photochemistry as sources of new types of pollutants...)

With the aim to integrate information about ecotoxicology at different levels of biological matter methodologies of the following directions will be interconnected:

- Biochemical ecotoxicology and genotoxicology
- Terrestrial and soil ecotoxicology

1C. Development of new test systems for xenobiotics in the environment

2. Study of the processes under real ecosystem conditions
   - Case study 1: Fate and impacts of PTS in model systems - use of model ecosystems from the view of the origin of current conditions, impact of principal abiotic factors including rock background and climatic conditions, effects on risk evaluation;
   - Case study 2: Bioindication of the stress factors effects under real soil conditions - study of soil biological potential in relation to risk evaluation;
   - Case study 3: Bioindication of the stress factors impact under conditions of real aquatic ecosystems on the model of water basins Kníničky (Brno reservoir) and water reservoir Nové Mlýny;
   - Case study 4: Natural development of basic parameters of natural environment and their modification by human activity in the area of crystallic rocks - Dolní Rožínka area;
   - Case study 5: Natural development of basic parameters of natural environment and their modification by human activity in the area of sedimentary rocks - rosicko-oslavanska coal basin area.

3. Risk analysis, critical analysis of information sources and development of information tools

Risk assessment studies and their methodology

Ecological and human risk assessment can be characterized from the viewpoint of informatics as complicated processing of heterogeneous data (mostly retrospectively collected from various sources) leading to probabilistic estimation of some uncertain (prospective approach) or on the other hand relatively certain (retrospective approach) risk event. Key methodical steps of the whole process can be simply defined as follows:

1. Problem formulation and hazard identification. Introduction to any reasonably designed study. It includes recognition of the area of interest, collection and aggregation of required information and preliminary focus on identified principal pollutants (stressors), source of contamination and most vulnerable environmental components and biological receptors.
2. Multi-component exposure assessment. Exploration, identification and quantification of important exposure pathways. It includes modeling and summaries of accessible data as well as empirical estimates of environmental concentrations of proposed key pollutants.
3. Biological effect evaluation. Empirical phase focused on concentration-related or dose-related reactions of biological systems. Principal aim is to get parametric measures that identify biologically dangerous concentration levels. The process should not be limited only to laboratory testing, it works with ecosystem monitoring as well. Whenever

we have access to regional or national bio-monitoring network we should use this data as very powerful information background.

4. Risk characterization is completely computational process that leads to the probabilistic estimate of the risk. In fact it is stochastic aggregation of data from all the preceding methodical blocks.

In other words, there are many inputs required and only limited number of outputs provided, however always with serious impact. The whole process can be also visualized as a circle that takes very different data and aggregates them according to given rules. The circle is constrained to rotate due to never-ending chain of problems entering the system. The image of "circle process" is functional because not all phases must be necessarily employed in any type of problems. Different situations give to different phases very different weights. For example, the situation is thoroughly different if someone needs retrospective or prospective assessment than if it is sudden catastrophic situation like industrial accident or flood where we must in first line mitigate the immediate effects.

Informatics in ecological and human risk assessment

Informatics is incorporated in each methodical step of formal risk assessment, from data gathering and analyses, through risk estimation to final validation of results and minimization of uncertainties. ICTs assist in building of assessment scenario and are indispensable in optimizing of experimental design. To summarize, information technologies and data analysis give the assessment process all its desirable properties:

- evidence-based background
- sufficient information power
- credibility and confidence
- effectiveness and presentation skills

Writing about informatics in the EcoRA methodology, we should never forget communication of the results. Risk estimate itself is complicated end-point, conditioned by many items and circumstances. Risk should be communicated as probability of some hazard event, that however can reach different levels for different biological systems. Without adequate presentation, there is a danger of incorrect interpretation and the examined situation can be unacceptably underestimated or omitted. ICTs have the power to emphasise the right findings to the right people. We can make the results accessible even for general public or to provide interactive tools for the evaluation of different scenarios.

Gained information must be processed and the sources must be prioritized, filtered and then aggregated in order to get really usable input into assessment scenario. The information processing is typically projected into the area of interest and so most recommended tool for this phase is some type of geographical information system (GIS).

Here we must strongly emphasize very important dimension of any practically targeted risk assessment scenario, it means effectiveness and pragmatic simplicity. EcoRa is very laborious work and so there is only limited space for research activities. We cannot rely on scientific and progressive data trying or even hoping that it improves our understanding common ecological data. Instead of that, the simplest and already verified set of methods should be applied in first line and additional analyses should be applied only in the case of remarkable uncertainties.

The selection of proper biological end-points is the last important step that should be prescribed in the scenario. This step is extremely important because the risk estimate cannot rely only on chemical data:

- biological tests can reveal some new effects that cannot be predicted from chemical data (this holds namely for heterogeneous environmental mixtures of chemicals)
- bioindication or monitoring survey can indicate the effects in past, that cannot be detected by chemical analyses

There are basically two strategies in biological effects assessment: (1) model testing under defined conditions (mostly laboratory tests and bioassays) and (2) monitoring of real ecosystems that is often referred to as bioindication. Typically we employ different tests or tests using different biological models (receptors) to cover the heterogeneity and various food strategies of biological systems in the field.

Multiple biological tests of course require a wide spectrum of analytical methods as it will be explained in next paragraphs. At this point we should only emphasize, that outcomes of both chemical measurements (mostly applied during area recognition and exposure assessment - see Fig. 1, 2) and biological tests provide principally the same numerical output, concentration measure:

- environmental concentration (mostly obtained on the basis of chemical monitoring) as estimate of the real (or predicted) contamination of target matrices
- biologically safe concentration (obtained from laboratory tests, biomonitoring and/or *in situ* assays) as the estimate of the concentration that does not cause biologically harmful effect or on the other hand, the concentration that causes some degree of the effect.

Both types of concentration estimates are then mutually related in probabilistic models or ratios to estimate the probability of risk event. We typically mutually relate two or more probabilistic distributional models and try to find concentration cut-off point that determines the highest acceptable environmental concentration that is still biologically safe.

Most important aspects of analysis of environmental data and related research topics

Data analysis plays strategic role namely in the following fields:

- Data models, auditing and validation of information sources. Relevant arrangement of input information, description of the situation, hazard identification.
- Regionally specific aggregation of accessible data, quality control and GIS models of the area of interest, mapping of exposure pathways and levels.
- Hierarchical structure and prioritization of biological indicators according to ecological criteria, susceptibility to stress factors and accessibility for measurements. Application of data from large-scale biomonitoring networks. Searching for biological "hot spots" and reference standards for biological systems in the area of interest. Selection of proper biological receptors. Currently, more and more sophisticated techniques are being applied in this field, namely data mining technology.
- Standardization of laboratory tests and their outputs (i.e. concentration measures that are related to some level of biological effects: NOEC, LOEC, NOAEL, LOAEL, ID_x, LD_x, ED_x, IC_x, LC_x, EC_x). Practical implementation of these outputs in decision making includes following topics:
    - standardized and reliably estimated concentration measures
    - estimation and formal mathematical description of different types of dose-response curves (because the shape of the relationship is important as well)
    - typology of dose-response curves for different situations and stressors
    - mathematical processing of complicated, but real dose-response patterns.
- Benchmarking of ecosystem abiotic and biotis characteristics, risk characterization and regionally specific interpretation. This approach generates more complicated data structure than laboratory biostests with the following specifics:
    - It is impractical to measure these complex parameters in predictive design, where the conclusion must be made before any large-scale release and effects can occur, the evaluation is then retrospective not prospective.
    - In fact it is virtual reconstruction of the state of the injured environment prior to the pollution release so that it can be compared to the injured state.
    - In the case of such complex parameters, standard statistical methodology fails or we have no time to verify hypotheses in repeated experiments.

- An alternative methodology to common statistical scoring must be used and it is multivariate statistical modeling: a) processing of so called calibration data set that is representative for the ecosystem or b) work with environmental gradient data. We rank hazardous and clean sites using a linear discrimination with the support of training set of well characterized sites that are assigned to categories on a scale hazard. The site attributes are used to establish a discriminant function. If the function separates the categories sufficiently, new sites are classified on the hazard scale by applying the discriminant function.

Conclusion

Integrated approaches for determination of environmental and human risks of persistent toxic substances will be presented on the examples of integrated approach which use the integrated long-term monitoring as a basic tool for the study of environmental processes and effects, laboratory and field methods of environmental chemistry and ecotoxicology with approaches of environmental modelling and informatics and human and ecological risk assessment.

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ADVANCED MINIATURIZED PLASMAS AS ATOMIC SPECTROMETRIC DETECTORS FOR ELEMENTAL DETERMINATIONS AND SPECIATION IN ENVIRONMENTAL SCIENCES

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Introduction

The development of miniaturized plasmas is a frontier field of development in plasma spectrochemistry, which has got impulses from the availability of a wide range of microstructuration technology and from developments in microelectronic on one side and is driven by the field of applications, namely by the demand for field-usable instrumentation, for instrumentation with low instrument and operation costs, for small and highly sensitive element-specific quantitative detectors, and for dedicated instrumentation, on the other side. In plasma spectrometry inductively coupled plasmas developed to a high degree of maturity since their introduction in the 1960s and are now together with CCD-based emission spectrometers and since the 1980s as ion sources for mass spectrometry the working horses for trace and species determinations in industrial samples, biomedical samples and environment-related samples, where especially determinations in solutions are made. For determinations in solid samples a number of direct solids sampling techniques in ICP-based plasma spectrometry were established, especially in combination with laser ablation for the case of compact solid samples also with spatial resolution capabilities and for powders after mixing them with additives and briquetting pellets. Further especially for powder analyses, slurry sampling in the graphite furnace, direct sample insertion in plasmas or slurry nebulisation with suitable nebulisers such as the Babington nebulisers can be applied. As alternative especially x-ray fluorescence methods are to be mentioned, however, with restrictions for the light elements. Here because of the high absolute power of detection total reflection x-ray fluorescence spectrometry is attractive, as for fine powders work with slurries also is possible and for minute samples such as aerosols sampled on substrates by impaction calibration through picodroplet deposition and drying on the samples widens the possibilities for quantification considerably. This approach also is of use for the analysis of environmental aerosols after impactor-based sampling. Miniaturization in plasma spectrometry is possible with any type of plasma, be it dc arc discharges, dc or rf glow discharges or high-frequency or microwave discharges at atmospheric pressure. This can in any of these cases be persued until the respective source can be provided on a chip where the energy is brought to the plasma by microstrips produced by metal vapour deposition through plasma assisted techniques or by galvanic techniques.

DC microplasmas

Through microstructurization techniques microstrips powering the electrodes of a dc arc gap in a glass, quartz or even polymer substrate can be realized. An intensive discharge here can be produced, as first shown by Eijkel et al. [1] with a discharge under reduced pressure. They could even provide a miniaturized gas chromatographic column on the chip in addition to the dc discharge. Gas chromatograms with considerable resolution were obtained when band heads were monitored. With a such approach one can already obtain cleaner chromatograms than with non-selective detectors and the system could be useful for in-situ monitoring of health-relevant substances e.g. in air. However, due to the electrode sputtering the lifetime of the sources is limited, which remains a limitation for any type of microplasma operated between electrodes.

Low- and middle-frequency electrodeless discharges

Here the electrodes are electrically isolated from the plasma and e.g. one could be provided as a grounded metal block on one side of the substrate and the other as an antenna at the other side of the substrate.. These antennas can be given a well-defined form according to the needs of the device and provided by galvanic or plasma vapour deposition on the substrate. Here it is favorable, to use a substrate with a cylindrical channel, which is parallel to the surfaces of the substrate and extends from one edge to the other.

Bass and Chevalier [2] described a high-frequency plasma operated at atmospheric pressure and showed that at reduced operation power and with a very simple structure for powering the discharge a stable plasma with a diameter of below 1 mm and a few 10 mm in length can be sustained. A number of spectral features were found to be related with the high sensitivity, so that the source has potential for practical use as element-specific detector in gas chromatography.

The miniaturization of the ICP to a low-pressure source has been consequently realized by Hopwood et al. (see e.g. Refs. [3]). Here a mini-coil is provided as microstrip on a quartz substrate and also the generator has been made small and portable. The system could be used as a source for atomic emission spectrometry. It was possible to determine sulphur dioxide down to the ppm level in gases and to obtain a linear calibration over several orders of magnitude [4].

A further line are the barrier-layer discharges, being ac discharges of which the electrodes can not be contacted by the plasma. They also are mostly operated under reduced pressure and powered by rectangular high voltage waveforms up to frequencies in the MHz range and known as silent discharges. Such sources proved to be suitable absorption cells, where excited levels of the halogens can be well populated, so that with diode laser radiation in the IR wavelength range their determination by atomic absorption becomes possible. With this approach detection limits for CCl_2F_2 of 400 ppt v/v and 2 ppb v/v in helium using the Cl 837 nm and the F 686 nm lines, respectively, could be obtained and the source is very stable. The system has been shown to be very useful for the determination of halogenated hydrocarbons by gas chromatography, where detection levels in the gas flows of the order of pg/s are obtained, as shown by Kunze et al. [5].

Other lines of development made use of glow discharges. This field is very interesting as the sources can be operated not only at low pressure as known from a long development (for a treatment see Ref. [6]) but since rather recently also at atmospheric pressure. Here, it is interesting to see how with glow discharges of which the liquid serves as one of the electrodes a stable source can be realized with which cations and anions in solutions can be determined. This sources, going back to the work of Kim et al. [7] are very promising with respect to power of detection. They can also be miniaturized, and consequently could serve as detectors for liquid chromatography, as shown by Davis and Marcus [8] and Webb et al. [9]. Here they really correspond to a need as with all other sources discussed the sensitivity to moisture is high and the detection capacity very quickly deteriorates when switching to wet aerosols.

Microwave discharges

Microwave discharges finally are very stable sources at atmospheric pressure. They became already at the end of the 1970s available as small sources through the work of Beenakker. He used, however, very bulky resonator structures to produce the standings waves required to sustain microwave discharges of about 1 mm in diameter and up to some 10 mm in length. Through the use of microstrips Engel and Bilgic et al. [10] in 2000 could realize a miniaturized microwave plasma operating inside a channel inside a quartz plate, where the microwave energy was provided through microstrips, deposited on the quartz by chemical and plasma deposition techniques and microstructuring through the use of photoresists. This plasma could be sustained in argon as well as in helium at atmospheric pressure and operated with gas flows in the 50-100 $ml.min^{-1}$ range and at a power of less than 40 W. This plasma is ideally suited for the excitation of analyte species, after they have been brought into the gaseous phase. The longterm stability of the discharge here was excellent and no deterioration of the device occurs even not hundreds of hours of operation. However, it should be emphasized that the microplasma does neither tolerate wet vapours nor aerosols of aqueous solutions as it than extinguishes. Through optimization of the structure and especially of the extra load provided as a side-strip one can obtain structures in which either an argon or a helium discharge can be operated and through optimization the plasma could be operated inside the wafer or it exit the wafer. The latter type of plasma can better serve as a source for optical emission or mass spectrometry, due to the absence of space angle limitations. At any case details such as the use of flattened corners to improve the ratio of forward to reflected power and the adaptation of the antenna length to the gas used and the plasma were found to be essential. For both argon and helium plasmas high excitation temperatures (depassing 4000 K) were measured but the gas temperatures, as estimated from the rotational temperatures were rather low (about 600 K), which lets expect a good excitation but a poor evaporation and atomization capacity. As the source can be operated with argon as well as with helium, also the non-metals can be excited efficiently. The latter makes the source of potential interest for being used for element-specific detection in the gas chromatographic determination of environmentally relevant analytes in a wide variety of samples [12].

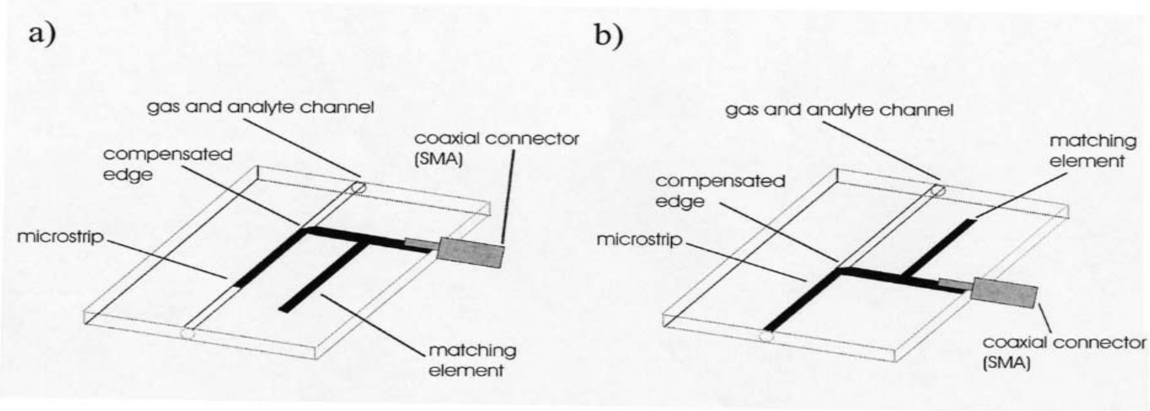

Fig. 1. Miniaturized microwave plasmas operated in a quartz wafer and powered through microstrips. Plasma operated inside the wafer (a) and plasma sorting at the edge of the wafer (b) [11]

The source was found to be an excellent emission source when combined with all types of chemical gaseous analyte species generation devices.

For the case of mercury, of which both the element and its species are of high environmental interest, the cold vapour technique known from atomic absorption spectrometry is highly useful. In the case of $SnCl_2$ as reducing agent a detection limit of as low as 50 pg.mL^{-1} could be obtained. Through improvement of the microstrip arrays, it is possible to allow the discharge to exit from the excitation channel in the wafer. Then space angle limitations do no longer limit the use of the source as radiation source for atomic emission spectrometry [11]. It then becomes easy to couple a miniaturized CCD spectrometer through an optical fiber with the microplasma making the complete instrumentation compact. Both a helium and an argon plasma can be operated in the microstructure based device. However, as the detection limit for mercury in the case of a helium plasma is higher than in the case of argon, the latter is the better choice. It further also is possible to use $NaBH_4$ instead of $SnCl_2$ as reducing agent in the case of the mercury cold vapour technique [13]. Indeed, through the strong coupling via the microstrip the plasma seems to be rather robust to the excess of hydrogen introduced with the working gases into the source. Nevertheless, the background emission intensities in the case of an excess of hydrogen increase, which leads to a deterioration of the detection limit. The optimum detection limit with a plasma exiting from the wafer and when using $SnCl_2$ as reducing agent is some higher than the one stated in Ref. [10], which certainly relates to the lower resolving power used in the case of the miniaturized monochromator (Table 1).

With the microstrip MIP also the elements, which form volatile hydrides can be determined, when $NaBH_4$ is used as reducing agent. Here the power of detection for the case of helium as working gas are lower. In the case of electrochemical hydride generation and a helium plasma detection limits for the volatile-hydride forming elements were again lower, as here the amount of hydrogen produced can be better controlled and the generation of less hydrogen leads to a lower noise, especially [14]. The procedure could be well used for the determination of As and Sb in dissolved environmentally relevant reference materials such as sewage sludge and coal fly ash but also in production waters from the galvanic industry.

Table 1. Detection limits of the cold vapour technique and of chemical and electrochemical hydride generation coupled to various types of MSPs in OES [14-16].

	c_L in ng.mL^{-1}
Hg with cold vapour technique ($SnCl_2$) inside the wafer with	
40 W Ar MSP	0.6
40 W He MSP	1.1
Hg with cold vapor technique ($SnCl_2$) exiting from the wafer with	
40 W Ar MSP	0.11
Hg with cold vapor technique ($NaBH_4$) exiting from the wafer with	
40 W Ar MSP	9
Chemical hydride generation with 40 W Ar MSP inside the wafer	
As	18
Sb	31
Chemical hydride generation with 40 W He MSP exiting the wafer	
As	16
Sb	22
Electrochemical hydride generation with 40 W He MSP exiting the wafer	
As	6
Sb	7

Table 2. Determination of Hg, As, Sb, Br, Cl and S in environmentally relevant samples [13-17].

Hg in environmental samples using an argon MSP exiting the wafer and $SnCl_2$ [13]			
	certified value	spiked	found
domestic sludge	3.64 + 0.25 μg.g^{-1}		3.55 + 0.41 μg.g-^{1}
NIST SRM 2781 after			
dissolution1 % (m/v)			
NaCl solution		0.2 μg.mL^{-1}	0.186 + 0.06μg.mL^{-1}
As and Sb in environmental samples using an argon MSP inside the wafer with chemical hydride generation [14]			
	ICP-OES	spiked	found
galvanic bath with 2.5 % (m/v) Ni_2SO_4			
As		45 μg.mL^{-1}	43.7 + 4.1 μg.mL^{-1}
Sb	6.89 + 0.18 μg.mL^{-1}		6.41 + 0.85 μg.mL^{-1}
	certified value		found
As in coal fly ash NIST SRM 1663a	145 + 15 μg.g^{-1}		144 + 4 μg.g^{-1}
Cl^-, Br^-, and S^{2-} in tap water samples using a helium MSP exiting the wafer [17]			
	ICP-OES	spiked	found
Cl^-	20.0 + 0.2 μg.mL^{-1}		20.3 + 0.3 μg.mL^{-1}
Br^-		10.0 μg.mL^{-1}	9.90 + 0.25 μg.mL^{-1}
S^{2-}		10.0 μg.mL^{-1}	10.0 + 0.2 μg.mL^{-1}

The generation of volatile speciers through the use of suitable chemical reactions also can be used for the determination of elements like S, Cl, Br, and C, which are of environmental interest. Here applications for water analysis are very attractive (Table 2).

A further field of application for miniaturized microwave plasmas is the determination of metals in air for monitoring purposes. Here, it is not useful to lead the air through the discharge, as this makes the discharge unstable. However, with an MSP exiting the wafer mercury e.g. could be determined in the air surrounding the plasma. Here certainly ways to make the excitation as efficient as possible have to be developed. Eventually mass spectrometric measurements, where the plasma is anchored between the plasma channel and the sampler could be useful as well. In any case it should be mentioned that in optical emission spectrometry also molecular bands were found depending on the compounds sampled by the argon working gas, so that a differentiation between different compounds could be made, which for environmentally oriented problems also could be made use of.

Conclusions

Miniaturized plasmas can be well used for determinations of the elements in a wide variety of environmentally relevant samples. All analytes, which can be brought in the gaseous phase can be easily determined with a wide diversity of microplasmas, whereas in liquids glow discharges where the sample solution serves as one of the electrodes is useful. For monitoring metals in gases also possibilities are available. The range of applications of the devices certainly still can be widened considerably when using mass spectrometry detection. By on-line combinations with chromatography the devices certainly also are very useful for metal speciation work.

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FROM RISK ASSESSMENT TO EVALUATION OF EFFECTIVE MEASURES - IMPLICATIONS OF MONITORING ANALYSES IN THE IMPLEMENTATION OF EU ENVIRONMENTAL POLICIES

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EU Environmental policies, in particular the so-called "framework" legislations, are often based on stepwise approaches and technical milestones such as characterization of "risks" (e.g. pollution risks), analyses of pressures and impacts of human activity, monitoring and design of action programmes. A good example of such legislation is the Water Framework Directive 2000/60/EC, which additionally includes a component of integrated river basin management. Other examples can be found in the sectors of waste, industrial emissions and agriculture policies. In this context, besides other data, chemical data often represent one of the pillars of policy-related decision-making. In particular, chemical monitoring data are aimed to provide information on initial assessments of risks, assessments of long-term changes both from natural and human activities, compliance requirements (e.g. assessment of "water status"), etc. Chemical information is also used for investigating risks due to specific activities or installations, and is used for permit granting procedures as well as for checking possible impacts of given activities and the effectiveness of action programmes. The effectiveness of policy actions highly depends on the ability of Member States laboratories to measure a wide range of chemical parameters in different types of environments. Measurement data, therefore, represents the foundation of the EU policy implementation system. This lecture will illustrate the policy cycle (from risk assessment to evaluation) with selected environmental policies (in particular water-related policies) and highlight the importance of monitoring with regard to EU policy implementation.

SATELLITE REMOTE SENSING OF THE BALTIC ECOSYSTEM

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The spectrum of radiation originated from sun and sky in the visible region, which emerges from below the sea surface after being scattered upward at subsurface depths is commonly described as ocean color. It is influenced by concentrations and optical properties of various organic and inorganic constituents of seawater. Ocean color can be measured from space to provide synoptic global information on subsurface oceanographic parameters representing the upper ocean from the surface to a few tens of meters depth.

These capabilities were first demonstrated by aircraft measurements in 1970 [1] and the proof-of-concept NASA's satellite mission of Coastal Zone Color Scanner, CZCS in 1980 [2]. Building upon the CZCS heritage, significant efforts have been made in the recent past to develop ocean color satellite missions (SeaWiFS, MODIS Terra and Aqua and many others) with improved spectral and radiometric performance, spatial and temporal coverage, and quality of data products.

To date, satellite retrieval of the water parameters based on ocean color has focused largely on oceanic waters for which simplifying assumptions about the optical properties can be made. This doesn't apply to the most of coastal and inland water bodies usually much more optically-complex. Such waters require new algorithms based on new approaches for dealing with both atmospheric correction and retrievals of bio-optical properties from water-leaving radiance. The Baltic Sea is such a case.

Large discharge from rivers, limited exchange with marine waters of the North Sea, and relatively shallow sea floor, significantly influence the optical properties of the Baltic. In addition to the high concentration of CDOM that exerts a profound effect on the absorption properties [3], the Baltic waters are also rich in nutrients.

On the other hand, the Baltic Sea is of great importance to the countries surrounding it and its ecosystem is evolving as a result of human activities. This requires a regular monitoring of environmental processes in the Baltic which, together with in situ analysis at selected sites and times, can only be effective with the implementation of remote sensing technology. Taking it into consideration, the Remote Sensing Lab of the IOPAS carried out development of remote sensing algorithms for the Baltic Sea for more then ten years, with significant results, (e.g.[4]), which will be presented.

Also recently, a comprehensive national project DESAMBEM - Development of satellite method of the Baltic ecosystem monitoring (PBZ-KBZ-056/PO4/2001-2005) was executed in years 2002-2005. The mathematical models and algorithms for the remote sensing of the Baltic ecosystem with its primary production at the end, were developed and can be applied in the future. It was proved that the new algorithms have a strong potential in terms of monitoring the Baltic ecosystems from space.

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WATER ANALYSIS: KEY FOR UNDERSTANDING AQUATIC SYSTEMS

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1.Introduction

Water as vital resource has become a severe limitation for the growth of human population and its industrialisation in wide areas of the world. Hand in hand with the availability of water go the quality standards for its use. Therefore water analysis has gained a key position for the development of mankind.

Milestones in the development of analytical tools for water quality assessment date back to the early days of analytical chemistry. First there was mainly fecal pollution; increasing industrialisation led to an increase of salt and metal loads of rivers. Organic xenobiotics followed, and in our days, questions on the bioeffects of the determined analytes wait for reliable answers.

Ion chromatography, atomic spectroscopy and high-resolution chromatography with mass spectrometric detection have become milestones in identification of water constituents and their quantification down to the sub-micro molar concentrations even in complex matrices like waste water. Element speciation, metabolic pathways and mass balances including different phases have been developed for aquatic systems and the technical treatment of polluted water. Pragmatic sum parameters found their way into environmental legislation and have been applied routinely [1].

This contribution wants to give actual examples for the application of analytical tools serving the assessment of aquatic systems and their sustainable use.

2.The fate of pesticides

Plant and crop protection depends to a good part on synthetic pesticides. The past decades have shown that some pesticides and their uncontrolled application can lead to a severe pollution of ground water regions. This is of great relevance for the public drinking water supply, which often relies on ground water. Hence, a maximum allowed parameter value of 0.1 μg/L has been introduced in the EU legislation on water for human consumption [2]. This challenge for analytical sciences has led to the development of a suite of experimental steps which guarantee reliable determination including sample treatment, concentration processes and chromatographic separation, high-performance identification and quantification with specific standard deviation. Due to standardised methods [3], the results became well comparable for different sources. Broad ground water monitoring programs resulted in regional hit lists of compounds. Their assessment led to a partial ban of products. Pesticides with long-term application like atrazine also give rise to metabolites which reveal the pathways of natural attenuation.

Other reaction products with toxic relevance like the recently found *N*-nitrosodimethylamine (NDMA) [4] raise the question on their proper regulation. From the analytical point of view, the emerging metabolites have shifted the identification from the target analytical approach to the search for unknown substances.

3.Sum parameters lead the way

In complex matrices like waste water, the determination of individual substances can be tedious and questionable. Sum parameters, however, give valuable information on material balances. Parameters like total organic carbon (TOC), dissolved organic carbon (DOC) or on activated carbon adsorbable organic halogens (AOX), chemical and biochemical oxygen demand (COD, BOC) or carbon-based UV absorbance (CbUVA) have become well established surrogate parameters which can help to quantify the efficiency of water treatment processes. The limited structural information which is typical for most of the sum parameters can be overcome by resolving the detection chromatographically, e. g. according to molecular size or polarity (Fig. 1). These hyphenated methods are well suited to identify hot spots of pollution and to characterise integrated functionalities of water constituents [5].

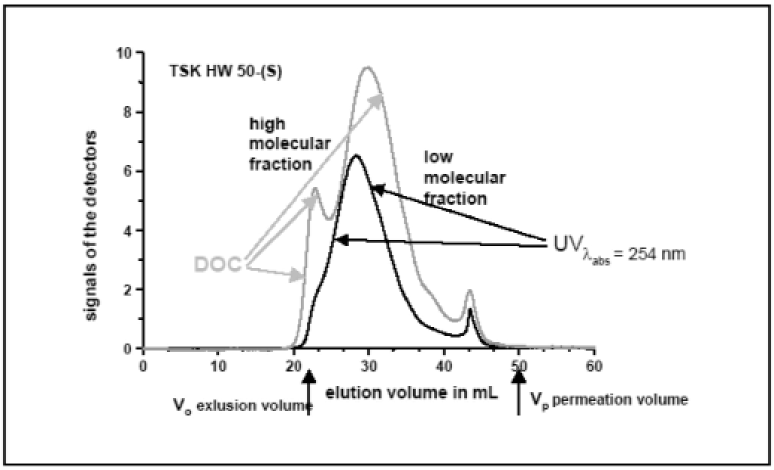
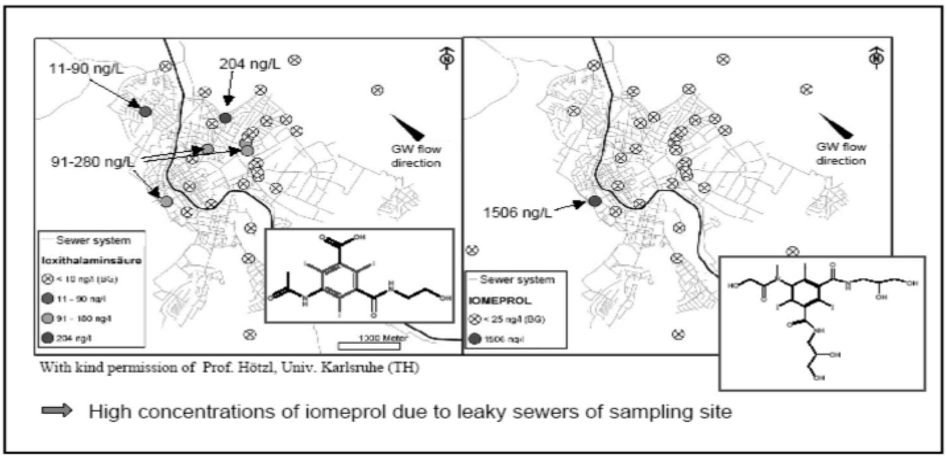


Fig 1. Size-exclusion chromatography with organic carbon and UV detection. Chromatogram of water from a brown-water lake. DOC: 17 mg/L.

Characterising the solid residue of an aqueous sample, e.g. by magic-angle spinning nuclear magnetic resonance spectroscopy (MAS-NMR) [6] is another powerful method to obtain detailed structural information. The costly approach turns out to become reasonable in case of careful sample selection based on preceeding sum parameter application.

4.Medical care and its consequences

Modern life style, health consciousness and an overaged society have led to an increased consumption of pharmaceutically active compounds (PhACs) including the use of diagnostic chemicals. The situation gets even more complicated by the wide application of veterinary pharmaceuticals. A good part of the PhACs find their way into the aquatic environment [7]. The resulting dilemma has stimulated analytical activities to trace the distribution and fate of the PhACs after their medical application. Most representatives of ionic and non-ionic iodinated X-ray contrast media (ICM) are highly water soluble and poorly biodegradable. As a consequence, ICM reach easily via waste water systems the receiving waters if no special care is taken. Individual ICM have been found in rivers and lakes up to a few micrograms per litre. Due to the highly reliable analytical identification, ICM can even serve as tracers for PhAC sources or leakages in the sewers (Fig. 2).



With kind permission of Prof. Hötzl, Univ. Karlsruhe (TH)

High concentrations of iomeprol due to leaky sewers of sampling site

Fig. 2. Iodinated X-ray contrast agents in ground water. Ground water sampling sites with concentrations of ioxithalamic acid and iomeprol. Background: Sewer system.

Fortunately most ICM are physiologically indifferent which is not the case for many of the other PhACs. Their analytical identification and the characterisation of their bioactivity has become one of the major tasks of water analysis.

5.Adding bio response

The classical assessment of the bioeffects of chemicals in drinking water is mainly based on human-toxicological data. For the assessment of aquatic systems, additionally ecotoxicological information has to be considered. The need for an assessment strategy which combines sound chemical and physico-chemical analysis with meaningful bioeffect data for the identical sample is obvious. There have been many investigations on the bioeffects of pollutants on aquatic organisms in the trophic chain. Some of them have found their way into the standardised test systems for water quality assessment. Recently molecular biology and molecular medicine have offered several test systems, e.g. for neurotoxic, genotoxic, reprotoxic or immunotoxic effects. Of special interest is a test for endocrine disruptors, for it focusses on the sensitive hormone functions. The yeast estrogen screen (YES) developed by Routledge and Sumpter [8] (Fig. 3) can be used for response curves which reach down to the pmol/L level of endocrine disruptors. Chemical contraceptives in aquatic systems can be monitored and fertilization rates can be correlated.

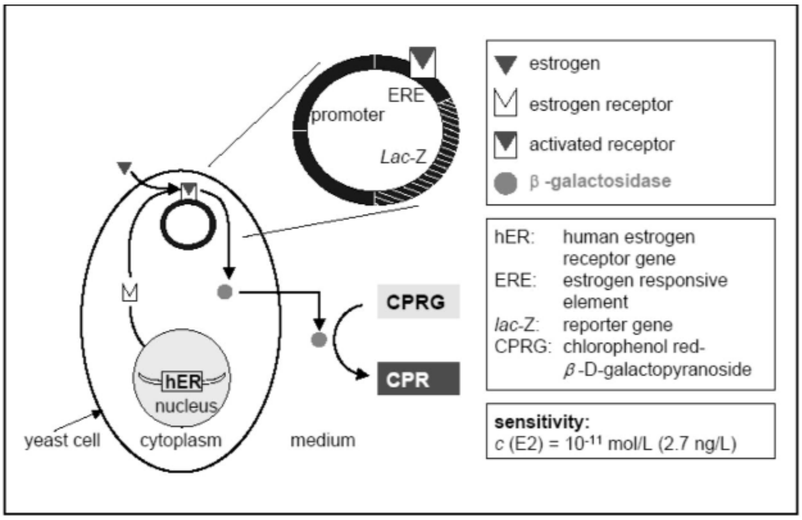


Fig. 3. Yeast estrogen screen (YES) [8].

6.Nano materials everywhere?

With the dawn of the nano age, nano particles have emerged as new environmental issue. In addition to the many known geogenic colloids, there is the new generation of engineered nano particles (ENPs) which after application find their way into the aquatic cycle. Reliable methods to follow distribution, fate and activity of ENPs in aquatic systems including sediments and biota are still missing, but there are promising systems from colloid chemistry with the potential to separate and identify the micro- and nano particles and to characterise their behaviour even in complex aquatic matrices [9]. Fractionation can be done in porous media columns or in flow field flow (F3) systems. The identification of the composition of the particles can be achieved by element specific on-line detection, e. g. using an ICP-MS system (Fig. 4).

The determination of particle size and surface charge will supply additional information for the assessment of ENPs and their behaviour in aquatic systems. It is clear so far that the aspects of analytical sciences will play a major role in understanding the impact of ENPs on the aquatic environment [10].

7.Sustainable water use

Water analysis is clearly a multidisciplinary task. From the many facets some interesting aspects have been highlighted, others, like physical and bio-sensors, online-monitoring or immuno-analysis were not covered. Even though it is obvious that water analysis has to aim for multidimensional quantitative information. That means, physical and chemical data have to be completed by bioeffect information to become meaningful. The holistic approach fits well to the overall aim of sustainability in water management. Water analysis plays a key role in it, for it can supply the necessary impulses for a sustainable design and a proper application of the products, and even for actions to be taken if aquatic systems are endangered.

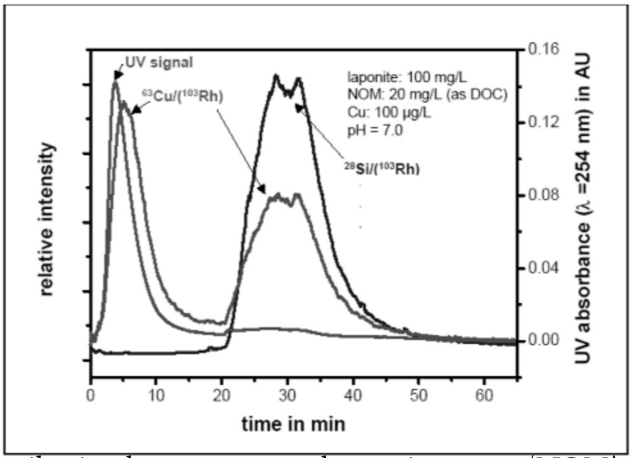


Fig. 4. Copper distribution between natural organic matter (NOM) and the synthetic three-layer clay mineral laponite (AF^4/UV/ICP-MS).

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ANALYTICAL PROBLEMS IN THE DETERMINATION OF DIOXINS AND DIOXIN-LIKE COMPOUNDS ARE STILL ACTUAL

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Polychlorinated dibenzodioxins, dibenzofurans and dioxin-like PCBs are to be found recently in most of the environmental and food samples in the nanogram per kilogram level. While chemical contamination may be a primary cause of food poisoning incidences food safety concerning chemicals is of critical importance. [1].

Sample extraction, enrichment and clean-up procedures have always played an important role in the determination of these toxic substances in picogram level in food and feedingstuff.

Determination of ultra trace concentration of those compounds require extraordinarily samples pre-treatment prior to the instrumental analysis. The sample final extract must be free of most contaminants before it is introduced into the analytical instrument. The matrix complexity of most food samples mean that the sample preparation and pretreatment may be a labour intensive and time consuming procedure. The most problematic is relatively high sample enrichment parallel to a severely interfering compounds removal. Therefore, the analytical procedure is a compromise between effective matrix component removal and high recovery of all investigated compounds [2]. Although dioxin and dl-PCB are chemically and biologically stable, they are prone to photo degradation, especially when dissolved in organic solvents. Therefore samples and sample extracts must be kept cool in the dark. Care has to be exercised to ensure that no one congener is decomposed or lost.

Ultra trace level analyses require special precaution to prevent cross-contamination or even carry-over. This is especially important when handling low and heavy contaminated samples. Contamination from solvents and reagents must be scrupulously avoided. It concerns also materials and equipment screening (e.g. re-used glassware). Adsorbents and drying agents as dehydrated sodium sulphate should be pre-washed and heated in appropriate temperature just before the use.

Extraction and clean-up procedures must be validated to determine their effectiveness. Surrogate compounds as dioxin and PCB ^{13}C and ^{37}Cl labelled analogues should be added to samples before extraction and clean-up to determine recoveries in individual samples and for correction of eventual losses during sample preparation. Concentrated sulphuric acid is the most often used for destroying bulk of interfering compounds in raw sample extracts. Further purification from co-extracted interferences are carried out using different preparative chromatographic separations.

Sample extraction, enrichment and clean-up procedures have always played an important role in the determination of these toxic substances in food and feedingstuff. The matrix complexity of most food samples mean that the sample preparation and pre-treatment may be a labor intensive and time consuming procedure. The sample final extract must be free of most contaminants before it is introduced into the analytical instrument.

The general procedure as follows: moisture removal, sample extraction, sample clean-up, preconcentration and enrichment. Final extract of as low as possible volume is analysed using gas chromatographic separation and selective detection method. Depending on the concentration of natural lipids, triglycerides, unsaturated fatty acids and other organic matrices as well as organic compounds such as food flavours, colorants and stabilising agents introduced in industrial processes this sample pre-treatment may be achieved using many individual preparation techniques such as: Soxhlet Extraction (SE), Supercritical Fluid Extraction (SFE), Microwave Extraction (MWE), Ultrasonic Extraction (USE), Solid Phase Extraction (SPE) and recently the most frequently used Accelerated Solvent Extraction (ASE) [3].

In most of extraction processes extract of heavy contaminated matrix is obtained. The use of semi permeable membranes (SPM) is a method of choice in this case. For lower molecular weight compounds like mycotoxins, dioxins, PAHs and other of relatively high toxicity permeability through the membrane is much higher than for matrix compounds. Therefore, very effective clean-up is available within 24 hours of dialysis through SPM membrane. Low amount of solvents, small laboratory area for single sample clean-up operation and no sophisticated instrumentation to be used make this method competitive to the other ones. Moreover, the recovery of analyte is on satisfactory level of 60 - 110% for most of non polar, chlorinated and brominated aromatic organic compounds of molecular weight up to 800 Daltons.

The appropriate mass of food or feedingstuff sample is freeze dried and extracted with dichloromethane to obtain fat extract. Then, the membrane is filed up with portion of 5g of animal or plant fat. Filled SPM tube is inserted in a large glass tube and hexane is poured into. Dialysis should be performed in light protected place for the minimum of 24 hours but not longer than 48 hours. After the equilibrate of analyte concentration the outer hexane solution is transferred to the measuring cylinder and the final volume is recorded (see figures 1 - 4).

Generally, all dioxin and dl-PCB congeners are recovered in one single chromatographic fraction by an enrichment procedure. The analyte are in most cases diluted in the presence of a large volume of solvent used for extraction and clean-up. Before analysis, if the volume of solvent to be removed is not very large purified sample extract is concentrated to sufficiently small volume (even up-to 10 microlitres) by means of a stream of nitrogen. Care should be taken that the solvent is removed only by evaporation in gently stream of inert gas. If some small solution droplets are lost as aerosol the analyte is losing along with it.

However dioxins are not highly volatile compounds, in ultra trace analysis evaporation to dryness must be absolutely avoided. It may cause sever dioxin loss. Evaporation should stop before the sample reaches dryness. To prevent complete dryness, a small volume of low volatile solvent - so called "keeper" such as dodecane is added before evaporation procedure is an option.

For laboratories which analyse routinely dioxins, PCBs, Pesticides, and PAHs in food samples the use of Power-Prep™ (available from FMS -USA) as a high speed sample processing workstation should be considered. It is designed to automate the extraction and cleanup of those toxic compounds from environmental, biological and food samples. The Power-Prep System uses pre packed disposable columns. Dedicated columns are made from PTFE polymer and contain multi layer silica, alumina and carbon [2].

For quantitative analysis of dioxins and dioxin-like compounds in final extract a gas chromatographic separation and high resolution (GC-HRMS) or double fragmentation ion-trap (GC-MS/MS) mass selective detection is recently applied. Both methods are the utmost selective in the determination of ultra trace dioxin concentration whereas the other organic interferences that are present in considerably higher mass do not interfere.

HRMS technique has been the ultimate detection method since the beginning of dioxin determination in 70s. For PCB congener specific analysis the electron capture detector (ECD) is the most widely used. The detector response depends on the chlorine atom number and position in PCB molecule. However, for the determination of dioxin-like PCB congeners mass spectrometry detector is currently the only technique able to provide extremely low sensitivity and high enough selectivity. Recently, miniaturized pressurized liquid extraction (PLE) with in-cell purification and subsequent gas chromatography with micro-electron capture detection (GC-micro-ECD) have been investigated for PCB congener specific analysis if food and feedingstuff samples [4]. However, the GC and MS combination is the only technique that permits entirely separation and specific determination of all 17 dioxin as well as 12 dl-PCB individual congeners with detection thresholds in the less than 1 nanogram per kilogram range.

The system that can provide double fragmentation of the molecule of analysed compound (GC-MS/MS) can be considered as a compromise between investment and operating costs and demands to reach high selectivity of separation of analytical systems [5].

Fig. 1. Single, new SPM membrane

Fig. 2. Membrane filled with fat extract

Fig. 3. Pouring of a collective solvent

Fig. 4. Sample ready to dialysis

GC-MS/MS system can be regarded as a newer version of quadruple detector or ion trap upgraded for detection of the so-called secondary ions formed in collision with the atoms of helium. The performance of the systems can be compared to the high-resolution, magnetic GC-MS systems if the secondary ions are formed in the optimized conditions. In recent years, the new ideas appeared for mass detectors - GC-MS/MS systems. The basics of their work are similar to that of the ion trap. PCDDs and PCDFs molecules after leaving the chromatography column are directed to the ion source where they undergo ionization with the thermal electrons usually with energy of 70 eV. In these conditions M^+ molecular ion for a PCDD or a PCDF molecule is formed. Moreover, fragmentation ions are formed but the number of them is much smaller. Molecular and fragmentation ions, which were formed, are directed through the so-called ion optic into a ring-shaped electrode (ion trap). Altering potential of this electrode enables to keep the ions in the area around the electrode and further, selective release to dynode of the photoelectric multiplier. However, it is possible to introduce a small amount of helium into it through a special valve.

As a result, molecular (primary) PCDD/F ions are accelerated in the ion optic system and undergo the collision with the atoms of helium. It results the formation of so-called secondary or daughter ions. The secondary ions are formed by splitting out of COCl particle from the molecular ion M^+. In this case the $(M\text{-}COCl)^+$ ion is produced. Computer programs enable detecting either the molecular ions or the secondary ions. This is possible because the signals for the secondary ions are detected only when the molecular ions are present. This is the "sine qua non" condition. Therefore, even if molecules of contaminants other than PCDDs or PCDFs molecules undergo fragmentation and form ions of the same mass (or m/e value), it is very unlikely that they can form the secondary ions of the same mass obtained from the collision fragmentation of PCDD or PCDF molecular ion. This is the reason why the selectivity of this method is very high, which may be compared to high-resolution mass spectrometers. Application of MS/MS method makes possible to obtain high selectivity of analysis and very high level of detection of the analyte as 0,1 pg of 2,3,7,8-TCDD for a single injection of animal fat extract.

The use of bioluminescence methods rely on the production of light by an enzyme-catalysed reaction is a method of choice. DR CALUX® cells have been developed so that they produce light in a dose responsive way when exposed to certain chemicals as dioxins and dl-PCBs [6]. PCDDs, PCDFs, and PCBs share a common mode of action. These compounds bind to an intracellular receptor, known as the aryl hydrocarbon (Ah) receptor. Binding to the Ah receptor is followed by transportation of the PHAH-Ah receptor complex into the nucleus of the cell and subsequent binding to specific sequences in the DNA. The same mode of action applies for other chemicals (BioDetection Systems, The Netherlands). The DR CALUX® bioassay could be a valuable tool for rapid screening of complex pollutants in environmental and biological samples; it could lead to relatively quick and cheap identification of samples likely to exceed specified limits for organic pollutants without the necessity of costly (chemical) analytical methods [7].

Accordingly to the new European Union regulation published in Commission Regulation (EC) No 1881/2006 of 19 December 2006 setting maximum levels for certain contaminants in foodstuffs, dioxins (sum of polychlorinated dibenzo-para-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs), expressed as World Health Organisation (WHO) toxic equivalent using the WHO-toxic equivalency factors (WHO-TEFs)) and sum of dioxins and dioxin-like PCBs (sum of PCDDs, PCDFs and polychlorinated biphenyls (PCBs), are uniformly expressed as WHO toxic equivalent using the WHO-TEFs). WHO-TEFs for human risk assessment based on Van den Berg [8]. Typically analytical result is expressed in pg WHO-PCDD/F-PCB-TEQ/g of fat for dioxins and dl-PCBs. The toxicity of a mixture is stated as TEQ (TCDD equivalents) and is assumed to be equal to the sum of the concentration of individual congeners multiplied by their potencies (TEFi) where:

$TEQ = \Sigma(PCDDi \times TEFi) + \Sigma(PCDFi \times TEFi) + \Sigma(PCBi \times TEFi)$ [2].

Quality control should always be verified by participation in inter-laboratory performance tests. Relevant information on problems related to the determination of dioxins and dl-PCBs is collected in reports from the International Intercalibration tests organized by prof. Bert van Bavel from Intercal AB, Södra Dylta, Dyltabruk in Sweden and by prof. Stefano Raccanelli from Consorzio Interuniversitario Nazionale La Chimica per l'Ambiente, Venezia in Italy.

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IMMUNOANALYSIS IN ENVIRONMENTAL AND FOOD CHEMISTRY

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Modern analytical chemistry is playing an increasingly greater role in the field of environmental and food monitoring. Often critics charge that only a few chemicals are monitored, that the number of samples is inadequate to ensure detection of contamination, and that there is too long a delay between sample collection and communications of results back to the client. Even with the best analytical methods, problems can arise when hundreds or thousands of complicated samples must be handled. Therefore, there are continuous efforts to develop rapid, low-cost, simple and reliable tests that could also be automated or carried out on-site (field-portable assays). Besides others, attention has focused on bioanalytics, especially on the development of immunological techniques. They are generally based on the recognition of an analyte by a specific binding protein - the antibody, which was specifically prepared against this target molecule.

1.The binder

Production of highly specific and affine antibodies against the target analyte is the fundamental work of any immunochemical methods. In the case of low-molecular-weight compounds (Mr<1000), the synthesis of a conjugate of the target analyte and a protein is required to obtain an immunizing antigen. The most widely used carrier proteins are ovalbumin, keyhole limpet hemocyanin, and bovine serum albumin. Methods used for such bioconjugation have been extensively reviewed [1]. For generation of ***polyclonal antibodies (pab)***, essentially any vertebrates can be used. Rabbits are the most commonly used laboratory animals for antiserum production, because they can produce moderate amount of antiserum. However, each polyclonal antiserum will vary in its composition and characteristics from animal to animal. Therefore, availability is limited thus reducing commercial utilization. Despite these shortcomings, the majority of commercially available tests kits for environmental contaminants is based on polyclonals.

For the production of ***monoclonal antibodies (mab)***, spleen cells of immunized mice and murine myeloma cells are used to obtain hybridoma cells. The latter can grow indefinitely in culture and secrete antibodies uniform in terms of structure and function. The potentially unlimited supply over a long period of time of a homogeneous well-characterized antibody reagent especially meets the demands of regulatory authorities for standardized reagents and methods. However, because of the high initial labor and costs needed, laboratories often hesitate to establish the hybridoma technology.

The recombinant DNA technology claims to overcome the disadvantages of hybridoma technology mentioned before [2]. Main advantage is that molecular modeling and site-directed mutagenesis of cloned antibodies (***recombinant antibodies (rab)***), may provide more cost-effective and efficient alternative to the tedious synthesis of haptens and accompanied numerous immunizations. Basic principle is to isolate genes that encode antibodies from an organism and purifying and reproducing them in another organism, e.g. E.coli, insect cells, yeast, and fungi. In addition, plants and crop species, in particular, have the potential to enable extremely cost-efficient production of antibodies (***plantibodies***). The technique is an exciting new possibility of more efficient manipulation of antibody binding sites to give desirable binding affinity, specificity, tolerance to physical parameters, and sensitivity to matrix constituents such as organic solvents.

Aptamers are artificial nucleic acid ligands, specifically generated against a target molecule [3]. They started as therapeutic agents and became interesting molecular tools for analytical applications as well. They are isolated from combinatorial libraries of synthetic nucleic acid by a systematic evolution of ligands by exponential enrichment (SELEX). So far, practically all analytical applications have been reported for clinical applications. Broadening into areas of food control and environmental monitoring, though being logical, has to be demonstrated yet.

Molecularly imprinted polymers (***MIPs***) also termed artificial antibodies, combine the stability, low cost and synthetic efficiency of synthetic polymers with the ability to tailor recognition properties of biological recognition systems. Preparation remains a disputed technique for the synthesis of high-affinity and selective synthetic antibody mimics for sensitive assays. A current effort is the exploration of different polymerization techniques to produce MIPs in any desired format, from bulk materials to nanospheres of highly defined shape and narrow size range (Fig. 1). Notwithstanding their proven usefulness for selective solid-phase extraction (SPE), a breakthrough as substitutes for natural antibodies in pseudoimmunoassays at relevant concentrations cannot be envisaged at this stage of development [4].

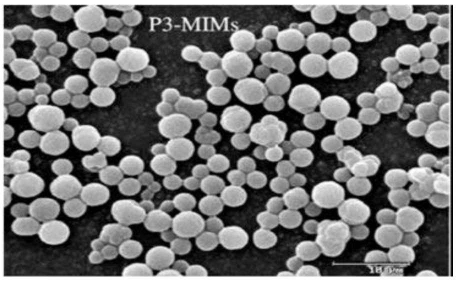

Fig.1. Scanning electronic microscopy (SEM) images of MIP polymer P3 (template = diethylhexylphthalate) synthesized by precipitation polymerizationin a round-bottom flask (dispersive solvent acetonitrile, crosslinker EDMA). Reprinted from [5] with kind permission of Springer Science +Business Media.

2.Assay formats

Immunoassays can be classified in several directions, (a) type of tracer used to quantify the target analyte (e.g. radioimmunoassay, enzyme immunoassay, fluorescence immunoassay, luminescence immunoassay), (b) applied amount of antibodies (antibody excess or analyte excess), and (c) separation of bound and free phases is required or not (heterogenous and homogeneous assays). Heterogeneous enzyme immunoassays involving the use of a solid phase, e.g. microtiter plates, tubes, or beads, for separation of bound and free analyte before enzymatic activity is determined are known as ***enzyme-linked immunosorbent assays (ELISA)***. They can be run as competitive or non-competitive formats. Both have been proven to work with environmental and food samples. Currently, ELISAs performed in a microtiter plate or test tubes are the most common techniques used for immunoassays. ELISA test kits are favored as high throughput assays with low sample volume requirements and often less sample clean-up procedures compared to conventional methods. They are rapid and simple to perform and portable for use in the field. However, with the demand for even shorter analysis time and user-friendly field-assays, other formats are being explored e.g. membrane based immunoassay such as ***flow-through assays*** and ***lateral flow tests*** (also called test strip or immunochromatographic test) and ***clean-up gel-based assay columns***. These methods do not require any special equipment and most any individual can perform the assay. A typical immunological test strip is composed of a sample pad, a conjugate pad (contains a mixture of the analyte-antibody gold particle complex and the anti-secondary antibody gold particle complex), a membrane, an absorbent pad and an adhesive backing (Fig. 2). On the test and control lines the analyte-protein conjugate and the second antibody are immobilized, respectively.

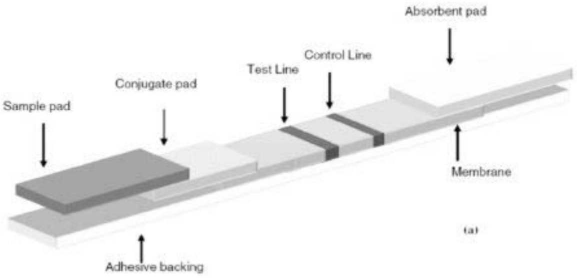

Fig.2. Usual configuration of a lateral flow test. Reprinted from [6], with kind permission of Springer Science+Business Media.

However, in environmental and food chemical analysis the technology can only provide semi-quantitative results, generally. The interpretation of results may be difficult when the analyte concentration of the sample is close to the method cut-off level.

The limited multianalyte capability of immunoassays is a major disadvantage compared with separative techniques. To compete, two main strategies are available for multiplex assays - ***microarray technology (immuno biochips)*** and ***encoded microsphere assays (bead-based microfluidic immunoassays*** [7]. Microarrays are a logical presentation of biomolecules laid out on a solid planar platform, generally a glass slide. The resulting presentation is referred to as an array or as a chip. In this format, individual molecules are separated from one another, allowing the user to interrogate each molecule independently but simultaneously. The scope of microarrays has expanded impressively in recent years. As a rapidly maturing technology, microarrays pave the way for high-throughput analysis. However, they are not only miniaturising microtiter plate to the size of a microscopic slide. They also show a new functionality due to the integration of a part or the entire detection system. This allows, on the one hand lowering of the operation times of the different test steps and on the other hand a real integration in a complete system incorporating particularly microfluidic parts. Complete systems integrate sample transportation and preparation, incubation and washing steps, and detection. Several companies are working to bring antibody chips to market. To date, the majority, as a research tool, is focused on proteome analysis. Only a few investigations are known which address the determination of small molecules in environmental and food samples. Bead-based microfluidic immunoassays employ microbeads as a solid support. There are a variety of surface modifications available on the beads, which will introduce multiple functionalities to a single microfluidic design. By encoding and creating a set of microcarriers for each analyte, the reactions can be tracked by decoding and identifying individual microcarriers. Therefore, multi-analyte analysis can be performed simultaneously in a single assay. In the interest of bead-based microfluidics, optical encoding using fluorescent dyes and quantum dots attached to microbeads used in flow cytometry appear the most suitable choice as solid supports. The extent of multiplexing is limited by the number of unique codes.

3.Detection principles

In enzyme immunoassays, the immunochemical reaction is visualized with enzyme labels such as horseradish peroxidase and alkaline phosphatase, providing a colored end product (colorimetric detection). Other important labels are fluorescence and chemiluminescence (Fig. 3). Artificial particulate marker systems, both organic and inorganic, are of increasing interest for improvement of the performance of immunoassays, e.g. reducing detection limits and signal amplification by several orders of magnitude. The underlying detection procedure is usually based on optical techniques, for example surface-enhanced Raman scattering (SERS), time-resolved luminescence (TRL), and back-scattering interferometry (BSI). Among the optical label-free assay platforms, surface plasmon resonance (SPR) has a prominent place. Especially the Biocore instruments have demonstrated the sensitivity required for environmental and food related analysis. Other label-free non-optical platforms such as differential calorimetry, electrical impedance, microcantilevers, and acoustic resonance are emerging [8].

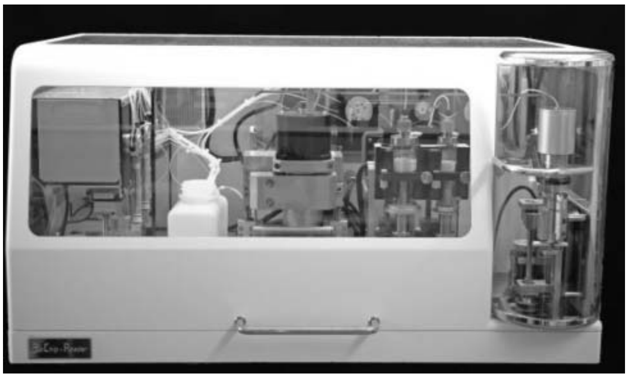

Fig. 3. In-house built microarray readout platform based on chemiluminescence.

4.Target analytes

To date, immunoassays for chemical contaminants were mainly developed for screening of aquatic and soil contamination but also for food and crop analysis. The vast majority of these methods was applied for ***pesticides*** including herbicides, insecticides and fungicides that are generally hydrophilic, non-volatile and stable in water. Approximately fifty poly- and monoclonal test kits either in plate or tube format are commercially available. Within the last years a number of investigations have been reported which clearly demonstrate the widespread occurance of ***pharmaceuticals and personal care products*** in the environment, notably in the aquatic compartment at ng/l to μg/l concentrations. Current knowledge about long-term effects of low-level exposure to such compounds is limited, and chronic effects may not become apparent for many years. In a wider sense, potentially serious environmental effects are often neglected, e.g. impacts on non-target species are practically unknown. Further, because of the potential of a wide range of xenobiotic chemicals (***endocrine disrupting chemicals - EDCs***) to interact and disrupt the endocrine systems of animals and humans, the presence of microcontaminants is of increasing public concern. Whereas a larger number of immunoassays have now been developed and used for the analysis of pesticides which are found at similar levels in aquatic systems, surprisingly, very few tests have been applied to pharmaceutical compounds this far. Only a few groups have shown the feasibility of adapting clinical assays to the analysis of water samples for the presence of pharmaceuticals, and these have tended to focus on hormones, antibiotics, and anticancer drugs. Recently, a highly sensitive and specific ELISA for the nonsteroidal anti-inflammatory drug *diclofenac* was developed and successfully used for its determination in influent and effluent wastewater samples [9]. ***Biotoxins (biological warfare agents)*** such as ricin and staphylococcal enterotoxin B (SEB), are perceived to be a new emerging threat to humans [10]. The possibility of bioterrorism has become more credible after the 9/11 attack in U.S. Properties of biotoxins such as its ease of low cost production, its high lethality and capability to incapacitate population, its ease of dissemination and its good stability after dissemination make them dangerous biological weapons. Thus, the development of rapid detection and quantification methods is urgently required.

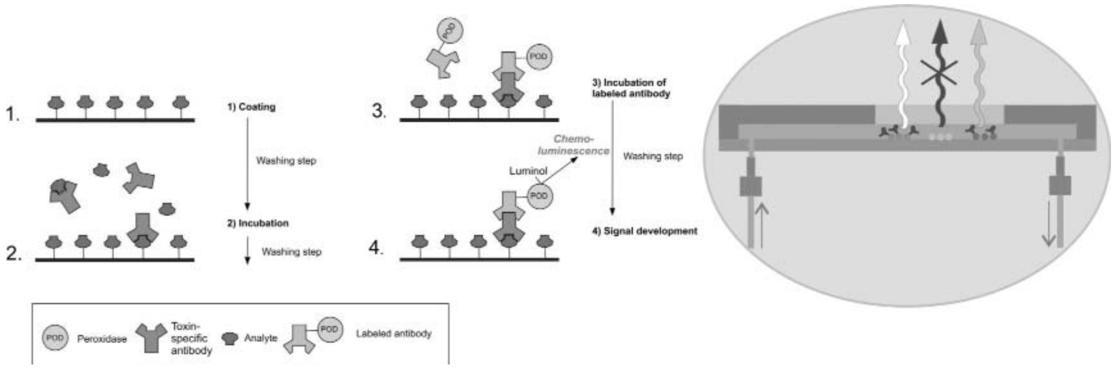

Fig. 4. Competitive flow-through immunoassay for the determination of aflatoxins. The luminescence signals are measured with an in-house developed chemoluminescence readout system (see Fig. 3).

Of the thousands of existing ***mycotoxins***, a few hundred are associated with food and only a handful present in food such as aflatoxins, trichothecenes, fumonisines, zearalenon, ochratoxin, and patulin, produce a wide range of adverse and toxic effects in animals in addition to foodborne hazards to humans. Conventional analytical methods employ solid phase column cleanup of extracts and immunoaffinity techniques to remove interferences to improve the determination of mycotoxins. These analytical methods applied to food or feed samples yield results within hours or days. Competition within food and feed industry forces them to reduce cost, employ cheaper labor and deliver costs rapidly. Thus rapid methods for mycotoxin analysis have become increasingly important. The miniaturization and mass production of microarrays will certainly contribute to practical application of these analytical devices as screening tools (Fig. 4). ***Authenticity testing of food products***, is important for labeling and assessment of value [11]. It is necessary to avoid unfair competition and assure consumers protection against fraudulent practices commonly observed in the food industry. To give some examples for the use of ELISA techniques, (1) meat, fish and milk species discrimination, (2) fruit juice labeling authenticitation, (3) genetically modified and irradiated food detection, (4) feedstuffs origin, and (5) allergen ingredients identification.

Finally, there is an increasing need in environmental and food analysis for clean-up methods that will result in more selective extraction of the analytes of interest, if possible, in a single step. ***Immunoaffinity chromatography (IAC, immunoaffinity extraction)*** which makes use of antibodies immobilized on solid supports such as silica or polymeric adsorbents is of increasing interest [12]. The sorbents are used in a manner similar to SPE cartridges. Several cartridges are commercially available, for example for the isolation of food nutrients, pesticides, EDCs, steroid hormones, and mycotoxins. In addition, immuno-extraction can be coupled directly with a chromatographic method thus giving rise to a hyphenated technique such as immunoaffinity/reversed-phase liquid chromatography (IA-RPLC).

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SOLID PHASE EXTRACTION SAMPLE PROCESSING FOR AAS DETECTION

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Atomic absorption spectrometry (AAS), despite its single-element capabilities, is a powerful tool to monitor many elements in different kind of samples. Whenever possible, the flame AAS serves as a common routine technique in thousands of analytical laboratories, owing to its large elemental coverage, remarkable selectivity, good precision and simple operations. When lower detection limit is required electrothermal AAS is the technique of choice. The samples with complex matrices very often cannot be directly processed as they pose severe matrix interferences, which often cannot be minimized even by existing efficient background correction devices. These difficulties may be sometimes overcome to various degrees by applying a powerful background correction. However, ETAAS cannot tolerate high contents of salt components and is sensitive to variation in matrix composition. FAAS is less sensitive for the matrix effects but offers lower detection limits.

The most effective way to avoid these problems is to perform appropriate sample pretreatment, which is aimed for analyte preconcentration and its separation from the matrix components. Additionally, applying appropriate sample pretreatment speciation analysis could be conducted for determination of specific oxidation states of species as well as inorganic and organic forms of elements. Successful matrix removal combined with an enrichment step of the analytes can be achieved by several techniques including solvent and solid phase extraction techniques, coprecipitation, generation of volatile compounds or dialysis. Among them solid phase extraction (SPE), also called sorbent extraction, with packed columns or knotted reactors proved to be particularly effective technique. The broad range of choice for sorbent materials along with various chelating reagents and eluents make this technique very attractive for sample pretreatment.

The separation/preconcentration procedures based on the sorption principles could be executed in off-line or on-line mode. On-line procedures could be performed in flow injection (FI) or sequential injection (SI) systems where all unit operations are executed with high reproducibility and where risks of sample contamination are minimised [1,2]. In addition to separation and preconcentration processes, on-line sample digestion using flow systems has been attracting considerable interest for some time as it is often the most rate-limiting factor of the method. Recently introduced the third generation of flow techniques, sequential injection lab-on-valve (SI-LOV), has specific advantages and allows novel application in micro-miniaturization of on-line sample pretreatment [3].

The sample loading mode in sorbent extraction is an important feature of a flow system. For pure separation purposes, as in the case of interference removal where sensitivity is not of much concern, usually injection of a defined sample volume from a sample loop will be the method of choice, both due to simplicity and reliability (Fig. 1A). In FI/SI preconcentration system, the sample volume processed directly affects the achievable enrichment factor, thus, time-based loading is preferred (Fig. 1B). In this system amount of sample processed is determined by the sampling flow rate and sampling time. For both systems, the loading flow rate is usually the main factor which determines the sample throughput. However, it should be taken into consideration that the maximum loading flow rates are limited by kinetic features of the retention system.

Column packings with adequate chemical and physical stability, fast kinetics in sorption of the analyte and its release with a suitable eluent, are very important for achieving optimal performance in flow system [4]. A number of different sorbents have been investigated and applied.

They include:

- common ion exchangers,
- chelating resins with selective functional groups covalently attached to copolymer matrices ,
- sorbents modified with chelating ligands (by ion exchange mechanism, ion-pairing or physical adsorption),
- activated alumina,
- natural and synthetic zeolites,
- carbon sorbents (activated carbon, fullerenes and carbon nanotubes),

as well as reversed-phase materials such as chemically modified silica or non-ionic polymeric sorbents. The species of interest are retained by portioning, hydrophobic or π-π stacking. These packing are applied mainly for sorption of neutral hydrophobic metal complexes, which are formed previously in a solution [5].

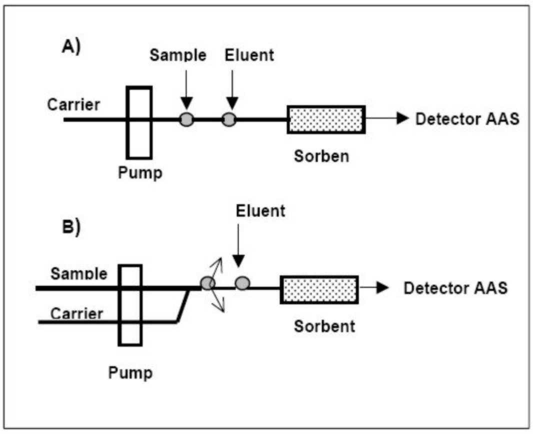

Fig. 1. Flow injection manifolds with column sorption; (A) volume-based system, (B) time-based system.

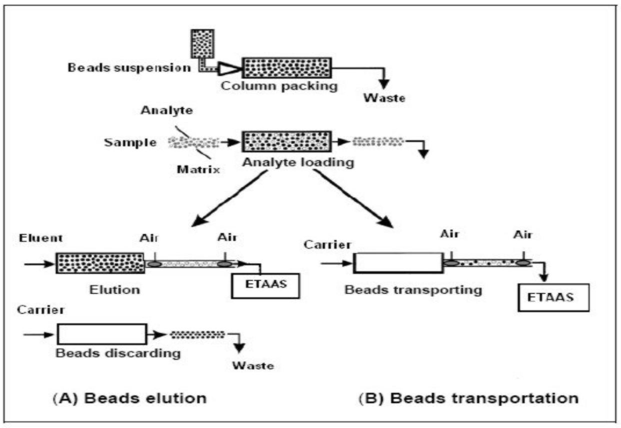

Fig. 2. Illustration of two possible schemes for dealing with analyte-loading sorbents in bead injection principles [6]. (A) The analyte from the loaded beads is eluted and determined by ETAAS. (B) The analyte-loaded beads are transported directly into the graphite furnace of ETAAS detector.

In conventional FI/SI on-line preconcentration systems, the column is used as a permanent component. However, their long-term applicability is often hindered by the progressively tighter packing of the column material, which might result even in drastic increase of flow resistance. The properties of surface sorbent might be also irreversibly changed after having been subjected to a large number of samples, either due to contaminants, deactivation or even loss of its functional groups. Such problems can be solved if the packing material of microcolumn is renewed for each measuring cycle relies on bead injection principle [3]. Using bead injection principle, two approaches are possible with ETAAS detection, which are schematically presented in Fig. 2 [6]. In the first one (Fig. 1A), the column is packed with beads of sorbent, analyte loaded and then eluted. After the eluate is transported to the detector for determination, the beads are discarded and the new ones are packed for the next loading cycle. In the second approach, instead of eluting the retained analyte from the microcolumn, loaded beads together with the analyte are transported with a carrier solution directly into the graphite tube, where they are pyrolized and the analyte is atomized and quantified (Fig. 2B). It should be noted, that this procedure could not be applied for determination of metals with low atomization temperature such as Cd, Pb, Bi, because pyrolysis of organic matrix temperature above 1000°C is required. Both approaches yield satisfactory results; limits of detection and enrichment factors being of the same order of magnitude. Although, the precision for beads elution is better.

As it was mentioned earlier solid phase extraction technique is very useful in speciation analysis for examples chromium speciation - it means determination of Cr(III) and Cr(VI). In the simple manifold without preconcentration and separation of these two chromium species - Cr(VI) could be determinated after complexation with diphenylcarbazide by spectrophotometric detection at 545 nm and then total chromium content by AAS. Using SPE, two different approaches could be distinguish. In the first one, Cr(III) or Cr(VI) is selectively sorbed on a microcolumn packed with a given sorbent and after elution is determined. Then after reduction or oxidation reaction, the total content of Cr is measured. Concentration of second chromium species is obtained by the difference. In the second concept for chromium speciation, each of species is retained separately on the sorbent with different functional groups; Cr(III) is sorbed on cation exchanger, while selective retention of Cr(VI) could be achieved on an anion-exchanger [7]. Sequential elution provides two signals of these species from continuously aspirated sample.

Another example is speciation analysis of vanadium, presented schematically in Fig. 3 [8,9]. In the presence of cyclohexane-1,2-diaminetetraacetic acid (CDTA) no retention of V(IV) on the cationic cellulose sorbent Cellex P was observed, as vanadyl ions form negative charged chelate with this complexing agent. Under these conditions vanadium(V) ions are quantitatively sorbed (Procedure A). However, it does not allow to enrich V(IV) as well as to separate it from the matrix components. In the procedure B, both vanadium species are enriched on the micocolumn (in the absence of CDTA) and then selectively eluted.

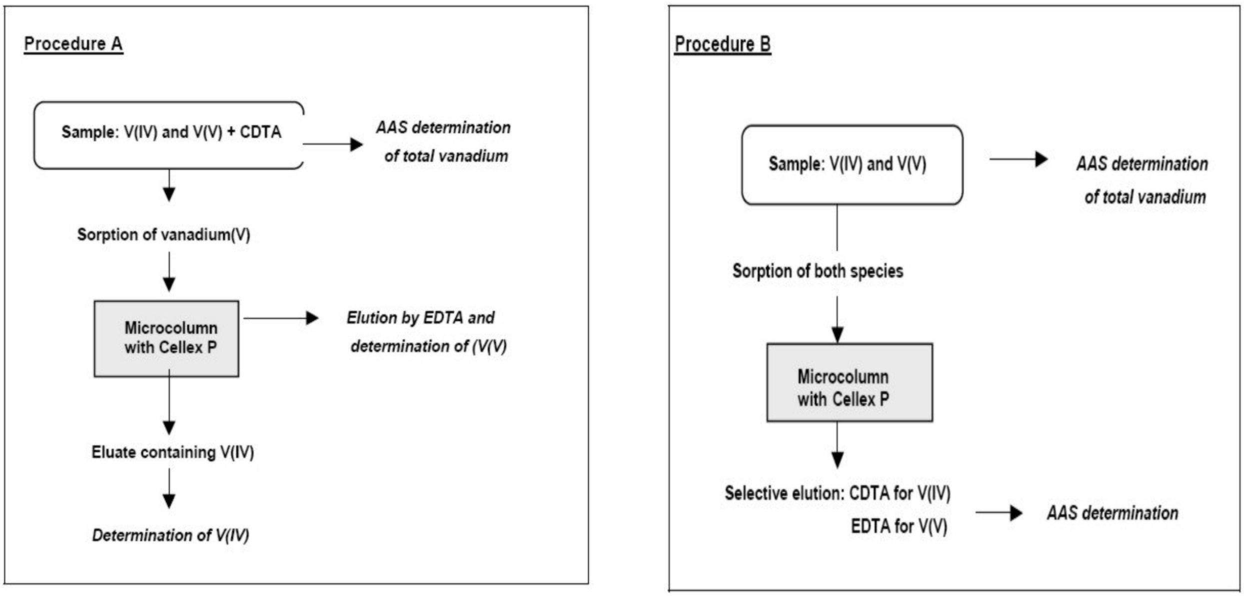

Fig. 3. Procedures for speciation analysis of vanadium

The column sorption approach could be also employed for field sampling technique [10], where water samples are processed in flow systems at the sampling site and trace elements of interest are retained on a packing material. The microcolumns may then be returned to the laboratory and directly inserted into a FI/SI system for on-line elution and quantitative analysis. In addition to flow methodology, this technique achieves improvement in collection, transportation and storage of the samples as the conventional sample preservation methods could be omitted. Sequences of columns packed with different sorbents have been used for fractionation of cadmium in natural occurring waters [11]. The systems with two or three columns, containing common ion exchanger, chemically bonded silica gel and a chelating resin enabled the evaluation of fractions of the labile metal species, organic fraction and strong complexes.

The presented examples have demonstrated high potential for appropriate sample processing using solid phase extraction. This method improve significantly sensitivity and selectivity of AAS measurements. Its application in flow systems gives high reproducibility and minimal risk of sample contamination.

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X-RAY SPECTROMETRY FOR PREVENTIVE CONSERVATION OF CULTURAL HERITAGE

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Analytical chemistry plays a key role in cultural heritage (CH) research, to study the techniques and methodologies the artists used, to identify forgeries and find the provenance of cultural heritage items, and to prepare for optimal restorations. It appears that X-ray spectrometry (XRS), in its many forms, including X-ray fluorescence (XRF) analysis and electron probe X-ray microanalysis (EPXMA), is one of the most relevant analysis techniques, in view of its non-destructive nature. Preventive conservation refers e.g. to studying the environment around works of art, with the intention to improve the environmental conditions and preserve the CH items better. Again, XRS appears to be important here since it allows to analyze optimally atmospheric aerosols, which are nowadays the main culprits for CH degradation, e.g. in indoor museum environments.

We have recently carried out studies in various museums and churches throughout Europe, Japan and the USA, to examine the effects of indoor and outdoor air pollution, mostly based on XRS. In each case, bulk aerosols and individual aerosol particles were studied, using i.a. XRF and EPXMA. For microanalysis of single particles, we have investigated a dozen techniques in the past two decades, but for wide, real-life applications, automated EPXMA has been the most rewarding (of all the techniques we tried out, we are, in practice, now still using micro-Raman spectrometry in addition to EPXMA, and no other ones). Different options for handling the large amounts of data generated by EPXMA, and for automated classification of particle types, have been examined. Recent methodological work includes the elemental speciation and low-Z element analysis using Monte Carlo quantification for thin-window Si(Li) detectors, analyses at liquid-nitrogen temperatures to avoid problems of volatility and damaging of sensitive particles, and specific surface layer analyses, all for micrometer size particles. Also gaseous pollutants (including sulphur dioxide, nitrogen oxides, ozone, benzene, toluene, ethylbenzene and xylenes) were analyzed by using passive gas diffusion monitors, and ionic aerosol compounds were also assessed by ion chromatography.

Using these technologies, we have, over the last decade, studied atmospheric aerosols in and around e.g. the Correr Museum in Venice, the Art History Museum in Vienna, the Royal Museum of Fine Arts in Antwerp, the Sainsbury Centre for Visual Arts in Norwich, the Metropolitan Museum of Arts in New York, the Wawel Castle in Cracow, and many other museums in Belgium. E.g. in the Correr Museum, it appeared that the particles, that were most threatening for the Bellini paintings in their specific rooms of the museum, were released by the deterioration of the plaster renderings in these rooms, and could in principle be avoided easily by painting the museum walls with a plastifying paint. In the Metropolitan Museum in New York, we found sodium nitrate particles (probably from the reaction of natural sea spray with nitrogen oxides from traffic) to be enhanced in some of the rooms and in some of the show cases, in e.g. the Egyptian wing; better filtration could remedy this. In the Wawel Castle, outdoor pollution particles, and especially soot particles (from diesel car exhaust) and salt road de-icing particles, were found to easily enter the museum, through leaks around the windows or in winter via the shoes of visitors, respectively.

Another study concerned the possible accumulation of air pollutants in the interspace between the original medieval stained glass windows and the recently installed protective glazings, in majestic cathedrals and churches in Cologne, Paris and Troyes. Because of the strong natural drafts in the interspace, no worrisome increase in the particle concentrations in the interspace air was noted. However, NO from candle burning proved to be a problem within the churches.

Also, the above-mentioned methodologies were applied to study the effects of different heating systems in a small church in the Italian Dolomites and in a wooden church in the Southeastern region of Poland; both contain valuable CH items and are in a climate where in winter strong temperature differences exist between moments with and without religious services, inducing strong physical expansion/shrinking stresses on the works of arts, in addition to chemical effects. In the former case, it was found e.g. that the combustion heating system introduced high NO levels and generated a strong air current, circulating and resuspending outdoor, candle soot and incense particles; together with the resulting strong physical expansion and dehydration phenomena; this was dramatically harmful for the 14th century wooden altar in the church. Installing a novel and especially designed electrical heating system in the pews proved to be beneficial for the CH items in this church.

In each case, XRS proved to be most useful to find the origin of the harmful particles, and hence to propose solutions in the realm of preventive conservation.

ORAL PRESENTATIONS

SIMULTANEOUS DETERMINATION OF URIC ACID AND DOPAMINE IN URINE SAMPLES USING DERIVATIVE SPECTROSCOPY

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In derivative spectroscopy, the derivative of a spectrum is used both for qualitative and quantitative evaluation. Many of the major applications of derivative spectroscopy in the ultraviolet and visible spectral region serve to qualitatively identify and analyze samples.

Uric acid (UA) is the waste product produced from the degradation of purines. In healthy human, uric acid is filtered and removed from the blood by the kidneys and excreted into urine. Because a number of kidney diseases are known to affect uric acid levels, uric acid determination is thus important and useful in diagnosing and evaluating kidney diseases. Dopamine is the most typical neurotransmitters which mainly exist in brain tissue and fluids, the change of dopamine concentration can cause some disease as Parkinson, uric acid is a main final product of purine [1]. Metabolic alteration, disease appearance or as control during the use of chemotherapeutic drugs, so the accurate determination of dopamine and uric acid is of great importance. Therefore, in the present work attempts were made for simultaneous determination of dopamine and uric acid in urine samples using derivative spectroscopy.

The present study involves individual and simultaneous determination of uric acid and dopamine using first and second derivative spectroophotomtery. Uric acid was measured at 302nm and 309nm individually while, dopamine was determined at 271nm, 239.5 and 294nm. Uric acid determined in the presence of dopamine at 250.2nm, 281.6 and 233nm using zero crossing technique. In other hand uric acid was determined at 235nm and 280nm in the presence of uric acid using first and second derivative spectroscopy. Good linearity, accuracy, precision and selectivity were found. The method is proposed for determination of uric acid in urine and dopamine in synthetic urine sample, and also determination of dopamine-hydrochloride in injections. High recoveries were obtained in the applications of the proposed method.

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BATCH AND FLOW INJECTION SPECTROPHOTOMETRIC DETERMINATION OF HISTAMINE IN FISH MEAT PRODUCTS USING P-NITROANILINE REAGENT

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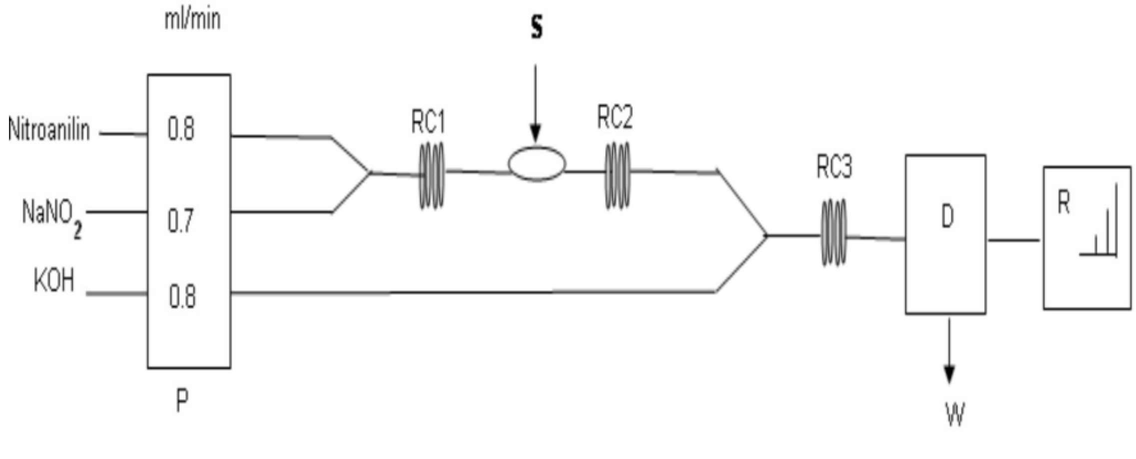
Biogenic amines are present in a variety of foods and have been widely documented as occurring in fish and fish products, meat, wine, cheese and fermented foods. Histamine, which is the most important biogenic amine, can cause poisoning as a result of the ingestion of food containing high levels of this amine, has also gained increased importance in medicine and pharmacology. Histamine is mainly found in food which was subject to microbiological and biochemical deterioration due to processing, ripening or storage [1]. The determination of histamine in fish meal samples is proposed. The analytical procedure is based on the formation of azo dye (λmax 473 nm) as a result of diazotization of p- nitroaniline and coupling with histamine in alkaline medium. A flow injection system was used for the determination of histamine with linear calibration curve over the range 0.5 - 22.0μg/ml and detection limits 0.30μg/ml. The sample frequency was 60 samples/h. The effect of common amino acids and some ions on the determination of histamine was examined. A synthetic sample of histamine (10μg/ml) and the interfering substance was injected to the carrier stream and the analytical signals were compared with that of histamine solution alone. The recommended FI procedure was successfully applied to the quantization of histamine in 5 commercial fish meals after appropriate sample treatment. The histamine contents in fish meal samples were found to be around 6.0 mg/100g of fish samples. In order to evaluate the proposed FI method, the results were compared with a standard method.



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FINGERPRINTING OF BILGE OIL SPILLS: A DIFFICULT CASE STUDY

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Bilge oils are mixtures of petroleum products used in vessels that are accumulated in the bottom of the ships, mixed with water. As the discharge of these oily wastes in water is prohibited, they should be collected in separator tanks from where oils can be off-loaded at the dock or burned on board, after their isolation. Despite these regulations and precautions, accidental or intentional discharges, unfortunately, occur.

Chemical fingerprinting of these oils is particularly difficult because their composition, reflecting the range of products used in a given vessel, namely middle and heavy fuel oils, as well as lubricating oils, is expected to be highly variable. Difficulties are more important when the spills occur in commercial/fishing harbours, where the potential sources are numerous. Moreover, sampling is sometimes cumbersome both on board and at sea, because in bilge tanks there may be an inhomogeneous distribution of the oil mixture even within the same tank, and the spills usually appear as thin and non uniform layers in the seawater surface. The presentation will discuss the approach to be followed in these cases, exemplified with the study of a spill occurred in a fishing harbour, where four potential transgressors were identified.

After ensuring a representative sampling, oil spill identification by GC-MS should first identify different regions of the TIC, revealing the boiling ranges of the products involved. Mixtures of light fuel oils and lubricating oils are normally easily detected because of the different boiling ranges of the two products, but heavy fuel oils (HFOs) and lubricating oils normally overlap completely in the higher-boiling region, and the detection is more difficult.

Specific distributions of hydrocarbon families and biomarkers within each type of bilge oil components should be used to characterize these oily discharges. Besides the classical n-alkanes/isoprenoid ratios, the ratios of alkyl-cyclohexanes and benzenes as well as individual C1-C4 alkyl-phenanthrenes and dibenzothiophenes, have been found adequate for the characterization of the middle fractions, whereas the aromatic steranes, not present in lubricating oils, have been found particularly useful for HFOs. These profiles are then considered for the correct interpretation of the sterane and triterpane biomarker distributions, present in both HFOs and lubricating oils.

MERCURY SPECIATION IN THE ENVIRONMENT: DETERMINATION AND MODELLING

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Mercury concentrations have increased in the world as result of industrial activities. It has been published that mercury emissions are mostly due to coal burning power stations, chlor-alkali facilities, mining and other industrial processes.

Mercury is present in the environment in different molecular forms with specific biogeochemical transformation and ecotoxicity. Inorganic Hg^{2+} is the main form in water and sediment samples. Special attention is given to transformations which lead to the *in situ* production of methylmercury. Concentration levels of organomercury species is very low (usually ng L^{-1}) in environmental aquatic environments but the toxic effect of these compounds can be significant due to their tendency for bioaccumulation and biomagnification in the food chain.

The determination of the total concentration of mercury is not sufficient to understand its fate in the environment. The development of a sensitive, reliable, simple, and cost effective procedure for speciation analysis of mercury in different environmental compartments is currently one of the principal research challenges in environmental analytical chemistry.

The objectives of presented study were to develop and optimise analytical procedures for mercury speciation analysis and they applications for analysis of water, sediment profiles, soils, plants, fish and human hair in the regions affected by environmental pollution due to reprocessing of old gold tailings damps and chlor-alkali factory. The study included collection of ancillary data (pH, redox potential) which are critically important for mercury monitoring program. The development of predictive models based on thermodynamic solution equilibria including mercury transformations, transport, fate and biological uptake are presented.

MULTIVARIATE EXPLORATION IN ASSESSMENT OF SPRING WATER CHEMISTRY IN SANCTUARY FOREST AREA

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The study was carried out over a period of 2004 year at the Zimnik and Czyrna catchments located in Silesian Beskid Mts. Region (southern Poland) by analysis of chemical composition of spring water samples. The multivariate exploration took into consideration type of spring outflow, geological conditions of the spring's surrounding area and different water' level related to seasonal variations in particular catchment ecosystem (high stage: beginning of the vegetation period; medium stage: vegetation period; low stage: final stage of vegetation period). The complex data matrix (more than 870 observations) consisting conductivity, water reaction, major anions (Cl^-, NO_3^-, SO_4^{2-}) and cations (NH_4^+, Na^+, K^+, Ca^{2+}, Mg^{2+}) determined by ion chromatography were treated by linear discriminant analysis, intelligent classification techniques and non-parametrical statistical testing. In case of both catchments obtained results indicate presence of two discriminant functions (DFs). The data variance explained by DFs is as follows: Zimnik - 1st DF: 73.6%, 2nd DF: 26.4%; Czyrna - 1st DF: 92.3%, 2nd DF: 7.7%. Springs located at Zimnik catchment can be distinguished according to low and medium/high water stage basing on 1st DF, which was mainly related to geological conditions (content of Cl^-, Na^+, NO_3^-, Ca^{2+} and electrolytic conductivity). The 2nd DF was related to NH_4^+, Mg^{2+}, SO_4^{2-}, K^+ and pH. In the contrary, springs located at Czyrna catchment can be distinguished according to high and low/medium water stage basing on 1st DF, which was mainly related to nutrient biocycle in the investigated ecosystem. The 2nd DF was related to electrolytic conductivity, pH, Cl^-, Ca^{2+}, Na^+, Mg^{2+} and NO_3^-.

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APPLICATION OF ATR-FTIR SPECTROMETERY AND CHEMOMETRICS FOR DETERMINATION OF MALATHION IN PESTICIDES

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Malathion is an organophosphate (OP) insecticide, which was introduced in 1950 by American Cyanamid Company as a new generation. It has a wide range of applications, e.g. in vegetable producing crofts, farms and fly dopes [1,2]. Some methods for determination of Malathion in pesticides have been published in Collaborative International Pesticide Analytical Council (CIPAC) reference book, e.g. gas chromatography with flame ionization detection (GC-FID) [3] or photometric determination procedure at 420 nm. Other procedures which have been proposed for Malathion quantification in pesticide are based on using GC with mass spectrometry as the detector [4], screen-printed enzyme electrodes [5], photometric determination with molybdenum at 825 nm [6] and indirect determination by atomic absorption spectrometry [7]. One of the most important drawbacks of foresaid methods is the use of solvent in most of them which is environmentally concerning. A simple and environment friendly method was developed for determination of Malathion content of analytical and commercial insecticide samples with no special preparation. Attenuated total reflectance-Fourier transform infrared (ATR-FTIR) spectra were characterized and 1000-2000 cm^{-1} region was selected for quantitative analysis utilizing partial least square (PLS) [8] and two wavelength selection methods: (a) principal component regression (PCR) [9] and (b) genetic algorithm (GA) [10]. Relative error of prediction (REP) was calculated in PLS, PCR-PLS and GA-PLS methods and was 3.536, 1.656 and 0.188, respectively. Proposed method is successfully applicable for quantification of Malathion in commercial grade samples and reliable results in comparison with known methods, confirms this idea.

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AN ANALYSIS OF LONG-DISTANCE ROOT-TO-LEAF TRANSPORT OF LEAD IN PEA PLANTS (PISUM SATIVUM) BY LASER ABLATION-ICP-MS

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Research on the ecosystem has indicated a strong link between plant tissue chemistry and soil chemistry. The concentration of elements in plants may be applied to monitor changes in environmental quality. Plants can take up and accumulate significant amounts of Pb without any visible changes in their habit or yield. Due to their ability to accumulate lead in tissues, plants can be used in the process of soil remediation and rhizofiltration. Phytoextraction is the most effective method for removing heavy metals from the soil. Initially, research on using plants in phytoextraction focused on plants which can grow in an extremely polluted environments and accumulate large amounts of metal in their leaves and shoots [1]. The strategies of lead tolerance in plants are poorly understood. Plants have a number of various mechanisms which protect them against the toxic effect of heavy metals, among which we can include the active translocation of metals, synthesis of peptides the ability to bind metal ions, e.g. metallothioneines or phytochelatins, storage of metals in the vacuole and many other adaptations [2]. A variety of instrumental techniques such as atomic absorption spectrometry with flame (FAAS), inductively coupled plasma with optical emission spectrometry (ICP-OES) or inductively coupled plasma mass spectrometry (ICP-MS) have been applied to determine total lead (and other elements) concentration in plant tissue. In most cases the samples are dried and dissolved. An alternative to these methods is laser ablation (LA) linked with ICP-OES or ICP-MS. A major application for LA-ICP-MS is as a tool for the determination of element distribution in solid samples 3].This technique is a useful tool for obtaining the information stored in the element concentration of plant material. This method which can enhance the possibility of improving our knowledge of how trace elements are distributed in tissues on a micrometer scale. It is a rather sensitive tool, with detection limits in the upper ppm range (1-100 $\mu g\ g^{-1}$). However, since the ionization of elements is strongly dependent on the matrix and therefore rather difficult to calibrate, this technique can be considered only as a qualitative method [4]. The application of many spectroscopy methods can indicate the total concentration of elements in tissue, although it is difficult to precisely localize trace elements. Therefore, the LA-ICP-MS technique was adopted to explore the possibility of determining elemental distribution and mapping its specific localization in the tissues of roots of pea plants (*Pisum sativum).*

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ANALYTICAL PROCEDURES FOR ATRAZINE, SIMAZINE AND METALS DETERMINATION IN TROPHIC CHAIN SAMPLES

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Monitoring the content of pesticides and metals in soil, plants and food (food chains) is necessary because of the toxicity of these compounds [1]. Moreover, some pesticides are able to translocate in whole ecosystem [2]. There is a risk, that even crops from free pesticides cultivation may be contaminated with these compounds. The heavy metals and herbicides concentration in soil and along trophic chains is an important issue with regards to human health [3].

Atrazine and simazine are widely used for annual and perennial grass. Atrazine has significant use in maize production, simazine is applied on corn and forestry. These compounds may be dangerous for human health because they are suspected to cause cancers, birth defects and interruption hormone functions [4,5].

The presented research concern the way of samples preparation, conditions of analysis, monitoring the concentration of atrazine, simazine and metals (Cd, Co, Ni, Pb, Zn and V) and translocation them along trophic chains: soil - grass - cow's milk, soil - cereal - hen's eggs, soil - vegetation - rabbit's meat and soil - vegetables roots - vegetables leaves. Emphasis was focused in shake - flask extraction, Soxhlet extraction, ultrasound assisted extraction and microwave assisted extraction as well as solid - phase extraction of atrazine and simazine from analysed materials. Triazines were analysed by means of high perfor-mance liquid chromatography and metals by means of ICP - AES [6,7]. Moreover, the results obtained by HPLC method were compared with results obtained by means of enzyme immunoassay. The optimal conditions for atrazine determination in trophic chain samples by means of an antigen - coated tube enzyme - linked immunosorbent assay (ELISA) were worked out [8]. The influence of human activity (industry, agriculture) on contamination the environment was also analysed.

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CHEMICAL EMISSIONS FROM TOYS-THE CASE OF STINK BLASTERS

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In the last years several communications to the Rapid Alarm System for non food products (RAPEX) were issued [1] concerning the presence of cyclohexanone in stink blasters (toys emitting characteristic smell after squeezing) and its possible impact on human health. The scope of the present study was to identify and quantify the emission of volatile organic compounds (VOCs) from this kind of toys and to evaluate possible health risks, in particular for children. Although the stink blasters are intended for outdoor use, a hypothetical indoor use (e.g. use by children in closed environments) has been considered relevant for exposure assessment studies. Specimens for testing were bought in a local market and are similar to the products mentioned in the RAPEX notification. The toys analyzed (following extraction with methanol) contain less than 0.2% by weight of cyclohexanone. Cyclohexanone was found in the sponge and the head of the toy (causing the characteristic smell, when squeezed) but also in the body. In addition to these preliminary experiments and in order to evaluate air exposure to cyclohexanone, the stink blasters were placed in the Indoortron facility, a walk-in type environmental chamber of 30 m^3 volume featuring automatic control of parameters such as temperature (T), relative humidity (RH) and air change rates (ach), and tested for emissions after squeezing several times under "real world setting" conditions (22 C, 50% RH, 0.5 ach). By this, the main compounds emitted were cyclohexanone and toluene with concentrations reaching values to 25 $\mu g/m^3$ and 32 $\mu g/m^3$ respectively. These concentrations are much lower than the indicative occupational exposure limit values of 40 mg/m^3 for cyclohexanone and 192 mg/m^3 for toluene [2]. However, within the frame of this study it is not possible to evaluate possible health effects, which might be expected from a chronic exposure to the aforementioned chemicals at low doses.

References:

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http://ec.europa.eu/consumers/dyna/rapex/create_rapex.cfm?rx_id=23
[2] Commission Directive 2006/15/EC establishing a second list of indicative occupational exposure limit values in implementation of Council Directive 98/24/EC amending Directives 91/322/EEC and 2000/39/EC of 7 February 2006

THE BENEFIT OF THE COMBINED USE OF ACCURATE MASS AND ISOTOPE PATTERN IN ENVIRONMENT AND FOOD ANALYSIS: A MULTI-COMPOUND STUDY

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Exact mass determination is a key technology for the generation of sum formulas for the validation of chemical entities or for the characterization of pharmaceutical impurities. Quality of these sum formula generations depends on: a) preciseness of the mass determination, b) use of the isotopic pattern information and c) accuracy of the isotopic pattern measurement. The accurate mass and the isotopic pattern provide two complementary dimensions, allowing a sum formula generation for compounds of masses up to ~500 Da. If molecular mass is higher, additional information has to be used. Exact mass alone is not sufficient here anymore since the required mass accuracy would be in the range of below 200 ppb.

For the statistical evaluation we analysed >150 known compounds of masses between 100 and 1000 Da by ESI-TOF-MS using external calibration. The sum formulas for these compounds were generated by the algorithm SmartFormula using the exact mass as well as the isotopic pattern information. We evaluated the achieved accuracy as well as the rankings based on mass accuracy as well as on the so-called SigmaFit value provided by the algorithm, which takes the isotopic pattern information into account. We also evaluated for larger compounds the additional use of exact mass and isotopic pattern on the MS/MS fragments, which must be a subset of the sum formula of the intact molecule.

The compounds which were analysed had elemental compositions ranging from 2-35 carbon atoms, 6-60 hydrogen atoms, 0-6 nitrogens, 0-15 oxygens, 0 or 1 phosphor, up to 3 sulfur atoms and up to 6 chlorine or fluorine atoms covering a large range of different compound classes. The evaluated compounds were all measured within the instrument specification of 5 ppm mass accuracy with external calibration. The absolute error was usually better than +/- 1 mDa. Therefore, every sum formula within this error range had to be regarded as equally likely. We observed that the additional use of the full isotopic pattern information provided significantly better results. While mass accuracy alone showed rank number 1 or two for the correct sum formula for only 27%, the use of the isotopic pattern increased this value the 68%. For the ranks 1-5 these values are 50 and 85%, respectively. In addition, we analyzed which mass accuracy would be required to obtain the selectivity, which arises from the combined use of accurate mass and isotopic pattern information on MS and MS/MS, thus basically four independent analytical dimensions. For the compound Taxol with a mass of 854 Da, we obtained 4 sum formula suggestions using this so-called SmartFormula3D approach. To achieve a similar result based on the MS mass accuracy alone, we would require a mass accuracy of 200 ppb. While it is possible to achieve such a mass accuracy by using internal calibrations in current instrumentation once in a while, one has to achieve this on a constant reliable base in everyday routine to be able to apply it for such an application. This is currently not possible and thus the combined use of the four dimensions provides a higher selectivity than any instrument can routinely deliver today.

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STUDIES ON METALS MOBILITY IN THE SEDIMENTS CORE - EARLY DIAGENESIS PROCESSES

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Sequential extraction is considered as a useful tool for examination of elements mobility in soil and sediments since the 1970ties. On the other hand, sediments play a decisive role in accumulation of metals from the water body, and their composition as well as physical and chemical properties may decide of the adsorbed elements and compounds fate in the water environment. Diagenesis is the process reflecting changes in chemical and physical structure of inorganic and organic compounds constituting the sediments.

By use of the sequential extraction procedure [1] early stages of diagenesis were observed in the sediments of the Dobczyce Reservoir. The core samples of the sediments were taken at two distinct locations: point 1 - shallow part (3 m) of the lake close to the Raba river inlet; point 2 - deep (24 m) part of the lake near the dam. The core samples were collected and divided into three 6 cm thick layers. The samples were dried, homogenized and their mineral composition was determined using X-ray diffractometry. Part of the sample was digested and analyzed for the total elements concentrations. The other part was used for the sequential extraction procedure. Concentrations of Ca, Fe, Mn, Cu, Cr, Pb, Zn were determined in the digested samples and in the sediments extracts by means of atomic absorption spectrometry method.

The extracts contained three fractions of the elements: A - bounded weakly to the sediments (in ionic or carbonate forms), B - adsorbed on Fe and Mn oxides and hydroxides, C - connected with organic matter and D - incorporated in mineral particles - residual fraction. It was found that: 1) the concentrations of elements in the organic and residual fractions changed little in the analyzed samples with the depth (age) of the sediments; 2) considerable shift in the elements concentrations was found between fractions A and B - the content of Fe, Pb, Cr, Cu and Zn in fraction A was increasing with the depth at the expense of fraction B. Probably, Fe compounds were reduced in anaerobic conditions what lead to change into ionic forms of adsorbed elements. These changes were only noted for the sediments in the sampling point 2 - no symptoms of diagenesis were observed at the sampling point 1.

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REFERENCE MATERIALS FOR ORGANICS TO COMPLY WITH THE WFD: A WATER "GRAIL"?

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Reference Materials (RMs) play a fundamental role in ensuring reliable measurement results, in particular also in view of the monitoring duties imposed on the Member States by the Water Framework Directive, (WFD) [1].

Chemical monitoring is focused primarily on the measurement of the so-called Priority Substances (Annex X of the WFD [2]) which currently includes thirty-three pollutants, most of which are organic compounds well-known as hazardous for environment and human health.

The analysis of organics in water still poses big challenges and presents serious gaps with regard to the availability of the necessary quality assurance/quality control (QA/QC) tools needed to achieve confidence in measurement results, e.g. validated analytical methods, Reference Materials and suitable proficiency testing (PT) schemes.

The Institute of Reference Materials and Measurements (IRMM) supports with various activities the proper implementation of the WFD at EU level in terms of QA/QC by the monitoring laboratories. These activities include exploitation of new strategies towards RMs for organic pollutants in water matrices, technical support to PT schemes [3, 4], development of new analytical methods [5] and expert advice to establish guidance documents.

An overview on the state of the art of matrix RMs for analysis of organics in water will be given. The latest achievements with regard to QA/QC tools developed at IRMM for water analysis in the field of organic pollutants will be presented.

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ANALYSIS OF ORGANOTIN COMPOUNDS IN BIOLOGICAL MATRICES BY GC-MS: COMPARISON OF TWO DERIVATIZATION PROCEDURES

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Organotin derivatives, such as tributyltin (TBT), dibutyltin (DBT), and monobutyltin (MBT) in biological matrices are commonly analysed by gas chromatography-mass spectrometry following a sample preparation procedure which includes several steps, in particular, extraction, clean-up and derivatization. Many Grignard reagents have been used to derivatize and increase the volatility of organotin compounds: hexylmagnesium bromide, pentylmagnesium bromide, propylmagnesium chloride, ethylmagnesium bromide, methylmagnesium bromide, and sodium tetraethylborate [1, 2].

In this work two among the most used derivatizing reagents were comparatively tested: methylmagnesium bromide [3], and n-pentylmagnesium bromide [4]. For the instrumental analysis, high resolution gaschromatography coupled with two different massspectrometric detectors has been used: quadrupolar ion trap (MS2) for methylated, and linear quadrupole (SIM) for pentylated analytes.

Commercially available pentylating reagents are known to contain impurities which systematically increase the limit of detection, whereas more volatile methylated compounds can be lost during the analytical procedure.

A comparison between the methods using the two derivatizing reagents was obtained by analysing organisms belonging to the species Nassarius nitidus sampled in the southern part of the Lagoon of Venice.

Gastropods were sorted in males and females and imposex levels were determined. Individuals were pooled according to imposex levels for subsequent chemical analyses with the two procedures.

The differences of the total butyltin concentrations (TBT+DBT+MBT) between the two analytical procedures resulted below 26%, with the best agreement for DBT and MBT.

In both analytical procedures sensitivity and selectivity to butyltin compounds were suitable for the analysis of complex matrices.

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SELECTIVE REMOVAL OF Pb^{2+} FROM AQUEOUS ENVIRONMENT BY CALIX[6]ARENE ESTER DERIVATIVES

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In this work we have explored the selective behavior of calix[n]arene ester derivative in two-phase extraction systems by polarographic technique. It has been revealed from the observations that calix[4]arene tetraester derivative shows remarkable Na^+ over Pb^{2+} selectivity; whereas calix[6]arene hexaester derivative shows Pb^{2+} over Na^+ selectivity. The interference of some selected cations (Na^+, K^+, Cu^{2+} and Mg^{2+}) has also been examined. No, significant effect of other ions was found except Na^+ on the selectivity behavior and extraction ability of these ionophores. The study reveals and explores first time that the calix[6]arene hexaester derivative is highly Pb^{2+} selective ionophore. It can be employed in the field of sensor as well as separation science and technology. The work also highlights the usefulness of polarographic technique in trace metal determination.

Keywords: Calix[n]arene; Lead Selectivity; Polarography; Solvent extraction.

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INVESTIGATION OF THE FATE OF MTBE AND BTEX COMPOUNDS IN A PETROLEUM CONTAMINATED COASTAL AQUIFER

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Petroleum hydrocarbons are among the most common groundwater contaminants. They enter the subsurface as the result of leaking underground storage tanks, improper disposal, or accidental spills. Water soluble fuel components such as benzene, toluene, ethyl benzene, xylenes (BTEX) and methyl t-butyl ether (MTBE) are of utmost concern from the perspective of human health. In addition to remediation strategies such as pump-and-treat, excavation, and air sparging, widely initiated by man, there is an increasing interest in natural attenuation as a promising alternative. Natural attenuation of MTBE and BTEX compounds in a petroleum contaminated shallow coastal aquifer in the Tel-Aviv area was investigated. Significant decrease in MTBE concentration and complete disappearance of BTEX compounds occur within 100 meters of groundwater flow. To evaluate natural processes occurring at the contaminated site, concentrations of the electron acceptors and biodegradation by-products in space and time were determined. Highly anaerobic conditions were found in the close vicinity to the spill source. In order to examine the contribution of microbial degradation to the attenuation process at anaerobic conditions, compound specific carbon isotope ratio analysis was employed. Carbon isotope enrichment of toluene, up to 2.4‰ along with the drop in its concentration, up to 80% was observed within 20 cm below the water table. The lack of isotope fractionation despite the significant concentration decrease for other studied compounds indicates significant contribution of abiotic processes to the natural attenuation

RISK ASSESSMENT OF POPS POLLUTION AND POSSIBILITIES FOR THE IMPLEMENTATION OF PHYTOREMEDIATION TECHNOLOGY IN MOLDOVA

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Moldova is characterized by the great number of POPs polluted sites. The actual problem is to develop an appropriate remediation technology for the reduction of negative impact to the environment and public health. The objectives of this work were to determine pollution risk from old pesticide storehouses and to assess phytoremediation technology for potential implementation in Moldova. The following tasks were developed: investigation of pollution levels following pesticide repackaging nears the foundations of old pesticide storehouses; risk assessment of pesticide pollution of surrounding agriculture territory; evaluation of the efficiency of the phytoremediation technology. Were determined that old pesticide storages are remain as high polluted sites and need remediation actions. The pollution level on that sites depends of the history of there utilization (better equipped sites have lover pollution level). The principal migration way of pesticides from polluted sites on local level are a transportation of the dust material by winds. The pesticide fate to ground water is limited on investigated site but is possible in favorable hydrogeological and geological conditions. The phytoremediation technology can be used for the remediation and needs individual design for every lot in view of local conditions. Investigators should to take into consideration all advantages and limitations of this technology: the time of agricultural phytoremediation is enough long and this technology needs an utilization complex approaches like using native plants, perennial plants, etc; the composting of obtained crops is an appropriate solution for the utilization of polluted plants after the pfytoremediation; the investigation of biochemical processes by the composting is actual for the better understanding of the further pesticide destruction. The implementation of modern analytical approaches and EU standards was important by the realization of any environmental investigation. The assessment of uncertainty and traceability, QC/QA procedure were very important tasks by the realization of presented work.

PREPARATION OF NEW RESIN GELS FOR DETERMINATION OF MERCURY BY DIFFUSIVE GRADIENTS IN THIN FILMS TECHNIQUE

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During the last twenty years, form the time when the diffusive gradients in thin films technique was introduced to scientific community for the first time [1], this technique has been intensively studied and developed [2]. The DGT technique was developed for measurement of phosphorous, sulfides, stroncium, cesium, technecium, lanthanoides, and actinoides, but only little effort was attended to measuring of mercury species [3], however they have attracted great attention in environmental contamination monitoring due their unique toxicity. In our laboratory DGT technique is studied 8 years and significant part of our research is only this exact issue - measurement of mercury by DGT. In given lecture, results from last 5 years in this topic will be presented.

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PERMEATION LIQUID MEMBRANE FOR TRACE METAL MONITORING IN ENVIRONMENTAL SAMPLES

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Chemical speciation studies are important for understanding the biogeochemical cycling of trace metals in natural waters. In natural waters, trace metals e.g. Cu, Pb, Cd and Zn, exist in various chemical forms and their bioavailability or toxicity to micro-organisms depend on the specific form, in particular the free metal ions are the most toxic. Speciation measurements are important for eco-toxicological risk assessment and for bio-uptake. The concentration of these metal ions in natural water is low (<100 nmol/L) and the free metal ions concentration is still lower (sub nanomolar). Very few methods that combine both sensitivity and speciation capability are available. Permeation liquid membrane (PLM), also known as Supported liquid membrane (SLM), an emerging analytical tool based on liquid extraction principles, allows the determination of free metal ions or bio-available species. Their attractive features are: - separation and preconcentration of species can be done in one step, thus minimizing sample handling; - it somewhat mimics biological membrane; - it can be used readily for in-situ speciation measurements. Previous studies demonstrated that only free metal ions and lipophilic complexes are transported by PLM [1-2].

Previously, PLM has been applied to in-situ speciation measurements of Cu, Pb, and Cd in natural waters, using a specially designed hollow fibre supported liquid membrane (HFPLM) device and the results showed that free metal ion concentration can be measured with a LOD in the few picomolar.

PLM was used to get information on the bioavailability prediction in the exudates of green algae Clamydomonas Reinhardtii. The results demonstrated indeed that free metal ions are measured. Validation of the application of SLM for trace metal speciation studies have been made by intercomparison with other techniques.

However, to our knowledge, trace metal speciation measurements in exudates of bacteria and in soil solutions or in exudates of rhizosphere, using HFPLM, has not been reported. The problem is that only small volumes of these are available and small sample HFPLM is required. Hence, small volume HFSLM device was specially designed. Trace metal speciation measurements in soil solution and exudates of bacteria were made using this HFPLM device [3]. Preliminary results showed that free metal ion concentrations are measured e.g. i) in soil solution and in exudates of bacteria. In this paper, the results of these measurements, compared to other methods, will be discussed. The application of HPLM for in situ trace metal speciation studies in various natural waters will also be presented.

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EFFECT OF CHEMICAL FORM OF MERCURY ON THE QUALITY OF THE RESULTS OF ATOMIC SPECTROMETRY TECHNIQUES USED FOR THE DETERMINATION OF MERCURY IN ENVIRONMENTAL SAMPLES

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Determination of mercury in environment is important because of its high toxicity. Mercury is present in trace amount in all environmental compartments as a result of natural and anthropogenic activities. It is also known that toxicity and ability of mercury to bio-acumulate in organisms depends on its chemical form. Besides well known environmental impact we also found out that the determination of mercury by any of atomic spectrometric technique (Atomic Absorption, Emission or Mass Spectrometry) depends on its chemical form. The are several reasons influencing the response of the instrument for the species present in the sample solution.

The aim of this presentation is to discuss the analytical performance of atomic spectrometric techniques used for the determination of the traces of mercury in various environmental compartments. It will be stressed that in all techniques the experimental conditions and analytical parameters depends significantly on the chemical form of mercury being present in the sample. In this respect, mainly two phenomena significantly influence the quality of the analytical results: (i) the sensitivity of the detector and (ii) memory effect. When neglected, those effects influence the calibration of the instrument, distracting the accuracy and traceability of the obtained results, thus preclude the determination of mercury. On the base of our results we are able to demonstrate the strategy towards assuring the uniform response of different measurement systems, independently on the mercury species being originally present in the sample solution.

The main aim of the presented research was focus on the developing the analytical procedure and optimize the measurement conditions as such to be able to calibrate the system with mono-compound mercury standard solutions. This was consider as of highly importance in a view of number of measurements of the mercury content in various environmental samples, which is drive by national and international requirements and regulation (e.g. European Directives).

DETERMINATION OF IONIC LIQUIDS IN NATURAL SAMPLES BY PREPARATION TECHNIQUES. PROBLEMS AND SOLUTIONS?

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Ionic liquids look like classical liquids and are molten salts. They are built of a bulky organic cation such as imidazolium or pyridinium, and an inorganic or organic anion such as tetrafluoroborate. These factors result in ionic liquids having reduced lattice energy and hence lower melting points. There is an almost endless number of ways of combining ions to make ionic liquids. Ionic liquids form a class of new environment-friendly compounds exhibiting low volatility, but also chemical and physical stability and recyclability. The specific properties of ionic liquids make them very useful in organic synthesis and catalyzed reactions, in liquid-liquid extraction, embalming and tissue preservation, and bio-catalytic enzymatic reactions. They were also advantageous as electrolytes for batteries, electrochemical devices, and germicide and fungicide applications. Due to their properties, ionic liquids have been used in a variety of separation methods, for example as stationary phase modifiers in gas chromatography, as carrier electrolytes in capillary electrophoresis or as additives to mobile phases in high performance liquid chromatography.

The wide applicability of ionic liquids will increase their production and utilization in industry. This will probably cause their appearance in water or soils. For that reason methods for their qualitative and quantitative determination must be developed. For this purpose an analytical tool can be used, namely reversed-phase high performance liquid chromatography (RP HPLC). Chromatographic analysis of ionic liquids on different types of packings gives interesting possibilities to determine main interactions between the stationary phase ligands and the analyzed compound. As a consequence, their retention mechanism can be defined. This could allow the prediction of principal interactions responsible e.g. for accumulation of ionic liquids cations in soils and biota.

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PERFORMANCE OPTIMIZATION OF A MEMBRANE ASSISTED PASSIVE SAMPLER FOR MONITORING OF IONIZABLE ORGANIC COMPOUNDS IN WATER

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A thin-walled silicone rubber hollow fibre membrane has been developed as a passive sampler. The inside of the tube is filled with an aqueous solution at an appropriate pH. The tube is sealed at both ends and then immersed in a water sample. In order for the ionizable permeating compounds to be trapped in the aqueous receiving phase, the pH is adjusted such that the compounds are ionized and trapped. The major advantages are its simplicity, low cost and high selectivity since only ionizable organic compounds are trapped. Additionally, the sampler uses no organic solvent. By adjusting the pH of the acceptor phase, it possible to control the extraction process and whether the sampler is used in the kinetic or equilibrium regime. Since it is very selective, no further clean-up of the extract is required. The membrane assisted passive sampler has been tested for extraction of chlorophenols under laboratory conditions. The extraction process was found to be linear over a 72-hour sampling period. Selectivity of the passive sampler in river water was demonstrated and the extraction process was independent of sample concentration even at lower concentration levels of analytes. Detection limits (three times signal to noise ratio) was dependant on sample matrix and type of detection system and ranged from 0.05 μg L^{-1} to about 1 μg L^{-1} with UV photodiode detector in water samples from one river and 1.0 μg L^{-1} to 20 μg L^{-1} in another but with ordinary UV detector. The obtained sampling rates compared well with those of other samplers such as the MESCO and CHEMCATCHER.

Keywords: passive sampler, water bodies, silicone hollow fibre rubber, ionisable organic chemicals

MEASUREMENT OF CHEMICALS IN THE CANADIAN URBAN ENVIRONMENT

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Environment Canada, in conjunction with Canadian provinces and territories operates a National Air Pollution Surveillance (NAPS) network [1] for measuring the quality of ambient air. This network is predominantly urban with about a quarter of the roughly 300 stations located in rural areas. The network, apart from measuring the criteria air pollutants (SO_2, NO_x, CO, O_3 and Particulate Matter) also measures a wide variety of chemicals in the air at a subset of sites. Currently, it is possible to quantify concentrations of over 200 volatile organic chemicals using a technique based on Summa canisters collection and GC-MSD analysis. Semi volatile organics including dioxins and furans, and polycyclic aromatic hydrocarbons (PAHS), are sampled using filters followed by polyurethane foam plugs, and are analyzed by GC-MS. Particulate matter (PM) is collected using special samplers which also capture other volatile species such as ammonia and nitric acid. PM collected on Teflon filters is characterized for elements by XRF and ICP-MS, and for ions using ion chromatography. The results are stored in a national database [2]. This presentation will discuss the various methods and outline future work. Some results of significance of selected chemicals found in Canadian ambient air will be presented.

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SUPERCRITICAL FLUID EXTRACTION OF PCB COUPLED WITH HYDRODECHLORINATION CATALYZED BY POLYMER-STABILIZED Pd NANOPARTICLES IN SUPERCRITICAL CARBON DIOXIDE

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This study investigated the feasibility of extraction a pentachlorinated biphenyl from contaminated soil and sand samples using supercritical carbon dioxide ($ScCO_2$) at 200 atm and different temperatures. Nearly all polychlorinated biphenyls (PCB) were removed quantitatively from solid matrices. The extracted polychlorinated biphenyls can be converted into nonchlorinated products by hydrodechlorination catalyzed by palladium (Pd) nanoparticles stabilized in high-density polyethylene (HDPE) beads. The technique studied here demonstrates that supercritical fluid extraction (SFE) of PCB followed by hydrodechlorination may have wide applications for the decontamination of toxic materials in various mixed wastes in environment samples.

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EVALUATION OF A PROFICIENCY INTERLABORATORY EXERCISE ON THE ANALYSIS OF TOTAL MERCURY IN DIFFERENT ENVIRONMENTAL MATRICES

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Mercury is a toxic trace metal of great environmental concern. Precise and accurate quantification of mercury is therefore very important for both monitoring and scientific purposes. Different analytical techniques and procedures are carried out by different laboratories for the analysis of mercury, turning essential the guarantee of the accuracy and comparability of results [1,2]. Thus, external quality control tools are very important for the evaluation and improvement of analytical performance of laboratories [1,2,3]. Twenty five European laboratories took part in a Proficiency Testing (PT) scheme which was organized to evaluate the state of the art concerning total mercury determination in three solid environmental matrices: soils, sediments and fish tissue. Both contaminated and not-contaminated soils and sediments were considered in the study. Participants used their regular in-house analytical methods and the reference values were determined from the obtained analytical results. The evaluation of the PT scheme was based on Z-scores and most of the participants obtained satisfactory records. The PT campaign allowed singling out laboratories which should revise their procedures. Most precise results were obtained for the biological matrix (fish muscle tissue) while concerning soils and sediments, the lowest relative standard deviation (RSD) from the mean was obtained for contaminated samples. Comparing the results of similar interlaboratory exercises for total mercury [4,5], the overall performance of participants in this exercise demonstrate that the ability to produce results of acceptable quality for this metal appears to be improving.

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O-25

RADIOACTIVE DISEQUILIBRIUM AS EVIDENCE OF URANIUM LEACHING FROM GOLD TAILINGS DUMPS IN THE WITWATERSRAND BASIN

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One of the environmental consequences of gold mining in the Witwatersrand Basin has been the release and distribution of heavy metals (including uranium) into the ground and surface water systems as a result of acid mine drainage (AMD) arising from oxidation of pyrite (FeS_2) in the tailings dumps. Uranium in the form of uraninite (UO_2) and brannerite (UTi_2O_6) is normally associated with gold-bearing ores.

This research was aimed at the quantitative assessment, based on radioactive disequilibrium, relating to the generation and release of uranium from the source and understanding how it is transported to streams, dams and wetlands.

Analytical results for samples collected in the study area showed that uranium is decoupled from its progeny, leaches away and is precipitated in wetlands. Measurements of radioactivity (using gamma spectroscopy) and direct measurements (using inductively coupled plasma mass spectroscopy, ICP-MS) helped in identifying the anomalies associated with the distribution of uranium and its progeny.

Analyses of dump material indicate that U is being selectively separated from its decay products in the dumps, resulting in locally high concentrations of U. It is possible that such areas of enrichment may not be detectable by conventional gamma ray spectroscopy because of separation of U from its decay products. Separation occurs as U is oxidized to the U(VI) state. Geochemical modeling indicates that U occurs predominantly as uranyl-sulphate complexes in the water, which is soluble over a wide pH range. Neutralization of the acidic water in swamp environments is associated with removal of U. This is partly due to interaction with organic fractions, adsorption or co-precipitation on Fe and Mn oxides, and partly due to reduction of U to the U(IV) state. In contrast, the decay products of uranium (e.g. Ra-226, Pb-214) hydrolyse, are strongly sorbed to tailings particles, and/or form insoluble compounds that become more and more enriched in the tailings as this process continues in time.

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SUGGESTION OF A PERFORMANCE REFERENCE COMPOUND FOR IMPROVING THE QUANTITATIVE MONITORING OF POLAR HERBICIDES IN FRESHWATERS WITH THE POCIS

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In this work, we performed an *in situ* calibration of the recent Polar Organic Chemicals Integrative Sampler (POCIS) [1] and suggested the use of a performance reference compound (PRC). The PRC approach was initially developed for the Semipermeable Membrane Devices (SPMDs) [2]. PRCs are (analytically) non-interfering compounds with moderate to relatively high fugacity from SPMDs, which are added to the lipid receiving phase prior to the field deployment. The determination of the dissipation rates of these compounds is essential for correcting the effects of several environmental parameters (e.g. biofouling, flow velocity, temperature, etc.) on the sampling rates. Multiple PRCs are generally needed to cover the wide range of environmental exposure conditions and for this purpose we determined the desorptions of several herbicides from the POCIS sorbent. The atrazine-desisopropyl (DIA) was characterized by a really high elimination kinetic constant in comparison with the other compounds. Thus, we suggested the use of the DIA as unique PRC and we investigated its in situ dissipation kinetic rate. The field validation of the PRC approach was performed with the comparison between the time-weighted average (TWA) concentrations estimated with either the POCIS or with an automated sampler. The POCIS estimates were dramatically lower than the concentrations obtained with the automated sampler whereas the corrected values (with the PRC use) were really closer. Such a result showed that the use of the DIA as unique PRC might give an acceptable correction of the sampling rates and a good estimate of the TWA concentrations of several triazines.

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IMPROVING THE SOLID-PHASE EXTRACTION PROCEDURE FOR THE DETERMINATION OF GLYPHOSATE AND AMPA IN ENVIRONMENTAL WATER BY LC-MS/MS AFTER FMOC DERIVATIZATION

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Glyphosate [*N*-(phosphonomethyl)glycine] has been one of the world's most widely applied herbicides since it came on the market in 1970s under the trade name Roundup. It is used for weed control in agriculture, forestry and gardens, and also on railway embankments. Glyphosate is rapidly adsorbed in soil and degraded to aminomethylphosphonic acid (AMPA) - its major metabolite and then transported to groundwater and surfacewater. The permissible level for individual pesticides including glyphosate and AMPA for drinking water is set at the pseudo-zero value of <0.1 μg/L by EU Directive. The high polarity and water-solubility of glyphosate and AMPA has, until recently, made their analysis in water samples problematic, especially at low levels. The aim of this study is to improve the extraction protocol in choosing the appropriate solid-phase extraction (SPE) sorbents in order to pre-concentrate the traces of glyphosate and AMPA and then the analysis is performed by method of high-performance liquid chromatography combined tandem mass spectrometry detection (LC-MS/MS) [1]. Due to a lack of adequate chemical groups (e.g. chromophores, UV absorption, fluorogenics), glyphosate and AMPA are derivatized with 9-fluorenylmethylchloroformate (FMOC-Cl) to form fluorescent derivatives and to reduce also the polar character of the analytes facilitating the chromatographic retention prior to the separation on column.

Due to their strong polarity and in most cases ionic character, anionic and cationic resins have shown great effectiveness in the enrichment and clean-up of samples [2]. For SPE, the study is realized on reversed-phase, strong anion-exchange and mixed-mode sorbents. The combination of the Oasis® HLB, PS-OH and Oasis® MAX cartridges are used for sample preparation to achieve high and reproducible recoveries (> 90%) for analysis of glyphosate and AMPA at low levels. Glyphosate and AMPA derivatized with FMOC then are separated in Sunfire™ C18 (50mm x 2.1mm i.d, 3.5μm) column prior to the determination on LC-MS/MS.

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OPTIMIZATION AND VALIDATION OF A SOLID-PHASE MICROEXTRACTION FOR GAS CHROMATOGRAPHIC DETERMINATION OF HALOACETIC ACIDS IN WATERS OF DISTRIBUTION

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Haloacetic acids (HAAs) are formed during the disinfection of drinking water by the interaction of chlorine with naturally occurring organic matter. There are nine HAAs congeners that contain chlorine and/or bromine. Five of the HAAs are regularly found in drinking water including mono-chloacetic acid (MCAA), dicloro-acetic acid (DCAA), trichloroacetic acd (TCAA), monobromoacetic acid (MBAA), and dibromoacetic acid (DBAA). Because of the very high toxic and carcinogenic risks of some HAAs, fast and accurate analytical methods for these substances are needed to monitor their concentration in chlorinated waters of distribution. Headspace solid-phase microextraction (SPME) has been developed for the determination of HAAs in water. The analytical procedure involves derivatization of HAAs into their metyl esters with acidic methanol, headspace sampling using SPME with 100 μm poly(dimethylsiloxane) (PDMS) fiber, and gas chromatography electron capture detection (GC-ECD) determination. The derivatization process was optimized to achieve maximum sensitivity using the following conditions: Esterification for 10 min at 50°C in 40 μL methanol, 30 μL sulfuric acid and 0,1 g anhydrous sodium sulfate. The headspace SPME conditions were also optimized and good sensitivity was obtained at a sampling temperature of 25°C, an absorption time of 10 min and a desorption time of 2 min. The linear calibration curves were observed for the concentration ranging from 5 to 300 μg L^{-1} with the correlation coefficient (R^2) being greater than 0,99 and %R.S.D. less than 12%. The method detection limits of most analytes were below 5 μg L^{-1} except DCAA and MCAA that were 6 and 20 μg L^{-1} respectively. The optimized method was applied for determination of HAAs in drinking water from Bizerte, Tunisia.

Keywords: Haloacetic acids; Solid-phase microextraction; Derivatization; Drinking water; Disinfection by-product.

STRATEGY FOR THE SCREENING AND IDENTIFICATION OF POLAR COMPOUNDS IN WATERSAMPLES WITH LC-MS/MS ACCURATE MASS MEASUREMENTS

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In the Netherlands groundwater and surface water are the main resources for drinking water production. In order to assess and maintain the quality of drinking water and its main resources, both regular monitoring of target compounds and screening for unknowns in these sources is necessary. Target compound analysis and screening for unknowns was mainly performed using GC-MS and HPLC-UV. However, GC-MS analysis is limited to non- to medium polar, volatile and thermostabile compounds present in water. In recent years, attention is more focussed on the polar and highly polar compounds, since they are more mobile and may pass through (conventional) water treatment systems.

One of the main challenges in water research is the isolation, analysis and identification of potential threatening (polar) (un)known compounds which are usually present at relatively low concentration levels (sub μg/l). In the past couple of years several potential threatening unknown compounds were detected with both chemical and biological (early-warning) systems at monitoring stations near the river. With the use of accurate mass measurements using a Q-ToF MS and a LTQ-Orbitrap MS it was possible to identify and confirm the presence of various organic micropollutants in watersamples [1].

In this presentation we will show the strategy for the screening of polar compounds including several examples of how LC-MS accurate mass measurements are used in the research program of Kiwa Water Research [2].

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O-30

OBSERVATIONAL STUDY OF CONTENT OF HG IN FOG WATER RELATIVE TO AIR POLLUTION IN SUBURBS OF NANJING

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Using in situ fog water samples gathered in the suburbs of Nanjing city, China in December, 2006, with their analysis performed, an attempt is undertaken of relation of Hg content with air pollution. It is found that foggy weather is unfavorable for diffusing pollutants, resulting in the increase in concentrations of PM_{10}, CO and total hydrocarbon, followed by their drop, and the density of pollutants changes roughly in phase with fog genesis/lysis; posterior to fog dispersal the concentration of SO_2, PM_{10} and NO_x is 2.5 to 10 times as high as prior to fog. Hg concentration ranges over 2.965 to 7.205 μg/L, averaging 5.471 μg/L, the high value appearing in the fog maintenance. Correlation analysis is made of Hg with pollutants, reaching the coefficient of 0.939 between Hg and CO that accounts for their homology.

APPLICATION OF A NEW VOLTAMMETRIC METHOD TO THE QUANTIFICATION OF URBAN WASTEWATER ORGANIC MATTER

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Many environmental studies have focused on the properties of the refractory fraction of natural organic matter, usually referred to as humic and fulvic acids, because of the key role that it plays in the fate of trace metals and organic micropollutants. However, this fraction has been rarely quantified since the necessary analytical tools are lacking. Recently, we have proposed an electroanalytical method based on adsorptive stripping after accumulation of Mo(VI)-humic or -fulvic acids complexes [1, 2]. This method is quick and reliable, and consumes only small amounts of sample. It has already been satisfactorily applied to a myriad of relatively unpolluted freshwater systems [3, 4] and has proved particularly suited to systems containing low amounts of carbon. In the present study, the method has been applied to samples from sewage effluents. Although it is usually assumed that humic-type substances present in surface waters are formed through the breakdown of plant and animal tissues by chemical and biological processes, sewage effluents, which contain large amounts of organic matter, are likely to be major contributors to the genesis of humic substances in major rivers. Thus, their contribution cannot be ignored when studying medium to high urbanized systems. In this study, the above mentioned voltammetric technique has been applied to different fractions (hydrophobic, transphilic and hydrophilic) isolated from effluents from the biggest wastewater treatment plant in Europe (Acheres, Paris) by following the isolation procedure described in [5, 6]. The response obtained is compared with that of well-characterised IHSS compounds.

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ALUMINIUM SPECIATION BY HYPHENATED TECHNIQUE HPLC-FAAS: A NOVEL METHOD FOR SIMULTANEOUS ONLINE DETERMINATION OF INORGANIC MONOMERIC ALUMINIUM

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The research presents a novel method for simultaneous online determination of inorganic speciation forms of aluminium: AlF_2^+, AlF^{2+}, and Al^{3+} by means of the high performance liquid chromatography hyphenated with a detection by the atomic absorption spectrometry with flame atomization (HPLC-FAAS). The separation of Al species with nominal charge of +1, +2, +3 required a run time of less than 8 minutes during a single analysis. The proposed method has been successfully used for speciation analysis of inorganic aluminium forms $AlF_n^{(3-n)+}$ in environmental samples. The suggested method for determination of inorganic aluminium forms in a combined online technique system (HPLC-FAAS) is a new solution which has not been applied in analytical chemistry to date. Optimized determination conditions for the HPLC-FAAS system allowed to obtain full separation of three forms AlF_2^+, AlF^{2+} and Al^{3+} during one analysis, which has not been achieved by other research centers before. The use of atomic absorption spectrometry with flame atomization as the detector enabled the determination of particular forms of aluminium fluoride complexes. The presented method enables to determine toxic form of aluminium present as free ion Al^{3+} in a sample and to separate and determine the remaining forms included in labile inorganic aluminium.

DETERMINATION OF ELEMENTS IN DIGESTED AND ASHED MOSS SAMPLES: A CASE STUDY, CENTRAL ALASKA AND SOUTH-CENTRAL POLAND

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The attraction of ICP methods is the possibility to determine 20-60 elements simultaneously. The lowest detection levels of trace elements are obtained by the ICP-MS technique. Of the different environmental materials, bioindicators require selecting an adequate procedure for sample preparation, i.e. digestion or ashing (and subsequent digestion), prior to chemical analysis. Ashing enables to substantially lower detection levels of elements. However, this should be treated with some caution due to the loss of volatile elements or semivolatile organic metal complexes at the ashing temperature.

The scope of this study encompassed preparation and element analysis of 44 moss samples (*Hylocomium splendens* and *Pleurozium schreberi*) collected in two remote areas, i.e. Denali and Wrangel-Saint Ellias National Parks (central Alaska) and the Holy Cross Mountains (south-central Poland) in the summer of 2007. Each sample was split into two subsamples; one (0.5 g) was digested with $HNO_3 + H_2O_2$, and the other (5 g) ashed at 500°C (0.1 g ash) and then digested with $HCl + HNO_3 + HClO_4 + HF$. In all, 34 elements were determined in the digested samples and 37 elements in the ashed ones, using inductively coupled plasma-mass spectrometry (spectrometer ELAN model 6000, Perkin-Elmer). Dry ashing enabled to lower detection limits of all the elements examined, especially Pt, Ag and As (Table 1), as well as the other elements poorly detected in the digested samples: Be (<0.03 vs 0.0006 mg×kg^{-1}), Bi (<0.06 vs 0.0012 mg×kg^{-1}), Li (<0.03 vs 0.006 mg×kg^{-1}), Ti (<40 vs 0.8 mg×kg^{-1}), Th (<0.1 vs <0.002 mg×kg^{-1}), Tl (<0.08 vs <0.0016 mg×kg^{-1}), U (<0.02 vs 0.0004 mg×kg^{-1}).

The results obtained from the ICP-MS analysis of the ashed samples enabled to better understand the geochemical relationships between the mosses and potential pollution sources. It is interesting to note that the Alaskan mosses show higher levels of As and Pt compared to those from the Holy Cross Mountains. This evidence suggests that geogenic sources (igneous and metamorphic bedrock) play a significant role in the spatial distribution pattern of these and other elements. Thus, Pt cannot be used as an exclusive indicator of vehicle emissions.

Table 1 Concentrations of Pt, Ag and As in the moss species *Hylocomium splendens* (H.s.) P*leurozium schreberi* (P.s.) from Alaska and Poland (reported on original whole plant basis)

Element	Moss species	Digest moss samples	Ashed moss samples					
			Alaska			Poland		
			m:n	GM	Range	m:n	GM	Range
Ag mg·kg^{-1}	H. s.	<2	14:14	0.024	0.012 - 0.052	10:10	0.048	0.036 - 0.071
	P. s.		14:14	0.031	0.021 - 0.103	10:10	0.043	0.031 - 0.055
As mg·kg^{-1}	H. s.	<1	14:14	0.376	0.134 - 1.550	10:10	0.207	0.133 - 0.262
	P. s.		14:14	0.329	0.145 - 1.860	10:10	0.193	0.136 - 0.246
Pt mg·kg^{-1}	H. s.	n.d	6:14	0.39	<0.4 - 1.60	3:10	0.28	<0.4 - 0.74
	P. s.		4:10	0.31	<0.4 - 1.03	2:20	0.27	<0.4 - 1.11

NOTE: Symbol < means below detection limit for a given chemical species; n.d. - not determined; m:n - number of samples above detectable concentration level relative to total number of samples; GM - geometric mean

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STUDY ON THE DETERMINATION OF INTRINSIC HORMONES IN *ARTEMISIA VULGARS L.* BY HPLC WITH GRADIENT ELUTION

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A gradient elution method for quantitative determination of intrinsic hormones of *Artemisia Vulgars L.*, such as gibberellin (GA_3), 3-heteroauxing (3-IAA), 6-benzylamino-purine (6-BA), abscisic acide (ABA) and α-naphthalene (α-NAA) was developed. The method employed a high performance liquid chromatography equipped with a Hypersil ODS C_{18} column and an ultraviolet alterable wavelength detector. The mobile phase, flowing at 0.8 mL/min, consisted of methanol, acetonitrile and acetic acid buffer solution of gradient ratios, and coupled with wavelength shift. The five hormones could be successfully isolated in 12 minutes. Recoveries of the individual hormone ranged from 91.39% to 95.98%, and the lowest detection limits varied from 0.02 μg/g (6-BA and ABA) to 0.3 μg/g (GA_3). The calibration curves showed a good linearity ($r>0.998$) for all components in standard sample under the concentration range of 10-800 μg/g. The method was applied, and proved suitable, for the determination of intrinsic hormones of *Artemisia Vulgars L.*

USING THE SYNERGY OF ACQUITY UPLC AND TANDEM QUADRUPOLE MASS SPECTROMETER FOR ENVIRONMENTAL ANALYSIS

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The introduction of Ultra Performance Liquid Chromatography (UPLC) capabilities allows reaching high chromatographic resolution level; in addition it affects positively the sensitivity and the MS data quality. Moreover, the use of UPLC has a significant effect in the return on investment of costly tandem quadrupole by decreasing substantially the run time.

To benefit the quality improvement of the LC data, the Mass Spectrometer has to be compatible with the new UPLC performances. The synergy of UPLC and MS will be outlined for the analysis of persistent pollutants; resolution of the 5 Hexabromocyclododecane (HBCD) diastereomers and of Perfluorinated compounds.

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COMPREHENSIVE TWO-DIMENSIONAL GAS CHROMATOGRAPHY FOR FIELD ANALYSIS OF THE SEMI-VOLATILE ORGANIC FRACTION OF AIR PARTICULATE MATTER

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Comprehensive two-dimensional gas chromatography (GCxGC) is one of the most powerful separation techniques available today. In GCxGC, two capillary columns coated with stationary phases of different polarities are used. The first column typically has standard dimensions and is coated with a non-polar stationary phase, while the second column is usually much shorter (1-2 m) and coated with a polar stationary phase. The two columns are connected through a special interface (modulator), whose role is to trap the effluent from the first column and periodically inject it as a narrow band to the second column. The modulation period typically lasts a few seconds.

Among the various modulation techniques developed over the years, cryogenic GCxGC modulation is the most widespread technique. It has important advantages, including efficient modulation of volatile compounds and improved signal-to-noise ratio of the chromatographic bands. On the other hand, the technique is not ideal for semi-volatile analytes, and it requires a constant supply of a coolant (liquid CO_2 or liquid N_2) for the operation, which makes it unsuitable for field applications. To overcome these limitations, we have developed a novel thermal modulator requiring no cryogens or moving parts for an automated *in-situ* instrument for the analysis of the semi-volatile fraction of organic compounds found in atmospheric aerosols (so-called 2D-TAG). The modulator is based on a segment of Silcosteel tubing coated with a film of a chromatographic stationary phase, placed outside of the GC oven. Analyte bands exiting the first GC column are trapped in the stationary phase kept at ambient temperature, and released rapidly by thermal desorption accomplished through resistive heating of the tubing. Dual stage modulation is ensured by alternatively heating two separate trapping zones.

The modulator was tested using compounds covering a wide range of volatilities. With proper adjustments to the trapping and release parameters, it proved to be able to modulate compounds with volatilities falling within the range of the C_6 - C_{40} *n*-alkanes. Programming of the temperature of the cooling air was tested in order to improve the transfer of the least volatile compounds. Suitability of the system for semi-continuous analysis of air particulate matter was demonstrated over a 24 hr period.

The 2D-TAG system offers unparalleled separation power for the organic fraction of ambient air particulate matter ($PM_{2.5}$). It is the first example of the application of GCxGC in the field.

PRELIMINARY STUDIES OF THE SORPTIVE CAPABILITIES OF SEDIMENTS FROM THE DOBCZYCE DRINKING WATER RESERVOIR TOWARDS IBUPROFEN

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Pharmaceuticals in the aquatic environment, which thousands of tons are used annually in human and veterinary medicine, has been recognized as one of the emerging issues in an environmental analysis. Because of their environmental persistence they may avoid degradation in the sewage and drinking-water treatment plants [1]. The introduction of drugs into the environment is a function of a combination of several factors: the quantity manufactured; the dosage (amount frequency and duration); the excretion efficiency of parent compound and metabolites; the adsorption/desorption on soil capability; and the metabolic decomposition in sewage treatment [2]. Ternes at al. predicted that, in general, two processes are responsible for this reduction, namely i)sorption and ii) biodegradation [3]. Additional problems are caused by the fact that pharmaceuticals in the aquatic systems occur as mixtures and not as individual contaminants [4]. Ibuprofen is a non-steroidal anti-inflammatory, analgesic, antipyretic and non-prescription widely uses drug. It is weak, carboxylic acid with pK_a value 4.52. In Germany, diclofenac and ibuprofen, consumed in quantities of ~75 and 180 tons per year, respectively, have been particularly recognized as important contaminants in the water cycle. For example, they were found in sewage and surface water samples in Greece, Canada, Finland, Spain, Slovenia, United Kingdom and Switzerland. Consumption of antiphlogistic drugs in 2005 stated 22% in all OTC (over the counter) pharmaceuticals market in Poland with a transaction volume of Euro 250 million. The aim of the study is to determine the chemical and physical properties of the sediments taken from the Dobczyce drinking water reservoir (southern Poland). Sediments sorptive capabilities have been examined towards ibuprofen.

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CHANCES AND OBSTACLES FOR A METHYLMERCURY DETERMINATION IN THE ENVIRONMENTAL SAMPLES

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Mercury is a toxic environmental contaminant and in particular a form of a methylmercury (MeHg) is a dangerous neurotoxin. From an analytical point of view the determination of MeHg in environmental samples is a special challenge. In most cases the determination procedures are complicated. The most unstable part of the MeHg determination is the derivatization step. Several different derivatization procedures were described in literature [1, 2], but the considerable instability of the result appear when they are applied. Another problems are the following: the MeHg decomposition, the stability of Solid Phase Micro Extraction (SPME) fibre properties, the influence of the equipment construction on results.

The system for the mercury speciation in the environmental sample has been designed and ensembled. The system of mercury speciation consists of three analytical lines: Gas Chromatograph (GC) - pyroliser - Tekran 2500 Atomic Fluorescent Detector (AFS), Gold/Tenax traps - GC- pyroliser - AFS, - GC-Mass Spectrometric Detector (MS).

The first line enables the determination of mercury organic compounds. The second line has been designed for the determination of a total mercury using US Environment Protection Agency (EPA) 1631E method. The third line is used for control and study the MeHg extraction process.

For the MeHg determination in the environmental samples the procedure with SPME fibre was applied (SPME fibre is more simple in use than Tenax trap). For the analysis the 1% sodium tetraethylborate in potassium hydroxide solution, pH 5 buffer solution and varied amounts of methylmercury standard were used. The SPME fiber was exposed to the head space. After the extraction and derivatisation the fiber was transferred into the injection port of GC. The detection was conducted using two detectors: Atomic Fluorescent Spectrometer (via pyrolyser) and Mass Selective Detector.

The comparison of the analytical lines led to the selection of the GC - quartz column pyrolizer - Tekran. Currently the MeHg determination procedure is being optimised. Due to the instability of the derivatization process the double SPME fibres are applied. This enables the control of the most important parameters of the procedure.

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ANALYSIS OF SULFONAMIDES IN SOILS: A COMPARATIVE STUDY OF EXTRACTION TECHNIQUES

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Sulfonamides are antibiotics widely used in veterinary medicine. Drugs which are not metabolised by treated animals are excreted and spread into the agricultural fields when manure is utilised as fertiliser. The fate of the drugs in soils depends on their sorption. Relatively polar compounds, such as sulfonamides, do not experience strong sorption, and as a consequence leaching and surface runoff can occur and this leads to groundwater and surface water contamination. Potential concerns from the environmental occurrence of these compounds, such as the development of antibiotic-resistant bacteria, the effects on the aquatic ecosystems, etc. have been lately reported.

Analytical methods for the quantification of sulfonamides in soil samples are relatively scarce. They are based on liquid chromatography, and the most critical issue is the extraction of the analytes from the soil sample. Different extraction agents, as well as different extraction techniques, have been proposed. Since recovery ratios can strongly depend on the soil characteristics it is difficult to conclude which system is the most advantageous.

In views of this, a comparative study using soils of different physicochemical properties is presented. Different extraction solutions have been assayed. Conventional mechanical shaking, microwave assisted, ultrasound probe and pressurised liquid xtraction techniques have been applied and the effect of soil aging on extraction recoveries has been also considered.

ANALYSIS OF FRESH & WASTE WATER USING TOTAL REFLECTION X-RAY FLUORESCENCE (TXRF)

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Total reflection X-ray fluorescence (TXRF) spectroscopy is a well-established and versatile method for the trace element analysis of liquid samples [1].

Applied to fresh and waste water analysis TXRF reveals its unique capabilities. Due to the thin film sample preparation, matrix effects are irrelevant and quantification is performed by means of internal standardization. Additionally, corrosive matrix components like acids or bases, common in industrial waste waters, can be analyzed without any risk to the analytical instrument. Due to the compact design of the spectrometer even mobile use for measurements on-site or in the field are possible.

The capabilities and limitations of TXRF spectroscopy for the trace element analysis of fresh and waste water samples are evaluated in this paper.

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A SENSITIVE SPECTROPHOTOMETRIC DETERMINATION OF TRACE AMOUNT OF BENZENE IN VARIOUS ENVIRONMENTAL SAMPLES

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Spectrophotometric method using two different reagents is being described for the determination of benzene. In this method benzene is drawn into nitrating mixture to form m-dinitrobenzene, which is further reduced to m-phenylenediamine and diazotized. The diazonium salt is subsequently coupled with NEDA in acidic medium to form a purple colored dye having λ_{max} 545nm. Second method involves direct-reaction of m-phenylenediamine with diazotized p-aminoacetophenone in alkaline medium to form yellowish-red colored dye having λ_{max} 450nm. Beer's law was obeyed over the concentration range 0.2 - 2.4 μg mL^{-1} (molar absorptivity 2.7 x 104 L mol^{-1}cm^{-1}) for NEDA and over the range of 0.16-2 μg mL^{-1} (molar absorptivity 2.9 x 104 L mol^{-1}cm^{-1}) for diazotized p-aminoacetophenone. The communicated method is simple, sensitive and free from non target species. The dye is extractable by using solid phase extraction (amino cartridge) and therefore the method can be successfully applied for the determination of trace amount of (0.016 ppm) benzene in various environmental samples. The methods have been validated by applying it for the determination benzene in petrol vapours, coke oven effluents and cigarette smoke.

Keywords: Spectrophotometer, Benzene, D-p-aminoacetophenone, NEDA.

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SPE COUPLED WITH CONTINUOUS POWDER INTRODUCTION MICROWAVE INDUCED PLASMA OPTICAL EMISSION SPECTROMETRY AS A TOOL FOR ENVIRONMENTAL ANALYSIS

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Sorption techniques such as solid phase extraction are commonly used for preconcentration and separation of analytes before determination. However, desorption of analytes could be sometimes troublesome owing to irreversible binding of some elements. Additionally, the desorption step leads to sample dilution decreasing the analyte enrichment factor. Sometimes, matrix effects caused by the eluent present in the sample solution are observed in the determination step. These problems may be omitted by analyzing the analyte-on-sorbent particles directly by solid sample introduction into the plasma. A direct solid sampling technique based on continuous powder introduction and coupled with microwave induced plasma optical emission spectrometry (CPI-MIP-OES) is presented. Several methods for direct analyte-on-sorbent introduction have been previously described for ICP-OES, including ETV, DSI and CPI techniques [1]. However, an important advantage of MIP-OES is its compatibility with various sample introduction techniques. The use of external calibration with the aid of synthetic standards obtained by multielement sorption of analytes on a suitable support material is attractive for the determination of trace elements by CPI-MIP-OES. This provides identical preparation procedure for samples and standards including sorption efficiency. Additionally, matrix matching and particle size matching is easily attainable.

The analytical potential of the SPE-CPI-MIP-OES is shown during the reliable analysis of some environmental samples. The reliability of the CPI-MIP-OES method with preconcentration of heavy metals on activated carbon was validated using water CRMs [2]. A total enrichment factor of 1000 is attainable when 1 g of the sorbent is used for a sample volume of 1 L. Thus, the detection limits (3σ) from 20 to 70 ng L^{-1} for Cd, Cu, Cr, Fe, Mn, Pb and Zn were obtained with respect to the aqueous sample. The second example of application of the method coupled with analyte preconcentration is the determination of precious metals in the platinum ore SARM-7 and in the Chinese soil CRMs [3]. The possible matrix effects caused by alkali and alkaline earths elements are eliminated at the preconcentration stage as these metals are not retained on the activated carbon. Additionally, the presence of carbon in the plasma improves plasma stability and analyte excitation.

Among plasma sources, the helium-MIP is much sensitive toward fluorine determination. Sorption on zirconium-modified activated carbon or calcium hydrogen phosphate was used for separation of aqueous fluoride. The absolute DL of 4.7 μg was achieved. It gives the possibility of determining the aqueous fluoride at the ng per ml level including analyte preconcentration by a factor of 1000.

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ORGANIC XENOBIOTICS IN AGRICULTURAL SOILS; EVALUATION OF THE CONCENTRATIONS AND SOURCES OF POLYCYCLIC AROMATIC HYDROCARBONS

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Contamination with chemical substances is one of the main soil threats specified in the EU Soil Thematic Strategy (*COM(2006)231 final*) which can generate direct and indirect risk for most of soil functions (habitat, retention, production). Agricultural soils used for crop production are the most "sensitive" part of the soil environment as regards human and ecological risk, hence, application of the reliable and sensitive methods for determination of the content of those contaminants in soils is of an utmost importance.

The aim of the studies was to provide a comprehensive and scientifically sound information on the contemporary levels of persistent organic contaminants, namely polycyclic aromatic hydrocarbons (PAHs) in arable soils in Poland. Over 200 soil samples were collected in 2005 from the whole country territory with a special reference to the areas of high exposition to anthropogenic pressure [1]. 16 PAH compounds (US EPA List) were included in the studies. Analytical procedure comprised extraction of soil samples with CH_2Cl_2 in Soxtec apparatus, cleaning-up extracts on silica gel and determination of individual PAHs content applying GC-MS technique [2]; resolution of PAH compounds has been achieved according to the ISO 18287 standard [3].

The content of PAHs in arable soils in was assessed according to Polish regulation [4] and the IUNG classification proposition for agricultural soils [1]; the results were compared with other relevant European soil quality standards. The concentrations of PAHs in Polish soils were on about the same level as in other European countries ranging from 80 to 7264 $\mu g \Sigma 16PAHs \cdot kg^{-1}$. The molecular markers pointed to prevailing pyrogenic origin of PAHs in Polish arable soils with prevailing contribution of coal combustion and minor participation of liquid fuel and traffic emissions. Generally, based on the sum of PAHs evaluations, about 90% of soils can be considered as unpolluted besides the "hot-spots" concentrating in the most industrialised South-West areas of the country. Polish regulations [2] including evaluations based on the BaP content appeared to be the most restricted one.

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COMPARISON OF SELECTED CHEMICAL METHODS TO PREDICT THE PHENANTHRENE BIOAVAILABLE FRACTION IN SOIL

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Bioavailability of organic contaminants such as PAHs in soils is the subject of many recent publications but there is still no agreement between scientists on its definition. Additionally, taking into account the factor of time, it becomes even more complicated. An effort of clearing up the concept of bioavailability in relation to organisms, pollutant and soil properties as well as time factor have been discussed in the ISO/DIS 17402 standard [1]. The document also emphasis the need for application of appropriate chemical methods for quantitative assessment the bioavailable fraction of pollutants in soils.

Several different procedures such as adsorption to solid phase (Tenax, XAD, cyclodextrines, SMPE), mild solvent extraction (water+organic solvent) and oxidation with persulphate to evaluate the PAH bioavailable fraction have been described in the literature and correlated with the results of bioassays such as degradation efficiency and uptake of contaminants. However, data on applicability of chemical methods for the assessment of PAH bioavailability/ecotoxicity to different soil microorganisms are still insufficient.

The aim of the work was to test selected chemical methods to predict phenanthre (PHE) bioavailability in ecotoxicity studies with nitrifying bacteria. Soil material, collected from the upper horizon of sandy soils from agricultural area was applied in the study.

Four different chemical methods of extraction of PHE bioavailable fraction from soil were applied: adsorption to Tenax for 1 hour (actually bioavailable fraction T1), adsorption to Tenax for 20 hours (potentially bioavailable fraction T2), mild solvent extraction with water+ethanol (2:3 v/v) and extraction with n-propanol. In all cases GC-MS method of phenanthrene determination was applied according to the ISO 18287 standard [2]. Ecotoxicity studies included 7 days experiment (20°C and 60% of full water holding capacity) with soil samples artificially contaminated with phenanthrene at the levels of 10, 50, 100, 500 and 1000 mg of PHE *per* kg of soil. Potential of nitrification (PN) was determined at the beginning and at the end of the studies according to the ISO 15 685 method [3]. Correlation of the results of chemical and biological tests indicate on the adsorption on the Tenax as method being the most perspective for evaluation of the fraction of PHE available to nitrifying bacteria. Further testing of this method for other groups of organisms may be useful for simplifying the ecotoxicity studies.

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SPECIATION OF ARSENIC AND PLATINUM COMPOUNDS IN PLANT TISSUES. STUDIES OF DETOXIFICATION PROCESSES

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Speciation analysis is one of the fastest developing area of analytical chemistry as determination of total amount of element in biological samples is not sufficient to evaluate its essentiality and toxicity, follow its pathways in the environment and recognize its metabolism in biological systems.

Recently the increasing interest in the investigation of different elements species in plant samples is observed. Especially that there are plants which are able to accumulate high concentration of toxic elements without visible side effects.

Some of them transform the more toxic form to the other one which are non-toxic to organism, which is very well documented in case of arsenic in water ecosystem where inorganic arsenic compounds are transformed to much less toxic MMA or DMA or AB and AC in marine organism. Attention of many scientists is currently focused on synthesis of phytochelatins in plant tissues, what is postulated as a very effective process of detoxification of heavy metals in plants.

Phytochelatines (PC) are glutathione-derivatived peptides with general structure $(\gamma\text{-Glu-Cys})_n\text{-Gly}$ (n=2-11). It is known that they play an important role in decreasing the toxicity of such cations as Cd^{2+} or Pb^{2+}. Some authors proved that arsenic may also be complexed with phytochelatines in terrestrial plants. This mechanisms was confirmed in *Brassica juncea* or *Rauvolfia serpentina.*

In case of Pt information about the nature of its compounds present in plant tissue is very narrow. In native plants growing in area with increased Pt content, platinum was found in high molecular mass fraction (160-200 kDa). It is also suggested, that platinum can take place of calcium in the structure of polygalacturonic acid, or can be bound with glutathione and small phytochelatins.

To identify As and Pt compounds present in plants mainly hyphenated techniques such as HPLC ICP MS or HPLC ESI MS are applied. But to determine the presence of phytochelatins in plant tissues alternatively to mass spectrometry also electrochemical methods can be used. Pulsed amperometric detection (PAD), that involves applying to a gold electrode a repetitive potential pulse sequence, by which amperometric detection is combined with pulsed potential cleaning, allows to detect any compound in which the sulphur atom has an unshared pair of electrons.

The aim of undertaken studies was characterization of chemical forms of platinum and arsenic present in Indian mustard plants (*Sinapis alba L.*), hydroponically cultivated in nutrient solution with addition of platinum and arsenic compounds. Additionally speciation analysis of arsenic in plants naturally growing in highly contaminated area was performed. After chromatographic separation of arsenic and platinum compounds in plant extracts mass spectrometry and pulse amperometric detector were applied.

EVOLUTION OF INTELLIGENT DATA ANALYSIS ON THE BASIS OF TURAWSKIE LAKE DATABASE

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Careful environmental monitoring requires data collection from lake and river bottom sediments, as they reveal important characteristics of aquatic ecosystems.

Sediments can serve both as reservoirs and as potential sources of contaminants to the water column, and can adversely affect sediment-dwelling organisms, aquatic-dependent wildlife and human health.

In the present state of art one common approach is linking chemical concentrations to toxicity data. This is a typical univariate strategy which produces traditional Sediment Quality Guidelines (SQG). The problems of the SQG estimation procedure are connected with the bioavailability of sediment contaminants and the effects of covarying chemicals and chemical mixtures. Assessment of the real threat resulting from the presence of a mixture of various pollutants (due to a wide spectrum of compounds, their concentration levels and speciation forms) in the environment is extremely complex.

Using a relatively large dataset from Turawa Lake - an artificial reservoir - treated with intelligent data analysis projection and classification methods (cluster analysis, principal components analysis with multiple regression on the identified principal components, SOMs), several general conclusions have been reached. Studies have proven that sediments as a representative biomonitoring system should be considered dependent not only on their chemical composition but also on their ecotoxicity properties. Such information is difficult to obtain due to simple univariate analysis, for this reason it is reasonable to apply more complex multivariate statistical analyses.

The hereby work shows the evolution of intelligent data analysis applied to dataset of Turawa Lake and how the conclusions withdrawn from each method supplement each other.

RELIABILITY OF THE ANALYTICAL RESULT - A CRUCIAL ASPECT OF RESEARCH ON ATMOSPHERIC PRECIPITATION

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The study of the composition of precipitation is an important element in determining the type and direction of changes occurring in the natural environment. The widespread nature of this atmospheric event allows the collection of a vast body of data by a variety of research and monitoring institutions. They provide a basis for conclusions concerning atmospheric pollution, the deposition of contaminants in a substratum, and even climate change or the general state of the environment. That is why their quality must be ensured by true and reliable data. Of no less importance is a correct comparison of the composition of samples, which must meet the condition of an identical sampling procedure [1, 2].

This work presents the relationship between the analytical procedures employed and the results obtained. Also assessed are differences resulting from the way in which an experiment is conducted and involving such factors as the place, mode and frequency of sampling, kind of samples taken, duration and way of storage from the time of sampling to the time of analysis, preparation of samples for analysis, and the control and interpretation of the results.

Fundamental differences were observed in precipitation samples acquired by procedures varying in the mode and frequency of sampling. The differences in concentrations of individual ions for the respective samples of wet and bulk deposition exceeded 100%. The results of analyses of precipitation samples collected on a monthly basis - poured together in amounts proportional to the precipitation episodes - differed from the figures obtained for samples collected daily and averaged over a month. The greatest differences have been observed in the pH and in concentrations of NH_4^+, SO_4^{2-} and Ca^{2+}.

Also analysed were differences in the composition of precipitation following from the various procedures affecting the samples prior to physico-chemical analysis, including the way and time of their storage. While the kind of vessels in which the samples were stored had no effect on the obtained result, the samplers employed turned out to be of importance. Differences in results were noted for precipitation samples stored at a variety of temperatures, unfiltered and filtered, the filtering material itself being neutral to the quality of the result. The greatest changes were observed in the levels of NO_3^-, NO_2^-, and NH_4^+. Those in the pH of a sample during storage could even range over 1.2 units, which corresponds to more than a 10-fold difference in H^+ concentrations [3]. The preparation of data for statistical analysis also turned out to be important - in the case of environmental studies, it can lead to significantly different conclusions.

It was found that despite the large number of results of precipitation studies being published, the diversity of the analytical procedures employed often makes their comparison impossible. There is a great need for a precise use of the standardisation rules agreed on, so as to make the results of tedious fieldwork comparable.

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A NEW TOOL FOR THE SIMULTANEOUS INORGANIC NITROGEN SPECIATION ANALYSIS IN ENVIRONMENTAL SAMPLES

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There has been rising interest in the past couple of years to quantify nitrogen budget in the environment. It is of no small importance in what form and what oxidation state it occurs in different elements of ecosystems. That is why speciation analysis of nitrogen is a very important subject of environmental studies. Moreover, the environmental analytical chemistry has stimulated development of all kinds of methods allowing fast and routine speciation analysis of different elements [1, 2].

A new analytical method for fast and simultaneous determination of inorganic nitrogen species (NO_2^-, NO_3^-, NH_4^+) in environmental samples has been presented. This method is based on ion chromatography with UV-Vis diode array detection. The ions are separated in a strong ion-exchanger. Oxidized form are determined directly, while the reduced form is determined in the column hold up time after a post-column derivatization. On-line derivatization of ammonium ion is based on the Nesslerization method. The use of a diode array detector permits a simultaneous identification of the inorganic nitrogen species: NO_2^- at 208 nm, NO_3^- at 205 nm and NH_4^+ at 425 nm. The time of complete analysis was 8 minutes, and the retention times of particular ions were: NH_4^+: 0.72 min, NO_2^-: 4.47 min, NO_3^-: 6.66 min. Separation of nitrogen ions was realized with NaCl mobile phase. The detection limits obtained are: NO_2^--0.1 mg L^{-1}, NO_3^--0.05 mg L^{-1}, NH_4^+-1 mg L^{-1}. A good linear relationship between the peak area and the analyte concentration was obtained in a wide range of the concentrations. Experimentally established limits of detection (3σ of blank level, n=5) were: NO_2^- - 0.1 mg L^{-1}, NO_3^- - 0.05 mg L^{-1}, NH_4^+ - 1 mg L^{-1}. The precision of the method (for standard 5 mg L^{-1}, n=5) was obtained at the level 1 - 2.5 % [3].

This method has been successfully used for speciation analysis of inorganic nitrogen in rain water samples. Additionally, different environmental samples (also with more complicated matrix) such as drinking water, surface water (fresh and salt), ground water and soil leachates were tested.

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DEVELOPMENT OF AN UPLC-ESI-MS/MS ANALYSIS FOR THE DETERMINATION OF PHARMACEUTICALS IN SURFACE WATER

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Introduction: By consumption or improper disposal, pharmaceuticals end up in waste water, where they are not fully degraded, and end up in environmental waters. These chemical substances which are made to interact in living beings, have the properties to induce acute or chronic effects in the environment.

Objectives: The aim of this work was to develop a LC-ESI-MS/MS method using Ultra Performance LC instead of HPLC for five pharmaceuticals (from different classes, from one pharmaceutical company: flubendazole, pipamperone, propiconazole, domperidone, rabeprazole). A liquid chromatographic-tandem mass spectrometric (LC-MS/MS) method was already developed [1,2], with a sample preparation consisting of an extraction using a phenyl-phase SPE and a sample clean-up using an NH_2-phase SPE. Due to substantial matrix effects, a laborious standard addition method was necessary. With the aid of UPLC, a method can be developed using internal standards for quantification [3].

Results: An UPLC-MS/MS method was optimized and compared with the existing HPLC-MS/MS method. The same solvents (gradient elution) and sample preparation were used. The UPLC-method, using an Acquity UPLC HSS T3 column (1.8 μm, 2.1 x 100 mm), is faster (run time including equilibration): 9.6 instead of 24 minutes. With the UPLC-method matrix effects are diminished and in most cases even eliminated. Using internal standards (structural analogues) matrix effects are almost eliminated for all compounds (matrix effects ranging from 85 to 130%; CV%<15%, n=5), and are more similar for different surface water samples. This means that the standard addition method can be omitted and that calibration can be performed with internal standardization. In this way a less time-consuming and a more simplified method is achieved. If sample preparation was limited to the phenyl-phase SPE, thus without the clean-up step on the NH_2 column, matrix effects were still prominent. So sample preparation could not be simplified.

Limits of detection and quantification were calculated and for most compounds both were below 10 pg/l. Calibration curves were constructed with $r^2 > 0.98$. Recoveries for SPE were between 82 and 108%. Stability was already proven [2].

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SCREENING OF SEVEN NEW GENERATION PESTICIDE RESIDUES IN GRAPE AND WINE BY HPLC WITH UV DETECTION

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Plant protection treatments in vineyards could potentially result in pesticide residues in grapes that can pass into must and may remain in wine, affecting not only the wine-making process, but also the wine quality and, thereby, entering food chain causing.

Numerous analytical methods for determining pesticide residues in different fruits and vegetables, including grape and wine, have been reported, but only a few works have been found in recent literature concerning multiresidue methods for determination of more than one of new generation pesticides using HPLC - UV [1, 2]. A new analytical method was developed and validated using liquid chromatography for simultaneous determination of seven pesticides belonging to different chemical classes (azoles, strobilurines, benzoylureas, and a new oxazolidinone) in grapes and wine.

Solvent extraction of pesticides from grapes and wine was based on a method using a cyclohexane-dichloromethane (9+1 v/v) mixture, allowing the determination of various pesticide classes by other chromatographic techniques in the same extract [3]. The extract was cleaned-up by solid phase extraction using silica cartridges after elution with tetrahydrofurane. Pesticide separation (flusilazole, fenbuconazole, diniconazole, tebufenozide, famoxadone, trifloxystrobin and flufenoxuron) was performed by gradient elution liquid chromatography with a Hypersil ODS narrow-bore column in 30 min total time, using mixtures of acetonitrile-water as mobile phase at 2,6ml/min flow rate. Pesticides were detected and quantified with a variable-wavelength UV detector at 210nm (Injection volume 20μL).

Recoveries of pesticides from spiked grapes and wine at three levels (0,10-1,0-2,0 mg/kg for grapes and at 0,05-0,10-0,50 mg/L for wine) ranged from 79 to 107 % for grapes and 85% to 106% for red and white wine with an RSD between 3 and 11%. The limits of quantification (LOQs) of the method, as a signal to noise equal to 10, ranged from 0,01 to 0,10 mg/kg for grape and from 0,005 to 0,02 mg/L for wine samples. The "bottom-up" approach, according to the EURACHEM/CITAC guide was followed to estimate the expanded uncertainties for the selected pesticides in the two matrices. The estimated uncertainty associated to the analytical method was lower than 12% for all compounds tested.

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NEW APPROACHES TO MONITORING OF NON-IONIC SURFACTANTS IN THE ENVIRONMENT AND SURFACTANT BIODEGRADABILITY TESTING

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Surfactants create a huge stream of synthetic organic carbon directed into the aquatic environment due to their application in washing and cleaning, as well as in numerous industrial applications. Non-ionic surfactants (NS) have a similar significance as anionic surfactants (AS), while decationic and amphoteric surfactants are applied in significantly smaller amounts. Despite the common presence in surface water, NS are rarely monitored because of the high cost of determination. The development of NS separation in PTFE capillary trap (PTFECT), together with NS determination by the indirect tensammetric technique (ITT) significantly reduces the cost and time of single NS determination. NS separation in PTFECT is based on the fact that only the strongest surfactants are adsorbed onto PTFE surface. Adsorbed NS are easily eluted. ITT is the electroanalytical technique based on the recording of the differential capacity curve. The analytical signal in the ITT is the lowering of the tensammetric peak of the monitoring substance (usually ethyl acetate) due to competitive adsorption of surfactants-to-be-determined. The determination is tolerant to the presence of AS, which are the main potential interferent. The PTFECT -ITT technique is successfully applied for continuous NS monitoring in the River Warta and its small tributaries in the vicinity of Poznan (Poland).

Another area of PTFECT-ITT application is NS biodegradability testing. Primary biodegradation can be specifically, easily and quickly determined. This is significant for NS biodegradability testing in the presence of auxiliary organic nutrients, including dynamic continuous flow activated sludge tests. The opportunity of quick NS determination during biodegradation testing enables the isolation of bacterial strains responsible for NS biodegradation. Numerous tests with PTFECT-ITT concentration measurements were performed.

PTFECT can be also combined with HPLC or LC-MS NS determination. Multi-PTFECT was applied for the HPLC determination of such metabolites of alkylphenol ethoxylates (APE) biodegradation as short-chained APE and free alkylphenol. LC-electrospray MS was successfully applied for identification and quantitative determination of NS biodegradation metabolites .

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METHOD DEVELOPMENT FOR THE SIMULTANEOUS DETERMINATION OF ELEMENTS USING HYDRIDE GENERATION HIGH-RESOLUTION CONTINUUM SOURCE ATOMIC ABSORPTION SPECTROMETRY AND AN AIR-ACETYLENE FLAME

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For the last 30 years, several types of gas-phase sample introduction methods in analytical atomic spectrometry (AAS, OES, AFS) have been investigated and developed. The gas-phase sample introduction techniques can be roughly divided into four groups: i) hydride generation (HG), ii) cold-vapor generation of Hg, Cd, iii) chemical vapor generation (CVG) and iv) miscellaneous. This presentation surveys and discusses HG aspects of vapor-phase introduction, comprising the instrumentation for performing the reaction, the influence of the chemical reaction conditions, as well as the analytical application to real samples. The analytical figures of merit of the gas-phase sample introduction methods have been described in detail.

Atom trapping AAS is a technique that allows detection at ng/L level for several elements such as As, Bi, Sb, Se, Cd, Pb. The principle involves the generation of volatile species, usually by hydride generation using $NaBH_4$, *in situ* trapping these species at the quartz surface of an atom trap and finally re-volatilizing and atomizing analyte species by rapid heating of trap. The analysis of certified reference materials and real samples will be presented. This novel approach to hydride pre-concentration is fully competitive to *in situ* trapping in graphite furnace.

Finally, presentation summarizes and discusses the analytical methods and techniques for the simultaneous determination of elements using hydride generation high-resolution continuum source atomic absorption spectrometry and an air-acetylene flame.

DETERMINATION OF MICROBIAL VOLATILE ORGANIC COMPOUNDS: IS INDOOR MOULD DETECTABLE?

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Mould growth in indoor environment can be associated with adverse health effects. Beyond the fact that spores of mould may cause allergies and asthma [1] fungi produce plenty of microbial volatile organic compounds (MVOCs), which are suspected of being responsible for a wide range of specific and non-specific symptoms and discomfort [2, 3]. Measurements of the MVOC concentrations are therefore required for a proper assessment of the indoor air quality. In addition, the prediction of hidden indoor mould by detecting certain MVOCs might be a further challenge. For several years there has been a continuous interest in finding typical indicator components within the range of characteristic MVOCs originating from indoor mould. Some MVOCs have already been proposed as indicators of mould, e.g. 1-octen-3-ol, 3-octanol and several ketones, but it is still under discussion whether hidden indoor mould can actually be found by the detection of MVOCs. The main problems are seen in the very low concentrations ($<1\ \mu g/m^3$) in common rooms.

The present study contributes to clarify the correlation of indoor mould and MVOCs with six relevant mould species on two different substrates. We analysed MVOCs emitted from the mould species *Penicillium expansum, P. chrysogenum, Aspergillus versicolor, A. fumigatus, A. niger and Cladosporium cladosporoides* by means of solid phase micro-extraction (SPME) and GCMS. The mould species were cultivated on the synthetic agar dichloran chloramphenicol (DG 18) and on wet wall paper. The production of MVOCs was monitored over several weeks to detect changes in the emission rates between the initial stage and later periods of growth. The cultivation on the synthetic agar resulted in MVOC patterns with a wide variety of signals. In contrast, the growth on wet wall paper led to changed MVOC patterns with a reduced number of components. The emission rates were drastically diminished.

Components emitted by all six fungi species were 2-pentanol, 2-pentanone and 1-octen-3-ol. 2-Pentanol was only detected during the first days of growth whereas 1-octen-3-ol had a more constant emission rate over the whole period of growth. On the basis of our studies some MVOCs could be proposed as specific for single fungi, e.g. 1,3-dimethoxybenzene for *A. versicolor* and 2,4-pentandione for *A. fumigatus.*

Typical VOC patterns of apartments with mould burden are compared to our results.

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DETERMINATION OF POLYCYCLYC AROMATIC NITROGEN HETEROCYCLES IN ENVIRONMENTAL MATRIXES

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Polycyclic aromatic nitrogen heterocycles (PANHs) are present in the environment in broad range of concentrations. They are formed and released into the environment from similar sources like other polycyclic aromatic compounds (PAC) and have in many cases comparable toxic effects. PANHs accompanied by polycyclic aromatic hydrocarbons (PAH) and their derivatives, such as amino-, nitro-, methyl-, etc., may be found in comparable concentration levels [1]. Actual determinable amount of PANHs may vary depending on their fate in environmental samples. Successful identification and content determination of PANHs in complex mixtures requires efficient methods of their extraction from environmental samples, suitable preseparation, preconcentration and final analytical determination [2, 3]. Common extraction methods recommended for isolation of PAHs, their derivatives and analogues from solid samples may not be always suitable for aromatic heterocycles, such as PANHs. The very low value of final amount often determined in the complex mixture may be a result of significant difference in affinity of extracted pollutants for both applicable extraction solvents and real samples. Differences in extraction recovery of set of PANHs from soil observed using different extraction solvents and methods are presented. Separation and determination of a mixture of PANHs is often made by high performance liquid chromatography. Presence of PAH in contaminated soil samples and therefore in organic extracts from soil samples often complicates final chromatographic determination due to coelution of separated compounds with similar analyte-stationary phase interaction. The effective use of reverse-phase high performance liquid chromatography (RP-HPLC) for analytical separation and determination of polycyclic aromatic heterocycles in complex mixture with parent PAH is discussed. Optimised separation system enabling efficient HPLC separation of PANHs in the mixture with PAHs without pre-separation step is presented as a tool of selective and sensitive analytical determination of PANHs in particular environmental matrixes, .The use of different HPLC detection techniques for PANHs qualification and quantification in environmental matrixes is presented. Limits of detection obtained for HPLC detection techniques, are compared with those obtainable using other methods of PANHs determination.

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DETERMINATION AND STABILITY STUDIES OF CHOLESTEROL LOWERING STATIN DRUGS IN AQUEOUS SAMPLES USING HPLC AND LC/MS

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Cholesterol lowering statins are a group of pharmaceuticals, which are the most frequently prescribed agents for reducing morbidity and mortality related to coronary heart disease. Lovastatin (Mevacor®), pravastatin (Pravachol®) and simvastatin (Zocor®) have been introduced to the market since 1987. Lovastatin is a natural product; simvastatin and pravastatin are semi-synthetic products [1]. Statins exist in two forms, lactone and hydroxy acid in general. In vivo, the hydroxy acid forms are the active drugs to lower plasma cholesterol while the lactone forms are inactive (prodrug) [2]. Very few papers have been published reporting presence of statins in the environment. Regarding metabolites scarce data is available [3, 4].

Our research focused on statin stability under different, environmental conditions, like pH changes (from 4.5 to 8) and presence of sunlight. In order to supervise statins stability under laboratory conditions (sample preparation), various solvents were tested. Preliminary photodegradation experiments involved samples irradiation with the monochromatic Xenon light (254 nm). The study of toxicity and biodegradability has been carried out in order to determine compounds hazard to potential aquatic and terrestrial organisms.

Liquid chromatography coupled with electrospray ionisation tandem mass spectrometry (LC-ESI-MS-MS), in positive mode for all three compounds has been applied for the detection of selected compounds. A solid phase extraction was developed to enrich the analytes from aqueous samples. The method with advantages in terms of sensitivity for determination of pravastatin, lovastatin and simvastatin was put forward. Limits of detection for pravastatin was 19 ng/L, for lovastatin 14 ng/L and for simvastatin 16 ng/L, respectively. Method was linear up to 1000 ng/mL. The experimental values showed statins interconversions between lactone and hydroxy acid form, even at the room temperature, various pH and presence of sun light. The interconversion ratio varied according to different conditions from 2 to 30 %. This occurrence has been supervised in order to avoid its influence on the results of quantification. Biodegradability test proved that statin compounds tend to possess biodegradability. Preliminary toxicity test shows that statin drugs do not demonstrate toxicity to *Vibrio Fischeri* organisms.

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APPLICATION OF MEMBRANE EXTRACTION TECHNIQUES IN THE BIOMEDICAL AND ENVIRONMENTAL SAMPLE PREPARATION

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The complexity of environmental and biological samples forces the need of pretreatment stage proceeding. It means that either the isolation of the target substance and/or removing of the interfering molecules before the final analysis have to be proceed. This step must also bring the analyte of interest to a suitable concentration (detection) level, because in most cases they are present in the samples in trace amounts. It should be emphasized that very often, more than one technique or a combination of at least two of them, is necessary to proceed in order to isolate, purified and preconcentrate the analytes of interest from a complex matrices.

The most popular techniques in every day analysis are chromatographic methods or traditional liquid-liquid as well as solid phase extractions. Recently, also membrane extractions in various procedures have been introduced. Moreover, membrane separation is in special place due to offering various modes of separation and its flexibility on choice of suitable separation scheme. From the various membrane techniques supported liquid membranes (SLM) and microporous membrane liquid-liquid extraction (MMLLE) are of special interest because that combines the benefits of liquid-liquid extraction and membrane process. Membrane-based extraction techniques offer efficient alternatives to classical sample preparation techniques.

In this review a number of examples from the fields of environmental and biomedical analysis are discussed. High selectivity and enrichment factors, as well as the possibility of automated interfacing to chromatographic and other analytical instruments, are shown for quantitative analysis.

DETERMINATION OF NON-STRUCTURAL CARBOHYDRATES (NSC), INCLUDING INULIN AND STARCH, IN PLANT SAMPLES BY HIGH-PERFORMANCE ANION-EXCHANGE CHROMATOGRAPHY WITH PULSED AMPEROMETRIC DETECTION

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Carbohydrates are major constituents of plants. Their composition may vary with season, light availability and vegetative stage. Additionally, composition of non-structural carbohydrates (NSC) will reflect growth and variations in photosynthesis as well as abiotic stress phenomena, like hyperosmosis. Besides the importance of studying these biological properties of carbohydrates, their exact identification and quantification in plant material is also of vital importance to establish more precise and reliable carbon balances to study biogeochemical cycles and evaluate appropriate models.

For this reason, a rugged method for the reliable determination of non-structural carbohydrates (NSC), based on 12 sugar alcohols and carbohydrates, including the tri-saccharide raffinose, will be presented. Moreover, the polysaccharides inulin and starch, used for storage purposes by plants, are amenable to the procedure after appropriate hydrolysis. The method is based on High Performance Anion Exchange Chromatography coupled with Pulsed Amperometric Detection (HPAEC-PAD). A Dionex ICS 3000 ion chromatographic system equipped with a SP gradient pump, a column oven, an AS 40 autosampler and an ED amperometric detector with a gold working electrode is used throughout. Analyses are carried out using a CarboPac PA 10 column with 18 mMol NaOH as eluent at a flow rate of 1 mL/min. Overall analysis time including column regeneration is 30 min. The method is applied to a variety of plant samples: pine needles, tomato leaves and grass of the species "*Lolium perenne*". Identification of peaks is carried out by comparison of retention times with known compounds (mixture of standards) and, in case where peak assignment is obscure, by spiking the extract. Repartition of carbohydrates in the different plant samples will be reported. Besides "common" carbohydrates, like glucose and fructose, several other mono- and oligosaccharides were detected, indicating that composition of non-structural carbohydrates in plant samples is complex. Particular emphasis is given to the determination of both the polysaccharides inulin and starch which make up a considerable part of non-structural carbohydrates in plants.

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ICP-AES ANALYSIS OF METAL CONTENT IN SHELL MYTILUS GALLOPROVINCIALIS FROM CROATIAN COASTAL WATERS

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Marine organisms have been recognized as a useful tool in monitoring of the environment because of their ability to accumulate chemical elements and compounds in tissues. Mussels have wide distribution on all continents and, therefore, they are commonly used as bio-indicators of changes in marine environment. Bioaccumulation of metals and lipophilic organic compounds through extraction from sea water can lead to accumulation of species in contents above those in the abiotic environment, which is most often confirmed by chemical analyses of mussel tissues [1, 2]. However, analysis of crude shell samples is very rarely applied, despite that it could provide additional information in understanding of bio-mineralization process. In this study, metal content was determined in powdered shell samples by inductively coupled plasma atomic emission spectrometry (ICP-AES). Samples of *Mytilus galloprovincialis* were collected along the Croatian Adriatic coast, in vicinity of populated area, where greater anthropogenic influence was expected. Analytical procedure included total digestion of powdered shell samples and reference material, following by measurement of the contents of selected elements i.e., Al, Ba, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, Pb, Sn, Sr and Zn. Results have shown that samples collected near harbors, city waste or sewage, and chemical industry centers indicate the certain level of contamination. It is shown that shell analysis provides useful data in determination of environmental status and also in estimation of possible anthropogenic influences.

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PLUTONIUM ISOTOPES ^{238}Pu, $^{239+240}$Pu, ^{241}Pu AND ^{240}Pu/^{239}Pu ACTIVITY RATIOS IN BALTIC SEA ECOSYSTEM

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The principal source of plutonium radionuclides in the Baltic Sea is the atmospheric fallout from nuclear weapon tests. The other sources: plutonium releases from spent fuel facilities in Sellafield (UK) and Cap de la Hague (France) are less important. Since 26 of April 1986 it's been a new source of plutonium - Chernobyl plutonium, which should be taken under note in estimation of its radiological effects on the environment.

Experiments on plutonium sources in Gdańsk Bay and Gdańsk Basin indicated the main source of these radionuclides is rivers (mainly Vistula and Nemen) inflows which enrich these regions in 78% of its total content.

Marine plants and animals are capable to accumulate radionuclides from environment. That is why it's very important to recognize the impact of radionuclides on living organisms and possible transfer to human body through feeding way. In marine ecosystem the highest plutonium concentrations were found in sediments, but complex biogeochemical cycle of this element causes it is present in all environment compartments. The results of experiments indicate increasing of plutonium bioavailability in marine food chain of southern Baltic Sea as a effect of its desorption from sediments and accumulation in benthic organisms.

Plutonium ^{238}Pu and $^{239+240}$Pu concentrations were measured using alpha spectrometer. The results indicate the Baltic organisms do not accumulate them on the same levels. $^{239+240}$Pu concentration in marine animals from southern Baltic Sea ranged from 0,33 mBq.kg^{-1} w.w. (fish) to 95,7 mBq.kg^{-1} w.w. (priapulida), and the respective bioconcentration factors (BCF) were 100 to 27 000. However, almost whole plutonium (about 99%) amount is deposited in sediments. Because the area of Gdańsk Bay and Gdańsk Basin constitute only 1.2% and 4.4% of Baltic Sea area and the capacity 1.3% and 5.7% respectively, the results indicate the sediments of both regions are highly enriched in plutonium.

Activity of ^{241}Pu in environmental samples taken in 2 years after Chernobyl power plant accident was calculated using indirect method. The measurements of b-emitting ^{241}Pu were done through the measurements of its decay product - a-emitting ^{241}Am.

Plutonium released in the moment of reactor explosion existed as insoluble PuO_2, and almost whole amount fell as dry atmospheric fallout or with the wet fallout. Air filter analysis indicates after Chernobyl accident ^{241}Pu concentration increased suddenly over 3500 times and was decreasing slowly. In November 1986 got the level before the accident. Among analyzed organisms the highest ^{241}Pu concentration was found in brown algae *Pylaiella litoralis*, priapulida *Halicryptus spinulosus* and polychaeta *Antinöella sarsi.*

$^{240/239}$Pu activity ratios were measured using accelerator mass spectrometry (AMS). The nuclide compositions of plutonium in filter samples correspond to their means of production. AMS measurements of atmospheric fallout collected in April showed sufficient increase of ^{240}Pu/^{239}Pu atomic ratio from 0.28 from March to 0.47. Also such high increase of ^{240}Pu/^{239}Pu atomic ratio, cose to reactor core ^{240}Pu/^{239}Pu atomic ratio, was observed in September and equaled 0.54

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GERMANIUM SPECIATION:
IMPORTANCE AND ANALYTICAL METHODS

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Having obtained less attention than any other element of the 4th main group of the periodic table, germanium is a relatively uninvestigated element, although it possesses technological uses of major importance, such as being used as a technical catalyst in the PET (polyethylene-terephtalate) production, as material for optical components and glass fibres, and as base material for the semiconductor industry [1,2].

Relatively little is known about the environmental chemistry of this element, which exhibits, in contrast to its homologue silicon, not only siderophile, but also lithophile, chalcophile and organophile character. Even more concealed is the environmental occurrence and chemistry of organic germanium compounds, of which only mono- and dimethylgermanium are confirmed, however not trimethylgermanium [3]. Few reports exist in which even trimethylgermanium has been traced, but they appear to suffer from analytical artifacts. This emphasizes the need for reliable and accurate analytical methods for the speciation of organic germanium compounds.

We have developed therefore a suite of analytical methods suitable for the speciation analysis of germanium, which are based on GC/AED (gas chromatography with atomic emission detection), GC/MS and LC/MS. They are capable of determining both the fully alkylated Ge species (for example, tetraethyl- and tetrabutyl germanium), as well as the ionic alyklgermanium species.

Inorganic Ge can furthermore be detected based on its ability to form a volatile hydride (GeH_4) and a volatile tetrachloride ($GeCl_4$).

A further Ge species of interest is the so-called germanium sesquioxide (also called Ge-132 or *bis*-carboxyethyl germanium sesquioxide). Although not of direct environmental concern, this compound has attained importance as it is proposed as a medication or food supplement to combat a wide range of infectious diseases, including even HIV or cancer [4]. Not being officially approved nor produced under well controlled conditions, it is important to have analytical methods that monitor the potential contamination of this relatively harmless organic compound with the inorganic GeO_2 which, in contrast, possesses considerable toxicity for humans, so that several fatal cases have already been reported due to the uncontrolled intake of germanium sesquioxide-containing formulations. We will present various analytical approaches for the determination of Ge-132, useful for monitoring the purity of germanium supplementation products.

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DETECTION OF BIOTOXINS IN WATER USING IMMUNOASSAYS

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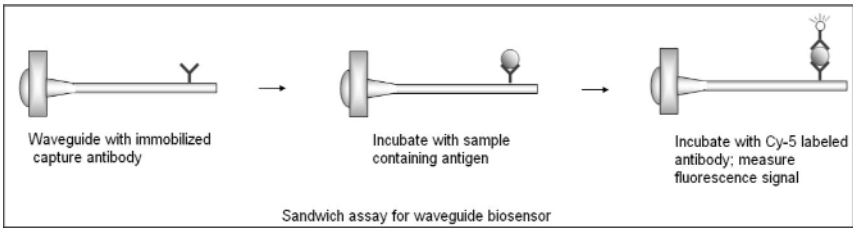
In this report, two types of immunoassays were employed to determine biotoxins in water. Protocol for detecting three potent biotoxins, including ricin, *Staphylococcal Enterotoxin B* (SEB) and botulinum, in water by commercial enzyme-linked immunosorbent assay (ELISA) kits was established and evaluated. Final results were obtained by this assay in eight hours and the detection limits were found to be 1 ng/mL for all three toxins. The validated assay was successfully applied to the determination of these three biothreat agents in emergency response program for the purpose of water security. The results showed that water samples were free from these agents. In order to reduce the assay time and enhance the ability of securing water quality, a fiber optic biosensor (RAPTOR, Research International Inc.) has been applied as another platform to rapidly analyze biotoxins in water. Ricin toxin was selected as the first analyte to be tested on this platform. Polyclonal anti-ricin antibody was captured on the waveguide through incubation. Four waveguides were assembled into each coupon, which could provide multiplex analysis in one assay run. Cy-5 labeled antibody was prepared by coupling Cy-5 dye with anti-ricin polyclonal antibody in 1M sodium carbonate buffer (pH 9.3). Labeled antibody was characterized by UV and MALDI-TOF. The prepared Cy5-labeled antibody was contained in the reagent vial and acted as reporter antibody during the fully automated assay. Preliminary results showed that 40 ng/mL of ricin toxin in water could be reliably detected. Spiked water samples with different matrices were analyzed using the biosensor and matrix effect was not observed. Based on readily assembled coupon, the assay run could be completed and the results reported in ten minutes. Thus, the biosensor has demonstrated to be a promising technology for rapid detection of biotoxins in water. In the future, more research work will be carried out to further improve the sensitivity and enhance reproducibility of the assay for the detection of ricin toxin. Furthermore, other biotoxins will be analyzed on this platform.



Sandwich assay for waveguide biosensor

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^{137}Cs ACTIVITY CONCENTRATION IN THE BALTIC SEA ENVIRONMENT

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The Baltic Sea is considered to be the most contaminated with caesium 137 (^{137}Cs) in comparison to any other part of the world ocean [1]. ^{137}Cs is an anthropogenic radionuclide with a relatively long half-life about 30 years. The main source of ^{137}Cs accumulated in the Baltic was the Chernobyl accident. After 1986, caesium isotope has dominated the radioactivity contamination of the Baltic water. It was estimated that the total input from this source was 4.7 PBq [2]. The knowledge about ^{137}Cs activity observed in the environment and about its transfer between marine environment elements (living and non-living) is of great importance.

^{137}Cs determination was performed in seawater and in fish soft tissue. Endemic species herring (*Clupea harengus*), perch (*Perca fluviatalis*), and flounder (*Platichthys flesus*), all of which being also of economic importance, were chosen for the analysis. Additionally an invasive fish round goby (*Neogobius malanostomus*) was analysed.

Seawater and biota samples were taken in the southern region of the Baltic Sea. Determination of ^{137}Cs in seawater was carried out using the radiochemical method, while for biota analysis a gamma spectrometry method was used.

In 1986, in the Polish economic zone of the Baltic Sea the average concentration of ^{137}Cs increased about 7 times in comparison to the level observed before the Chernobyl accident, and it reached the maximum value (100 Bq m^{-3}) in 1991. Starting from this year, there is observed continuous exponential decrease of the average ^{137}Cs activity.

In 2006, the average concentration of ^{137}Cs in waters of the Polish economic zone reached 41.9 Bq m^{-3} and it was still elevated in comparison to value observed in 1985 (12.6 Bq m^{-3}).

Generally, the average activity concentrations of ^{137}Cs found in herring samples were similar as regards sampling year, sampling place, and sex. In 2007, the average activity of ^{137}Cs in herring muscle tissue was 4.65 Bq kg^{-1}$_{\text{w.w}}$ in samples taken in the Darłowo fishery region and 3.81 Bq kg^{-1}$_{\text{w.w}}$ in samples taken in the Władysławowo fishery region.

Activity concentration of ^{137}Cs in a muscle tissue of perch, flounder, and round goby were lower than observed in herring muscle and they were 1.65 Bq kg^{-1}$_{\text{w.w}}$, 1.11 Bq kg^{-1}$_{\text{w.w}}$, and 1.72 Bq kg^{-1}$_{\text{w.w}}$, respectively.

Beside the fact that the radioactivity level in the studied fishes is higher than the one before Chernobyl, the risk connected with the fish consumption is negligible. This is confirmed by the estimated average committed effective doses related to annual intake from fish consumption in Poland.

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POSTERS

TOWARDS GAS CHROMATOGRAPHY-MASS SPECTROMETRY COUPLING PROTOCOLS FOR BOTH IDENTIFYING AND QUANTIFICATION ESSENTIAL OILS OF *AROMATIC AND MEDICINAL PLANT OF THE TUNISIAN FLORA*

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Essential oil of *Thymus capitatus* Hoff et Link is analysed by using four techniques: GC/pyrolyse/MS, GC/FID, electronic impact GC/MS (quadripole), and GC/MS (ion trap). Both major and trace components are analysed. The GC/pyrolyse/MS coupling provides reference to the exact mass compositions without any need of the previously purified references, neither for major or trace components. The comparison between this reference analysis and GC/FID shows that the FID response coefficients may vary by a mean 7% from one component to another. As it was expected, quadripole or ion trap response coefficients vary to a much greater extent (a mean 25%), although the two MS techniques response coefficients are first order consistent. We conclude that GC/MS coupling could be used not only as it is usual for reliable identifications, but also for a complete quantitative routine analysis of essential oils. Expected precision could be very similar to GC/FID precision provided correcting species by species the MS analysis by a mean value of the response coefficient measured for the MS 70 eV electronic impact ionisation technologies. The GC/pyrolyse/MS coupling is proposed as a relevant tool for analysing reference samples containing trace natural species that could not be purified.

HEAVY METAL MOBILITY IN SOIL FROM A MINING AND A RURAL AREA OF ROMANIA

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Soil contamination with heavy metals represents a potential risk to human health due to metals transfer in aquatic media, uptake by plants and subsequent introduction into the food chain. The aqua regia extractable metal content of soil is an indicator of the contamination level, but does not provide any information about metals mobility. In order to evaluate the mobility of heavy metals in soil, the diethylenetriaminepentaacetic acid (DTPA) and water extractable metal contents were determined in soils from a highly polluted mining area and an unpolluted rural area. The results showed that despite the significant difference between the aqua regia extractable metal contents in soil from the two regions, the percentages of DTPA extractable metals were comparable for Pb and Zn, while those for Cu and Cd were higher in the polluted region. The water soluble metal content was below 5% of the corresponding aqua regia extractable content in the majority of samples.

Keywords: heavy metals, soil contamination, DTPA, aqua regia.

A SIMPLE AND ULTRA-SENSITIVE LC-MS/MS METHOD FOR ANALYSIS OF ACRYLAMIDE IN DRINKING WATER

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A simple and ultra-sensitive LC-MS/MS method has been developed and validated to analyse acrylamide monomer in drinking water using [$^{13}C_3$] acrylamide as internal standard (I.S.).

Analytes were extracted from tap water samples using a SPE spherical carbon cartridge and chromatographed on IonPac ICE-AS1 microbore column under isocratic conditions using acetonitrile-water-formic acid (43:52:5, v/v/v) as the mobile phase.

Mass spectrometry analysis was done on a triple quadrupole mass analyzer API-3000, equipped with turbo ion spray interface and operating in multiple reaction monitoring mode to detect parent → product ion transition for acrylamide and I.S.

The method was validated for linearity, sensitivity, accuracy and precision, extraction efficiency, matrix effect and stability studies. Linearity in water was observed over the concentration range 0.1-2.0 μg/L for acrylamide. Limit of detection (LOD) and limit of quantification (LOQ) were 0.02 μg/L and 0.1 μg/L, respectively. Inter-day and intra-day precisions (RSD, %) across three validation level (0.1 μg/L, 0.5 μg/L and 1.0 μg/L) were less than 14.8 %. The accuracy determined at these levels was within ± 4.9% in terms of relative error (RE, %).

PERFORMANCE ASSESSMENT OF ClO_2 GENERATORS WITH SUPPRESSED ION CHROMATOGRAPHY AND DPD SPECTROPHOTOMETRY APPLIED TO ON-LINE REDUCED AND PURGED EFFLUENTS

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An alternative water disinfectant to sodium hypochlorite is chlorine dioxide, which must be produced on site to avoid explosion risks during storage and shipping operations. A number of experimental surveys have proved that unwilled inorganic by-products such as chlorate and chlorine 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 such 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 order to overcome such problems, we have recently developed an on-line equipment to collect and pre-treat the concentrated chlorine dioxide effluent. A flow fraction of the generator output is drawn by a peristaltic pump and alkalinized in a mixing coil with Na_2CO_3 delivered by a HPLC pump. The concentration of ClO_2 in the resulting fluid is monitored on-line by a chromatographic UV-VIS detector. Subsequently, the flow is alternatively diverted to a purging system and to a reduction chamber by acting on a two-way valve. Residual chlorite, chlorate and chlorine are determined in aliquots of the purged effluent, while total chlorite (that is, ClO_2 + ClO_2^-) are dosed in the reduced eluent. The analysis of chlorite and chlorate is performed in laboratory by suppressed ion chromatography while the dosage of chlorine is carried out on site by N,N-diethyl-p-phenylenediamine spectrophotometry. The overall setup and the effect of experimental conditions on analytical recoveries have been described.

AMPEROMETRIC BIOSENSOR BASED ON TYROSINASE IMMOBILIZED IN NAFION/TITANIA GEL MATRIX FOR DETERMINATION OF PHENOLIC COMPOUNDS IN WATER

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Phenolic compounds, widely distributed in the environment, belong to organic pollutants which are highly toxic, carcinogenic and allergenic. Many efforts have been made to develop the simple and effective methods of the determination of phenols. Amperometric biosensors based on phenol oxidases, tyrosinase and laccase, have been regarded as promising methods for determination of phenols because of their effectiveness and simplicity.

For detection of phenolic compounds an amperometric biosensor based on tyrosinase immobilized in titania sol-gel was developed [1]. The biosensor exhibited high sensitivities towards phenolic compounds, however, the stability of response of the biosensor was not satisfied. In order to improve the storage stability Nafion, perfluorosulfonated ionomer, was employed in construction of biosensor. It was reported that incorporation of Nafion in the sol-gel-derived metal films enhanced the long-term stability of biosensors [2]. In developed biosensors tyrosinase was immobilized on the surface of carbon electrode in titania gel mixed with Nafion in ratios 1:1 and 2:1 (v/v). Analytical performances of biosensors with and without Nafion were compared. Apart from storage stability also repeatability, reproducibility, sensitivity and operating stability of biosensors were evaluated. The functioning of proposed biosensors with Nafion was checked to be useful in determination of catechol in environmental water samples.

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NADH ELECTROOXIDATION ON MODIFIED CARBON ELECTRODES

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Electrochemical oxidation of nicotinamine adenine dinucleotide (NADH) has attracted a great deal of attention in respect of developing amperometric biosensors, biofuel cells and bioelectronic devices associated with NAD^+ (the oxidized form of NADH) dependent dehydrogenases. Near 300 dehydrogenases are known which require nicotinamide coenzymes as co-reactants [1].

The main problem with direct NADH oxidation at conventional electrodes, such as platinum, gold and carbon, is connected with large overpotential (in most cases higher then 1 V) that would lead to the oxidation of other electroactive species present in the media. Moreover, adsorption of NADH oxidation products at unmodified electrode surface lead to electrode fouling [2].

In order to reduce the high NADH oxidation overpotential and minimise electrode fouling carbon electrodes modified with mediator, Meldola's Blue (8-dimethylamino-2,3-benzophenoxzine), immobilized in titania layers was proposed. The amorphous titania layers, obtained by sol-gel technique, were chosen due to their biocompatibility with biomolecules. Influence of several parameters (e.g. Meldola's Blue concentration, pH and electrode potential) on electrode response was evaluated. Obtained results, especially significant reduction of NADH oxidation overpotential, suggest that proposed electrode could be used as a platform for construction of biosensors based on NAD-dependent enzymes. These biosensors can be used for determination of analytes in environmental samples.

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DETERMINATION OF VOCs ON BOARDS OF CHEMICAL TANKERS

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Release of toxic vapors of a cargo to the atmosphere on the ship and in its close neighborhood is unavoidable. The fumes from the engines and vents of bunker tanks can also be considered as a possible source of toxic vapors. Several studies suggested a relation between sailing as a crew member on chemical tankers and increased risk of various types of cancer [1, 2]. Only few studies have dealt so far with on-board sampling and identifying the cause. The aim of this study was to give a general overview on the concentrations of toxic vapors in different locations on boards of two chemical tankers (112 m length, equipped with 17 cargo tanks, with an overall load capacity of 10.000 m^3). The ships were trading between Rotterdam and the Baltic Sea area. The sampling was performed during the sea voyages as well as during the stay in the ports. Radiello® (Fondazione Salvatore Maugeri, Padova, Italy) passive diffusive samplers and GC/MS analysis were used to determine the concentration of several volatile organic compounds (VOCs), namely toluene, ethylbenzene, o-, p-, m-xylenes, 1,2,4-trimethylbenzene and 1,3,5- trimethylbenzene, over varied periods of sampling (8-100 hours). The concentration of all measured compounds was found to be relatively high in the engine rooms (up to 608 μg/m^3 for toluene during the tank-cleaning and up to 1550 μg/m^3 during stay in port of Rauma). Accumulation of toxic vapors was found to take place indoors, what indicates insufficient ventilation (sucking the vapors by the ventilation intake). Personal exposure of different crew members was investigated. Engineers were exposed to the highest concentrations, with the exception for toluene vapors.

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THE STUDY OF TOTAL NITROGEN AND TOTAL PHOSPHORUS CONTENT IN SEDIMENTS FROM THE PORT OF GDAŃSK

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The wastes are the product of our civilisation, posing significant pressure on the environment. The nutrients such as nitrogen and phosphorus, which get into the environment in excessive amounts, are the wastes also. The nitrogen and phosphorus sink with organic matter through the water column to the sea floor, where they are deposited. In advantageous conditions remobilisation may return contaminants from the upper sediment layers to the water and then to the food web. The wastes disposal in Poland is very low (a few percent of the whole wastes) [1, 2].

The aim of this work was to examine the level of total nitrogen and phosphorus pollution in port sediments and estimate the danger for environment when these sediments from deepening port areas will be deposited in the dumping sites in the Gulf of Gdańsk. The 52 samples of sediments from the Port of Gdańsk, shipyard basin of the North Shipyard, areas of Martwa Wisła and Wisła Śmiała were examined. In these samples the concentration of organic matter, total nitrogen, total phosphorus and humidity were determined. The correlation of the amount of nitrogen and phosphorus and organic matter content were determined. The content of total nitrogen ranged from 59 mg N kg^{-1} d.w. to 2831 mg N kg^{-1} d.w. in surface sediments and from 14 mg N kg^{-1} d.w. to 15 756 mg N kg^{-1} d.w. in cores. The concentrations of total phosphorus in sediment from all analysed areas and ranged from 33 mg P kg^{-1} d.w. to 1250 mg P kg^{-1} d.w. in surface sediments and from 2 mg P kg^{-1} d.w. to 712 mg P kg^{-1} d.w. in cores.

The results of this study can be useful for local authorities and port administration in making a decision about deposition of port sediments in deeper areas of the sea.

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THE COMPARISON OF TOTAL NITROGEN AND TOTAL PHOSPHORUS CONTENT IN SEDIMENTS ALONG THE POLISH COASTLINE

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Nutrients enter the Baltic Sea via rivers, atmospheric deposition, or direct discharges from pollution sources located on the coastline. Nutrients may originate from point sources, such as industrial or municipal wastewater outlets, or from diffuse sources, such as farmland, homes in rural areas and atmospheric deposition within the Baltic Sea catchment area. Nitrogen and phosphorus are the main nutrients in the bottom sediments. The phytoplankton fixes the nutrients into their biomass through primary production. When excessive amounts of nutrients enter the sea, the primary production increases rapidly, and the natural ecological balance of marine ecosystem is disturbed [1, 2].

The aim of this work was to examine the level of total nitrogen and phosphorus content in sediments along the Polish coastline and to estimate its environmental impact. In the period 2002-2006 the 143 samples of sediments from areas of high and low nutrient discharge were examined. The roadstead and port areas of Kołobrzeg, Darłowo, Ustka, Gdynia and Gdańsk, the regions of Piaśnica river mouth, Płutnica river mouth, Reda river mouth, and the stations near Rewa, Dębogórze Jurata and Hel were selected for investigations. In samples from these locations the concentration of organic matter, total nitrogen, total phosphorus and humidity were determined.

The levels of total nitrogen and total phosphorus content were higher in samples from urban areas of high anthropogenic impact, than in samples from regions where the anthropogenic pressure was lower. This situation suggests that the local authorities and/or port administration should make an environmental decision cautiously, for example about deposition of the dredging sediments in dumping sites in the Baltic Sea, because the ecological balance is very easy to be violated.

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P-10 A

THE INFLUENCE OF RESINOUS AND Al_2O_3 PROTECTIVE COATS ON THE METAL IONS RELEASE FROM DENTAL WIROBOND C ALLOY INTO 0,9 % NaCl SOLUTION

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Nowadays, hundreds of various alloys are available for prosthodonic restorations. The factors which determine their choice are mainly economic and corrosion aspects. Also physical properties or biocompatibility may affect their selection. In recent years an increasing attention has been drawn to the so-called adverse effects connected with the application of metallic implant materials. It is a well-known fact that oral cavity is a very aggressive environment for restorative materials. As a consequence metal ions are released from implanted biomaterials causing several toxic or allergic aliments [1]. A large amount of elements incorporated into the human body can be harmful to our health. Thus, it seems to be crucial to monitor and control the release of metal ions from dental alloys in order to assess their safety and biocompatibility [2]. For a number of years, noble metals alloys have been used in prosthetic dentistry. However, their high cost limits considerably their application. Nowadays, cobalt-chromium alloys, which are famous for strength, hardness and resistance to corrosion are preferred [3]. The material employed for the investigations in this study was commercially produced and typically used in prosthodontics CoCr alloy - Wirobond C (Bego). The aim of the present work was to evaluate the release of ions from Wirobond C alloy coated with various protective layers into 0,9% NaCl solution. CoCr alloy samples coated with lightcured acrylic varnish (Megaseal/Megadenta-one and two layers), varnish mixed with composite material C-Fill Flow (Megadenta-one and two layers) and Al_2O_3 (one, two and four layers) were tested. Dental alloys were conditioned in 0,9 % NaCl medium for six months. The qualitative analysis of the investigated solutions was performed with a ICP-ToF-MS OptiMass 8000 spectrometer (GBC). Additionally, the concentration of Cr, Co and Mo, being a main component of Wirobond C alloy was measured using an atomic absorption spectrometer, SOLAAR M6 (UNICAM). The elemental determination was made twice: after one week and 6 months after placing the alloys in 0,9 % NaCl solution. These analyses were completed with the surface characterization of studied alloys by scanning electron microscope (SEM) Hitachi S-4700, equipped with energy dispersive spectrometer (EDS), Thermo Noran. This study could enhance the understanding of the safety and biocompatibility of the dental restorative materials.

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REFERENCE VALUES AND AFFECTING VARIABLES FOR BLOOD COBALT IN THE GENERAL POPULATION

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Cobalt is an essential oligo-element which shows adverse effects when its body burden become excessive. For the general population, food and beverages represent the main source of cobalt exposure. This study was devoted to assess the reference range of Co in blood as well as the influence of some variables on the cobalt content. The whole population was 109 subjects living in Rome, aged between 20 and 61 yrs (mean 42 ± 10 yrs), 36 were women (mean age 39 ± 10 yrs) and 73 men (mean age 44 ± 9 yrs). The entire experimental scheme was designed taking strict precautions to avoid alteration in the analytical determination of cobalt. The sector field inductively coupled plasma mass spectrometry was used as quantification technique. Unexposed humans have blood cobalt levels ranging from 0.06 ng/ml to 0.15ng/ml (25th-75th percentiles), with a mean value ± standard deviation of 0.12 ± 0.08 ng/ml. Gender, age, BMI, diet of participants, fish and milk consumption, sport practice, alcohol consumption and smoking habits, medical cobalt sources such as dentistry implants, are considered as potential variables influencing Co levels in blood. A Binomial Logistic regression applied on the data gave gender as the predictor variable of the Co content, i.e., a woman was 3.6 times the odds of a man having high content of Co. A smaller set of clinic parameter (Hb content, siderosis, erythrocytes) was correlated to the Co concentrations by Spearman correlation.

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DETERMINATION OF SEVERAL HORMONE DISRUPTERS IN WATER BY SOLID-PHASE EXTRACTION, LIQUID CHROMATOGRAPHY AND ELECTROSPRAY TANDEM MASS SPECTROMETRY

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An endocrine disrupter is an exogenous substance or mixture that alters function(s) of the endocrine system and consequently causes adverse health effects in an intact organism, or its progeny, or (sub) populations [1].

The main evidence suggesting that exposure to environmental chemicals can lead to disruption of endocrine function comes from changes seen in a number of wildlife species (molluscs, crustacea, fish, reptiles, birds and mammals) in various parts of the world [1].

Their effect on wildlife is well documented and includes the feminisation of male foetuses, reproductive dysfunctions, behavioural changes and developmental problems.

There is also some limited evidence in humans that adverse endocrine-mediated effects have followed either intentional or accidental exposure to high levels of particular chemicals. The clearest example of an endocrine disrupter in humans is diethylstilbestrol (DES) [1]. Chemicals with hormonal activity, i.e. potential endocrine disrupters, include natural hormones, natural chemicals, synthetically produced pharmaceuticals and man-made chemicals.

In order to evaluate the impact of some hormone disrupters in Lisbon drinking water supply system, we developed and validated an analytical method based on the on-line combination of liquid chromatography and tandem mass spectrometry after solid phase extraction.

In this work several endocrine disrupters were studied, like natural and synthetic hormones (17-β-estradiol, estriol, estrone, progesterone, testosterone, mestranol and diethylstilbestrol and some industrial products (nonylphenol, 4-tert-octylphenol and bisphenol A).

Several parameters were optimised in order to get the best formation conditions of the precursor ion for each target compound, using an electrospray source, namely ionisation mode (positive or negative), capillary voltage and cone voltage. Two different precursor ion - product ion transitions were selected for each compound, one for quantification and one for qualification, and these ions were monitored under time scheduled multiple reaction monitoring (MRM) conditions, after optimisation of the collision cell energy of the triple quadrupole.

This method showed excellent linearity ranges for all compounds, with determination coefficients (r^2) between 0.9962 and 0.9999 with coefficients of variation lower than 3%.

Determination limits (between 1,2 and 50 ng/L), precision (RSD < 10 %) and recovery (between 55 and 87 %) studies were also performed.

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DETERMINATION OF ORGANIC COMPOUNDS IN SEWAGE SLUDGE AMENDED SOILS BY HIGH PERFORMANCE LIQUID CHROMATOGRAPHY

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In the recent years, the number of wastewater treatment plants operating in the European Union has greatly increased. This fact has led, in most countries, to an increase in the production of sewage sludge. Disposal routes for sludge includes, among others, incineration, spreading on agricultural land, land spreading in forestry or land filling [1], being application of sewage sludge to farmland the cheapest disposal option. However, some hazardous compounds can be present in sludge which can cause negative effects to the ecosystem. Some of the possible pollutants in sludge are the organic compounds: linear alkylbenzene sulfonates (LAS), nonylphenols (NP), nonylphenol mono- and diethoxylates (NP_1EO and NP_2EO) and phthalates, being di-(2-ethylhexyl) phthalate (DEHP) the most common phthalate ester. These compounds are used as anionic (LAS) and non-ionic (NP and NPEO) surfactants in a wide range of commercial usages mainly in the detergent industry and as additives in PVC plastics (DEHP) used in various products such as waterproof clothing, footwear, toys, blood bags and heat-seal coatings on metals foil.

In this context, the European Union published in 2000 the third draft of a future Sludge Directive entitled "Working Document on Sludge" [2], where limit concentrations of 2600 mg kg^{-1} dry matter (dm), 50 mg kg^{-1} dm and 100 mg kg^{-1} dm are fixed for LAS, sum of NP, NP_1EO and NP_2EO, and DEHP, respectively, for land application of sludge.

Some methods have been reported for the determination of these compounds in soils amended with sewage sludge but no method has been found in literature for the simultaneous determination of LAS, NP, NP_1EO, NP_2EO and DEHP.

In this work, a method for the simultaneous determination of LAS, NP, NP_1EO, NP_2EO and DEHP in sludge-amended soils is presented. Sample treatment is based on sonication-assisted extraction of an amount of 0.5g of soil with 3mL of acetone in triplicate and further clean-up by solid phase extraction with Waters Oasis® MCX 3cc, 60 mg cartridges. Simultaneous analytical determination is carried out in 30 min by high performance liquid chromatography with diode array and fluorescence detectors using gradient elution with acetonitrile and water. Recoveries of all of the selected organic compounds were higher than 70%. The developed method was tested to be suitable for routine monitoring of the organic pollutants in amended soils in order to evaluate the contamination effect of sludge application to agricultural sludge.

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DETERMINATION OF PHARMACEUTICAL COMPOUNDS IN SEWAGE SLUDGE BY HIGH PERFORMANCE LIQUID CHROMATOGRAPHY WITH DIODE ARRAY AND FLUORESCENCE DETECTORS

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Several tons of pharmaceutically active compounds are consumed yearly worldwide being discharged to wastewater via urine or faeces or by direct disposal from toilets. Then, wastewater is often treated in wastewater treatment plants which are not specifically designed to remove pharmaceuticals so they can finally be discharged into the environment through wastewater effluents or adsorbed into the sludge generated during wastewater treatments [1]. Most studies focus on the determination of the concentration levels of pharmaceutical compounds in liquid samples, such as drinking water, domestic wastewater and wastewater from hospitals, but few studies analyze concentration levels in sewage sludge samples. Nevertheless, it is important to determine pharmaceuticals in sewage sludge not only to evaluate the removal efficiencies of pharmaceutical compounds in sewage treatment plants but also to determine the concentration levels in sewage sludge which conditions its application to agriculture land [2].

The development of methods for the simultaneous determination of several pharmaceutical compounds with different physicochemical properties in a complex matrix such as sewage sludge requires a considerable effort.

In this paper, an analytical method for the simultaneous determination of five anti-inflammatory drugs (acetaminophen, aspirin, diclofenac, ibuprofen and naproxen), two antibiotics (sulphametozaxole and trimethoprim), a ß-blocker (propanolol), three lipid regulators (bezafibrate, gemfibrozil, and the metabolite clofibric acid), an antiepileptic drug (carbamazepine) and a nervous stimulant (caffeine) is proposed for the routine analysis of these pharmaceuticals in sewage sludge. The procedure consists on ultrasonic solvent extraction using methanol and acetone, clean-up by solid phase extraction using Oasis HLB extraction cartridges and determination by high-performance liquid chromatography with diode array and fluorescence detectors on-line.

Chromatographic separations were carried out on a ZORBAX Eclipse XDB-C18 column using gradient elution with acetonitrile and 25 mM potassium dihydrogen phosphate solution as mobile phase. Recoveries of the selected pharmaceutical compounds were higher than 70% for all of the pharmaceuticals except for acetaminophen, which could not be extracted. The proposed methodology can be a useful tool to evaluate the contamination of sewage sludge with pharmaceutical compounds before land application of sludge.

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HIGH PERFORMANCE LIQUID CHROMATOGRAPHIC DETERMINATION OF THIRTEEN PHARMACEUTICAL COMPOUNDS IN DIFFERENT THERAPEUTIC CATEGORIES IN WASTEWATER

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Pharmaceutical substances are extensively used in human and veterinary medicine. The occurrence and fate of pharmaceutically active compounds in the aquatic environment has been recognized as one of the emerging issues in environmental chemistry [1]. Due to their high consumption, pharmaceutical compounds along with their metabolites are continuously introduced into wastewater. It has been reported that the elimination of some pharmaceutical compounds during wastewater treatment processes is rather low and as result, they are found in surface, ground and drinking waters. For this reason they could cause the same exposure potential risk as persistent pollutants [2]. Pharmaceutical compounds represent a wide group of chemical compound which are classified according to their therapeutic use. Many of them are biologically active, often with estrogenic activity, and as a result they could have a potential influence in the environment and in human health [3]. Their ubiquity in the environment has prompted researchers to identify the effects that pharmaceutical compounds could have on non-target species and to evaluate chronic exposure risk of aquatic organisms as well as of human beings [4].

In this work, the development of an analytical method that enables the measurement of pharmaceutical compounds from five different therapeutic categories in wastewater is presented. Pharmaceutical compounds selected were analgesics and anti-inflammatory drugs (diclofenac, ibuprofen, naproxen, paracetamol and salicylic acid), psychoestimulant (caffeine), antibiotics (sulfamethoxazole, trimethoprim), lipid regulators (bezafibrate, clofibric acid and gemfibrozil), an antiepilectic drug (carbamazepine) and a ß-bloker (propanolol).

Solid-phase extraction used for sample preparation was optimised through several preliminary experiments involving the following variables: type of solid-phase, pH value of the sample prior to extraction and elution conditions from extraction cartridges. HLB Oasis cartridges, acidification of wastewater prior to extraction and acetone as elution solvent were the conditions finally chosen. Chromatographic separation was carried out on a Zorbax Eclipse XDB-C18 by gradient elution with KH_2PO_4 25mM aqueous solution and acetonitrile. Determination was carried out by high performance liquid chromatography with diode array and fluorescence detectors on line. Recoveries obtained were ranged from 70% to 100%.

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ANTI-OXIDATIVE DEFENCES AND Cd ACCUMULATION IN *NICOTIANA TABACUM, BRASSICA JUNCEA* AND *SOLANUM NIGRUM*

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Agricultural soils in many parts of the world are moderately or even severely contaminated with Cd due to long-term use of phosphatic fertilizers or sewage sludge applications. Cadmium is not an essential element and represents a risk in the environment due to its toxicity towards humans, animals and plants. Heavy metals, including Cd, cannot be degraded like organic pollutants and the clean up of a soil usually requires their removal [1]. Phytoremediation relies on vegetation for the *in situ* treatment of contaminated soils, sediments and water. This plant-based technology offers a number of advantages over traditional clean up methods as well as over other bioremediation technologies. The phytoextraction of heavy metals has emerged as a promising, cost-effective alternative to conventional engineering-based remediation methods that usually involve removal of the contaminated soil layer, physical stabilization or washing of contaminated soils with strong acids that change soil properties. Throughout the world, over 400 species of terrestrial plants have been identified as hyperaccumulators of various heavy metals. These are capable of taking up and storing high levels of heavy metals without suffering from metal toxicity with cell damage. However, these species commonly accumulate biomass slowly and the amount of metals extracted in a certain period of time can be a factor that limits their extensive use. Plant species with a fast growth rate may actually extract more metal from soils if the concentration of the element in the aboveground tissues is not very low.

In the present study, the use of *Nicotiana tabacum, Brassica juncea* and *Solanum nigrum* to extract Cd from a soil (0-35 mg kg^{-1}) was investigated. The effects of the metal on plant growth, metal accumulation, and antioxidant response after 90 days of growth in pots were measured. The results indicated the ability of these plants to remove Cd from the contaminated soil, with *Solanum nigrum* presenting the highest concentrations of Cd in shoots and roots for the higher Cd soil concentration.

The oxidative stress induced by heavy metals in plants may derive from active oxygen species (AOS) such as superoxide radicals (O_2^-), singlet oxygen ($^1O_2$), hydrogen peroxide (H_2O_2) and hydroxyl radicals (OH·). These AOS cause lipid peroxidation, enzyme inactivation and DNA damage, resulting in dramatic reduction of growth and productivity, or even causing plant death [2]. Changes in the activity of antioxidant enzymes including superoxide dismutase (SOD), peroxidase (POD), catalase (CAT), guaiacol peroxidase (GPX), ascorbate peroxidase (APX) and the contents of malondialdehyde (MDA), were examined. The results obtained suggested that antioxidative defence in the plants studied might play an important role in Cd tolerance.

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MICROWAVE-ASSISTED EXTRACTION OF POLYCYCLIC AROMATIC HYDROCARBONS FROM OUTDOOR PM_{10} SAMPLES

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Airborne suspended particulate matter (PM) is an important marker of air quality [1]. PM is the sum of all solid and liquid particles suspended in air, many of which are hazardous [1]. Recent research studies seem to indicate that PM10 (particles with an aerodynamic diameter smaller than 10 micrometers) are associated with negative respiratory responses [2]. These particulates include organic and inorganic matter, nitrogen and sulphur compounds, several heavy metals, radionuclides and polycyclic aromatic hydrocarbons (PAHs) [1].

PAHs are produced by high-temperature reactions such as incomplete combustion. After formation, most of these compounds are adsorbed on to PM causing serious health problems and may, possibly, contribute to cancer [2].

The analysis of PAHs in air samples remains a challenging task and requires an extraction and enrichment step prior to the instrumental analysis, due to their low levels and matrices complexity [3].

In the present work, the combination of microwave-assisted extraction (MAE) and liquid chromatography (LC) with fluorescence and photodiode array detectors was investigated for the efficient determination of 17 PAHs in real outdoor PM10 samples collected at an urban site (Oporto Metropolitan Area, Portugal).

In order to select the appropriate MAE conditions, solvent volume and mixture, as well as, temperature and extraction time were studied. Using the optimized operational parameters for MAE (30 mL of acetonitrile at 110°C during 20 min) and for a spiking range of 0.0455 µg/g for indeno(1,2,3-cd)pyrene to 6.909 µg/g for acenaphthylene, PAHs were successfully extracted from air samples with recoveries ranging from 67.3 ± 5.7% for anthracene to 112 ± 1.1% for fluorene, except for naphthalene (57.8 ± 18%) and acenaphthylene (29.8 ± 3.9%). Relative standard deviations less than 24% were attained.

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MODIFICATION OF TITANIUM DIOXIDE NONOPARTICLES AND ITS APPLICATION TO THE PRECONCENTRATION AND DETERMINATION OF CADMIUM IN WATER SAMPLES

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In the present work, a method was developed for the preconcentration of traces of cadmium in environmental samples by using a new adsorbent. The surface of TiO_2 nanoparticles were modified with SDS surfactant and PAN. The adsorption properties of the prepared adsorbent towards cadmium were investigated. The preconcentration and separation of cadmium was performed in a micro column filled with modified TiO_2 nanoparticles and the measurement was carried out by Flame Atomic Absorption Spectrometry. The effect of experimental parameters such as pH, flow rate, sample volume and elution condition on the preconcentration as well as the effect of foreign ions on the recovery were investigated. The adsorption capacity of PAN-TiO_2 adsorbent was found to be 9.22 μg mg^{-1} for cadmium. In the optimum conditions the linear range of the calibration graph was 5 - 200 ng ml^{-1} and the corresponding detection limit was 0.96 ng ml-1. The proposed method was successfully applied to the determination of cadmium in several water samples.

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NEW CHIRAL STATIONARY PHASE BASED ON STABILIZED BY ORGANIC LIGANDS GOLD NANOPARTICLES ON SILICA SURFACE FOR SEPARATION ß-BLOCKERS

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Organic ligand-capped gold clusters have been known for a number of years. The practical formation of stable, isolable monolayer-protected clusters has only been demonstrated in 1994 year by Schiffrin and co-workers [1]. Gold Nanoparticles are also attracted much attention for their outstanding, size-dependent chemical, electronic, physical and optical properties. The dimensions of these particles make them ideal candidates for the nanoengineering of surface and the fabrication of functional monostructures. Functionality of different ligands is very important, which sorts define the scope of application of corresponding gold clusters. For some time past, much effort has been expended on construction of functional interfaces.

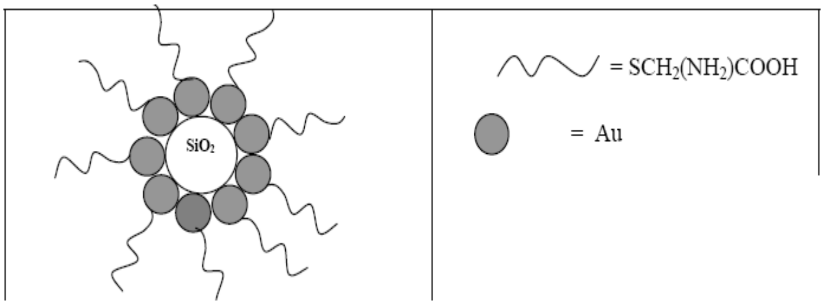

Fig. 1. Layout view of the adsorbtion of modified gold nanoparticles on the silicon oxide's surface.

Gold Nanoparticles have been prepared by reduction $HAuCl_4$] in an aqua solution by sodium citrate, and then they were modified by L-cystein. Prepared Nanoparticles have been adsorbed on silica.

Determination of optically active compounds is a subject of great interest in analytical chemistry, particularly in pharmaceutical domain. The fact that the enantiomers of the substances frequently exhibit differential pharmacological and toxicological properties has fostered the use of enantiomerically pure products.

The current interest in the resolution of the optical isomers is due to the growing awareness may be achieved by derivatizing the enantiomers with derivatizing agent, but much works in chiral separations have been directed to the development of new chiral selectors.

We suggest newest chiral selector for liquid chromatography - silica coated by adsorbtion of gold Nanoparticles modified L-cystein. The optimal conditions for enantioseparation of some ß-blockers in reversed phase mode and in polar organic mode were investigated.

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P-20 A

PITFALLS AND SOLUTIONS TO SILYLATION OF STEROID ESTROGENS FOR GAS CHROMATOGRAPHY-MASS SPECTROMETRIC ANALYSES: ARE WE UNDERESTIMNATING CONCENTRATION OF THE SYNTHETIC HORMONE 17α-ETHYNYLESTRADIOL?

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Silylation is a very common derivatization method used in the determination of organic compounds containing polar functional groups such as estrogenic hormones in environmental samples using gas chromatography-mass spectrometry (GCMS). Various reagents and solvents have been used to derivatise estrogens. Typical silylation reagents include the trimethylsilyl donor reagents such as *N*-*O*-bis-(trimethylsilyl)-trifluoroacetamide (BSTFA) and *N*-methyl-*N*-trimethylsilyltrifluoroacetamide (MSTFA) or the tert-butyldimethylsilyl donor *N*-(*tert*butyldimethylsilyl)-*N*-methyltrifluoroacetamide (MTBSTFA). Catalysts such as trimethyl chlorosilane (TMCS) together with trimethylsilyl imidazole (TMSI) or *t*-butyldimethyl chlorosilane (TBCS) and *t*-butyl dimethylsilyl imidazole (TBSI) are usually added to enhance derivatization. For example many previous studies have used BSTFA with pyridine, BSTFA with isooctane/acetone, BSTFA + 1% TMCS with pyridine, MSTFA with ethyl acetate, MSTFA + 1% TMCS with acetonitrile/pyridine, and BSA with dimethyl formamide. TBS derivatives of estrogens have been prepared using MTBSTFA with ethyl acetate, acetonitrile, dichloromethane, or hexane.

We have recently reported an improved derivatisation procedure [1] for the simultaneous determination of the steroid hormones 17α-ethinylestradiol (EE2) and estrone (E1) using GCMS after a re-evaluation of some of the common silylation procedures using MSTFA, BSTFA and MTBSTFA.

We found that silylation of EE2 using MSTFA or BSTFA+ 1% TMCS in ethyl acetate, acetonitrile and dichloromethane solvents produced multiple peaks corresponding to TMS-E1, and 3-mono-TMS-EE2 and/or 3,17-di-TMS-EE2 in variable proportions depending on the solvent used. When pyridine or dimethyl formamide solvents were used in the silylat ion of EE2 under the same reaction conditions, only 3,17-di-TMSEE2 derivative was formed. Derivatization using MTBSTFA reagents using ethyl acetate, acetonitrile, dichloromethane, pyridine and dimethyl formamide resulted in almost 100% conversion of mono-TBS-EE2 to the TBS-E1.

Therefore, we believe that typical methods used in some previous GC–MS determinations of E1 and EE2 in environmental water and/or sediment samples are subject to speculation. However, we can confirm that any of the TMS reagents can be used with either pyridine or dimethyl formamide under suitable reaction conditions.

We are currently testing our hypothesis using spiked samples and some environmental samples, analysed using different approaches including (i) conventional silylation method versus improved silylation using GC-MS and (iii) an LCMS-MS method which does not require derivatization.

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THE SEPARATION OF THE TRIAZOLE FUNGICIDES BY HPLC USING SILICA MODIFIED WITH CHITOSAN DERIVATIVES

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Pesticide residue analysis in environmental samples has received increasing attention in the last few decades. Triazole derivatives represent the most important category of fungicides due to their excellent protective, curative and eradicant power against a wide-spectrum of crop diseases. Triazole fungicides have a common structural moiety, the 1,2,4-triazole ring, which is connected to a hydrophobic backbone through position 1. Asymmetrical carbons are typically present in the molecule and makes chitality almost ubiquitous for triazole derivatives. Considering that the chiral centers of triazole fungicides are locater close to the 1,2,4-triazole ring, a key template in the binding of the fungicides, chirality is expected to play a crucial role in the bioactivities of triazole fungicides [1].

The separation and determination of selected triazole derivatives (diniconazole, penconazole, propiconazole, difenoconazole and tebuconazole) and their enantiomers by HPLC were investigated. The majority of chiral stationary phases (**CSPs**) are prepared by attachment of chiral selectors to the surface of silica gel microparticles. Among the most extensively studied chiral selectors are derivatives of cellulose and chitosan particularly their phenylcarbamates [2].

In our work chitosan have been used as starting material for the preparation of new chiral stationary phases. Aminopropylsilica modified by chitosan and nanocompositional chitosan-silica [3] were used as matrix of **CPSs**. Two methods a modification of immobilized chitosan is designed: 1) the total modification by 2,4-dimethylphenylisocyanate; 2) the modification of amino groups of chitosan by 1,2-phthalic dicarboxaldehide/ N-isobutyryl-L-cysteine reagent. The four new **CSPs** were prepared.

It has been show, that chitosan's derivatives are effective modifiers of silica for the separation of studied substances. The influence of the structure of sorbates, their size, bulkiness, hydrophobicity, steric effects, position of chiral center and polar groups was investigated. The retention and resolution of analytes in different modes of HPLC were studied. The best results were achieved in the normal phase mode. The mixtures of hexane with different polar additives (chloroform, propan-2-ol, 2-methylpropan-2-ol, ethylacetate, trifluoroacetic acid, triethylamine) were used as mobile phase. The effect of nature of polar additives to hexane on the separation of enantiomers depends of **CSPs** structure. The aim of our work is a comparison of the enantiorecognition of phenylcarbamate derivatives of cellulose and chitosan. The enantioseparations of tested compounds were achieved.

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CONDENSATION OF AROMATIC ALDEHYDES WITH POLYURETHANE FOAM AND ITS APPLICATION IN CHEMICAL ANALYSIS

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Schiff bases (imines) can be obtained by condensation of aldehydes or ketones with amines. They have been known for more than 130 years, but they became the subject of many investigations relatively recently. Last years there is a pronounced tendency of growing attention to the problems of synthesis and practical application of Schiff bases. The interest to these compounds in analytical chemistry is connected with the fact that their protonated form in aqueous solution is colored. This provides for possibility of using such type of reactions for photometric determination of aldehydes, ketones and amines. In spite of a lot of works devoted to the analytical application of the reactions of Schiff base formation, search for new forms of ketonic- and amino-components is still of current importance. This is connected with the fact that aromatic amines used in such a reaction are frequently carcinogenic. Besides, the crucial question is improvement of sensitivity of analysis due to the determination directly in the sorbent or chemosorbent.

We have found that terminal toluidine groups of polyurethane foam (PUF) can parti-cipate in condensation reaction with different aromatic amines resulting in formation of colored polymeric Schiff bases. The spectra of these products were recorded using diffuse reflectance spectrometer. The influence of phase contact time, acidity, temperature and concentration of carbonyl component on the yield of the polymeric Schiff bases has been investigated. It has been shown that Kubelka-Munk function of the polymeric Schiff base depends linearly on the concentration of aromatic aldehyde in the solution. This proves a fundamental possibility to determine the carbonyl components by the condensation with PUF using diffuse reflectance spectroscopy. The determination of major moiety in food vanillin has been made.

It has been shown that scanner, digital camera and computer data processing can be used for evaluation of color intensity of polymeric Schiff bases.

The main advantages of PUF as a polymeric chromogenic reagent are: relatively low cost, availability, mechanical durability, chemical stability in diluted acids and solvents. It can be easily separated from other components of the reaction mixture.

This approach is promising for monitoring aromatic aldehydes in environment.

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MERCURY CONTAMINATION IN THE VICINITY OF A CHLOR-ALKALI PLANT AND POTENTIAL IMPACTS ON LOCAL POPULATION

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A mercury-cell chlor-alkali plant operated in Estarreja (North-western Portugal) for 50 years and caused widespread contamination of the neighbouring environment. Although production by this process ceased in 2002, mercury (Hg) contamination from the existing plant still remains significant. The main objectives of this study were to investigate Hg impact on the nearby environment, since land surrounding the plant is used for crop growing and grazing cattle on a daily basis, and to evaluate Hg contamination of foodstuff (vegetables and fish), considering that this is one of the main routes for metal intake by humans.

To assess the level of contamination we collected soil samples from agricultural fields in the vicinity of the chlor-alkali plant, extending the study by taking samples of the predominant vegetation suitable for animal and human consumption, water samples from wells, and several fish species from a nearby coastal lagoon, with the aim of gaining a preliminary insight into the potential for contamination of the terrestrial and aquatic food chain. In order to determine population exposure to Hg, hair samples were collected from local residents.

Total Hg concentration in the 0-15 cm top layer of soil collected in Estarreja was found to be highly variable, ranging between 0,010 and 91 mg kg^{-1} (mean 5,4 mg kg^{-1}, median 0,41 mg kg^{-1}), although we found that Hg contamination of soils was restricted to a confined area nearby a stream used to transport the effluents from the plant.

Lolium perenne roots contained between 0,0070 and 2,0 mg kg^{-1} (mean 0,38 mg kg^{-1} and median 0,063 mg kg^{-1}), and there is evidence that root systems uptake Hg from the soil. Levels of Hg in the aerial parts of plants ranged between 0,018 and 0,98 mg kg^{-1} (mean 0,16 mg kg^{-1}, median 0,067 mg kg^{-1}). It appears that higher Hg concentration in soils and roots implies higher Hg concentration in leaves. This is likely to result from translocation of Hg to the aerial parts in *Lolium perenne* species or from the atmospheric deposition of airborne particles as well as absorption of atmospheric Hg.

Total Hg concentrations in water samples ranged between 12 and 846 ng L^{-1}, all samples presenting concentrations below the maximum level allowable for drinking water defined in the Portuguese law (1,0 μg L^{-1}), leading us to conclude that the water system is not significantly impacted by the metal.

Hg levels in all fish samples were below the maximum limit defined in the Portuguese law (0,5 mg kg^{-1}), ranging from 0,004 to 0,24 mg kg^{-1}. Also, vegetables collected presented maximum Hg concentration of 0,17 mg kg^{-1} (mean 0,058 mg kg^{-1}, median 0,040 mg kg^{-1}). These results lead us to conclude that, in general, food is not contaminated and should not be a responsible for major exposure to the metal.

Hg determined in Human hair samples (mean 1,3 mg kg^{-1}, median 1,0 mg kg^{-1}) can be considered within normal limits, according to WHO guidelines, suggesting that Hg is not affecting the resident population.

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SEQUENTIAL EXTRACTION OF HEAVY METAL IN SEDIMENTS AT RIVER AND MARINE OF MID-BLACK SEA COAST, TURKEY

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Heavy metals are present in river and marine waters in both dissolved and solid forms and play a role in many biogeochemical cycles. These metals are rapidly and efficiently removed to the sediment via adsorption onto surface particles, precipitation, and incorporation into biogenic material [1]. Sediments have proved to be excellent indicators of environmental pollution, as they accumulate pollutants to the levels that can be measured reliably by a variety of analytical techniques. The geochemical partitioning of heavy metals in sediments is of great importance in risk assessment and remedial investigation [2]. In this research, the sequential extraction procedure of heavy metal (Cr, Cd, Cu, Pb, Ni, Zn, Fe, Al, Mn) contaminated sediments have been investigated in order to provide better guidance on acceptable procedure for contaminated sediments to use in the development of the sediment treatment procedures. The extraction of heavy metal spiked into surface sediments with varying properties were investigated. After the routine analysis of sediment samples such as TC, TOC, IC, pH, water content, redox potential, electrical conductivity and particle size distribution; the extractable contents of heavy metal in five sediment samples collected from Yeşilirmak river, Abdal stream, Mert stream, Kizilirmak river and Kurupelit shore have been analysed using the sequential extraction procedure (SEP) [3]. In order to perform a mass balance, a five step has been include, i.e. digestion of digestion residue from the five extraction steps. Sequential extraction experiments have been shown provide a convenient means to determine the metals associated with principal accumulative phases in sedimentary deposits. Sequential extraction schemes provide information on the potential metal bioavailability and mobility of sediment-bound metal, design of remediation process and heavy metal bioavailability. The residue HF-$HClO_4$ digestion for recovery studies. Sediments samples ($<63\ \mu m$) were subjected to a total digestion technique (HF-$HClO_4$ conc.) and analyzed for selected heavy metals (Cr, Cd, Cu, Pb, Ni, Zn, Fe, Al, Mn) by this ICP-AES. The accuracy evaluated by comparing total trace metal concentrations with the sum of the five individual fractions, proved to be satisfactory. Validation of analytical results was checked by both recovery studies and analysis of standard reference material (BCR-701). BCR-SEP Community Bureau of Reference of the Europeans Union was validated using BCR-701 sediments certified materials. This research deals with the study of heavy metal speciation of contaminated river and marine sediments but still a long-term investigation with special emphasis on heavy metal search treatment technologies in contaminated sediments is required.

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CHROMIUM DETERMINATION FROM ROMANIAN WINES USING ATOMIC ABSORPTION SPECTROMETRY

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This paper presents a method for the determination of chromium in wine samples previously digested with HNO_3-H_2O_2 mixture using electrothermal atomic absorption spectrometry.

Chromium (III) is one of the essential trace elements in the human body that is involved in glucose and lipid metabolism [1,2]. The estimated safe and required dietary intake of Cr(III) is 0.05-0.20 mg/day [3].

The aim of the present research is to determine the chromium concentration from wines and the objective is completely justified, moreover that the wine could contribute an important fraction of the dietary intake of Cr [4,5].

The optimal temperature program of the furnace is defined according to pretreatment and atomization curves constructed in the presence of the white wines from Romania and for aqueous standard solution of Cr (10 µg/L). It has been investigated the optimal conditions of the furnace for both background corrections: Zeeman correction and deuterium lamp correction, respectively. The calibration curve was made using a chromium solution prepared using nitric acid 3,46 mole/L. The method accuracy was analyzed using white wine samples that were fortified with chromium at different levels of concentration. The recovery level for concentrations between 1-10 µg/L is in the range 80-107%.

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STUDIES REGARDING FOOD QUALITY MONITORISATION-HEAVY METAL CONTENTS IN FRUITS IN ROMANIA

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Determinations of chemical contaminants in food are important in environmental monitoring for the prevention, control and reduction of pollution as well as for occupational health and epidemiological studies.

The aim of this study was to determine the lead and cadmium concentrations from 7 varieties of apples and to establish if these fruits are suitable for consumption. Other objective of the research was to correlate previously published results regarding lead and cadmium contents in other fruits (plums, strawberries) with these new ones [1].

The presence of heavy metals in living organisms is harmuful, undesired, it may create health problems because of its tendency to bioacumulate and present no physiological function for human body [2]. Cadmium can disturb kidney functions, and some studies indicate a cancerous effect [3]. Sources of cadmium exposure are cigarette smoking, ingestion of food grown on contamined soil. It is known that phosphate fertilisers contain cadmium [4] and lately environment cadmium contamination through phospate fertilisers represent an increasing problem. Lead is a naturally occurring substance and can be found in organic and inorganic forms [5] that has the most significant toxic effect from the heavy metals. Sources of lead exposure are represented by leaded gasoline, leaded paints, pesticides, cans, battery manufacturing, drinking water, vegetal products grown on lead-contamined soil.

Heavy metals concentrations were achieved by electrothermal atomic absorption spectrometry (ETAAS). In order to effect the measurements it was used an atomic absorption spectrometer Zeenit 700 from Analytic Jena equipped with autosampler AS52 S for dilution. The lead content in plums ranges between 0,02 - 0,047 mg/kg, for strawberries between 0,006 - 0,038 mg/kg and for apples between 0,001- 0,049 mg/kg. The cadmium content in plums ranges between 0,007 - 0,023 mg/kg, for strawberries ranges between 0,016-0,138 mg/kg and for apples between 0,0005-0,014 mg/kg.

The levels of lead and cadmium was correlated with those set by Commission Regulation 466/2001 and Romanian legislation. Commission Regulation 466/2001 sets a lead limit of 0,1 mg/kg in fruits, 0,2 mg/kg in berries and small fruits, and a cadmium limit of 0,050mg/kg in all fruits. The same values were adopted by Romanian legislation, as well (Order no.1201/2003/106/2004).

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SPE-HPLC/DAD DETERMINATION OF TRIMETHOPRIM, OXYTETRACYCLINE AND ENROFLOXACINE IN WATER SAMPLES BEFORE AND AFTER RO/NF MEMBRANE TREATMENT

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The occurrence of veterinary and other pharmaceuticals in environment has led in the last ten years to increased research space in analysis of pollutants in surface water and sediments. As possible environmental threats of this compounds are still not well known, every information on pharmaceutical presence in water is of environmental relevance. Of all the emerging contaminants human or veterinary antibiotics are the biggest concern since their environmental emmissions can increase the occurrence of resistant bacteria in the environment, which can lead to unforseen consequences. One of the major sources of these compounds are industrial process wastewaters. To unburden surface recipients from pharmaceutical active compounds, their removal is recommended. As conventional water treatment processes are ineffective in the removal of emerging contaminants, methods such as carbon adsorption, advanced oxidation processes and modern pressure driven membrane processes nanofiltration and reverese osmosis (NF/RO) should be used for this purpose.

This work focused on the SPE-HPLC-DAD analysis method development of veterinary pharmaceuticals of three different classes in highly complex wastewater matrices and their removal by NF/RO membrane separation processes. The pharmaceuticals investigated include sulfonamide synergist trimethoprim, oxytetracycline, and fluoroquinolone enrofloxacine.

The analytical method involves pre-concentration and clean-up by solid phase extraction (SPE) on polystyrenedivinylbenzene Varian Empore extraction disks and determination by high-performance liquid chromatography (HPLC) on Varian ProStar500 HPLC/DAD with Varian RP-18 column. Detection and quantification was performed at 254 nm. The best separations were achieved with mobile phase 0.5 % formic acid and 1 % trifluoroacetic acid in 0.05 M ammonium acetate-methanol, 70+30, (v/v).

The removal of above mentioned pharmaceuticals from wastewaters was investigated by NF/RO membranes. The analytical results on pharmaceuticals in permeate streams showed complete rejection of all by tight NF membranes and RO membranes.

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^{210}Po, ^{238}U AND $^{239+240}$Pu INFLOW IN RIVER CATCHMENT AREA ASSESSMENT BY ADVANCES CLASSIFICATION TECHNIQUES

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The present study deals with the application of self-organizing maps (SOM) to classify and interpret a monitoring data set for Vistula river water quality basing on concentration values of radiochemical parameters. The data set represents analytical monitoring data for 3 alpha emitters (^{210}Po, ^{238}U and $^{239+240}$Pu) measured in surface water samples collected at 19 different sampling locations (8 in major Vistula stream while 11 in Vistula tributaries) within four seasons: winter, spring, summer and autumn in the framework of one year-term quality monitoring research. The advantages of SOM algorithm and its classification and visualization ability for environmental data sets are stressed. The neural-network based classification applied mate it possible to reveal specific quality patterns related to both seasonal and geographical variability. In the middle and upper part of Vistula catchment as well as in the right-shore tributaries an inflow of ^{210}Po and ^{238}U during summer and winter is the lowest. An inflow of ^{210}Po and ^{238}U increases significantly during spring and autumn in the Vistula river catchment, especially in the delta of Vistula river. The high concentration of anthropogenic originated $^{239+240}$Pu indicates "site-specific" character of pollution in two large left-shore tributaries located in the middle of the Vistula river. The efficient location classification could lead to an optimization of river radiochemical nets to a better tracing natural and anthropogenic changes along Vistula river stream.

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CHEMOMETRIC METHODS FOR EVALUATION OF MERCURY MOBILITY IN ENVIRONMENTAL SOLIDS

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The mobility of mercury in different soils and sediments has been evaluated by sequential extraction (SE). The procedure of SE involves five subsequent stages performed with the solutions of chloroform (organomercury species), deionized water (water-soluble mercury species), 0.5 M HCl (acid-soluble mercury species), 0.2 M NaOH (mercury bound to humic matter) and aqua regia (mercury bound to sulfides). Additional thermo desorption stage to determine elemental mercury was applied only for extremely contaminated samples. The contribution of mercury in particular fractions in the environmental solids can be only semiquantitatively compared with the analogous data reported by other authors because of the slight differences in the methods of fractionation. Mercury mobility in was assessed on the basic different contribution of mercury species in different sediments and soils using the same SE scheme. Chemometric evaluation allowed identification of uncontaminated, moderately and heavily polluted samples and shows different patterns for uncontaminated, moderately and heavily polluted samples.

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SAMPLING AND TEM STUDY OF ULTRAFINE PARTICLES IN THE URBAN ATMOSPHERE OF ROME: FIRST RESULTS

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Many toxicological studies have pointed out that particles in the ultrafine size range (<100 nm) pose special problems to the lungs [1] due to their high efficiency of deposition. At the same ponderal dose ultrafine particles (UFPs) have been reported to produce more inflammation in experimental studies with respect to respirable particles made from the same material. UFPs are characterized by large surface area and particle number per unit mass. Adverse respiratory and cardiovascular effects leading to morbidity and mortality in susceptible subpopulation have been associated with ambient UFPs. Moreover controlled exposures to carbonaceous UFPs [2] evidenced effects on the cardiovascular system. Several *in vitro* and *in vivo* studies have demonstrated that UFPs cause oxidative stress. In this context it is important to study UFP morphology and composition in urban areas. With this purpose UFPs have been sampled in downtown Rome. The sampling site was located in a street with high density of autovehicular traffic. Particles have been classified in the range 8 -50 nm electrical-mobility diameter using a TSI 3080 electrostatic classifier. The classifier operates drawing polydisperse aerosol through a Kr-85 radioactive bipolar charger, establishing a bipolar equilibrium charge level on the particles. The particles then enter the differential mobility analyzer and are separated according to their electrical mobility. Monodisperse aerosol are then either counted by TSI 3786 ultrafine water-based condensation particle counter or sampled by means of a TSI 3089 nanometer aerosol sampler. The sampler consists of grounded cylindrical sampling chamber with an electrode at the bottom of it. Particles are collected due to the electric field applied between the chamber and the electrode. Samples collected are investigated using energy filtered transmission electron microscope (EFTEM) in combination with energy dispersive X-ray spectroscopy (EDX) and electron energy loss spectroscopy (EELS). The first results have shown a seasonal variability of particle number concentrations, with average value of 23.000 cm^{-3} in the range of 20-760 nm in spring and average value of 42.700 cm^{-3} in autumn. EFTEM observations showed that most of the particles observed were carbonaceous. The lower levels observed during periods characterized by less intense traffic demonstrated that autovehicular emissions are the main source of these particles.

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PRELIMINARY RESULTS OF POTENTIAL CORRELATIONS BETWEEN GEOCHEMICAL PARAMETERS, METALS CONTAMINATION AND MICROBIAL DIVERSITY IN NORTH SEA SEDIMENTS

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Many coastal areas worldwide are contaminated by metals such as Cd, Cu, Pb, Zn, Hg and Ni, and these contaminants usually accumulate in sediments. On the Belgian Continental Plate, (BCP), metal concentrations in sediments are above, or just at the level of the Ecological Assessment Criteria (EAC), which are defined by the OSPAR Commission as concentration levels above which concern is needed.

As the most abundant organisms in the sediments, microorganisms play a key role in the biogeochemistry of benthic ecosystems, including a variety of processes which may affect metal mobility and bioavailabity. This may lead to both the alteration of microbial biodiversity and to metal bioaccumulation in higher trophic levels through increased leaching of metals from the sediments (metal upward fluxes).

Two sampling cruises have been carried out in February and July 2007 at 7 stations near and far from the Belgian coasts. Geochemical parameters such as oxygen at the water-sediment interface, pH, Eh, dissolved and particulate sulphides, granulometry specific surface area (SSA) have been measured in the sediments at various depths. Metals concentrations have also been evaluated in the sediment particles (after a strong mineralization using concentrated acids) and in porewaters by using DET and DGT probes. A soft leaching of sediment with a 1 M HCl solution has also permitted to calculate a toxicity index towards metals easily associated to Acid Volatile Sulphides (AVS) [1].

Finally, Microbial community (archaebacteria, eubacteria and microeukaryotes) has been determined in surface sediments (0-2 cm) and in deeper ones (8-10 cm).

Intermediary results clearly indicate that eubacterial taxon richness and diversity indexes are both reduced in heavy metal contaminated stations, when compared to the other stations analysed. This result is not an artefact due to differences in the surface areas considered because this factor was taken into account. Additionally, a surprising high biodiversity of microeukaryotes was revealed in some BCP stations.

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GAS CHROMATOGRAPHIC- MASS SPECTROMETRIC DETERMINATION OF VOLATILE FATTY ACIDS IN MUNICIPAL AND ANIMAL FARM WASTEWATER

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Volatile fatty acids (VFAs) are monocarboxylic acids containing from 2 up to 8 carbon atoms. They can be found in different environmental matrices due to numerous sources of natural and anthropogenic origin. They can have negative effects on the quality of some environmental compartments. On the other hand, VFAs play an important role in biological wastewater treatment. Therefore, VFAs should be monitored in environmental gaseous, liquid and soil samples, including municipal and animal farm wastewater as well as media at different stages of wastewater treatment.

This research was conducted to develop the method of determination of VFAs in aqueous samples and then to apply it to monitor municipal wastewater at different steps of treatment and liquid media from pig and cow farms for the content of these analytes.

The determination relied on extraction of pollutant volatile acids with organic solvent, separation of extract with gas chromatography (GC) and identification and quantitation of analytes of interest with mass spectrometry (MS), directly coupled with GC. The selected VFAs recoveries in the process of extraction from model aqueous samples and the corresponding detection limits were determined. Satisfying separation of VFAs in the extracts obtained was achieved using Stabilwax-DA (crossbond polyethylene glycol treated with nitroterephtalic acid) open tubular capillary column (30m x 0,32mm x 0,5mm).

In all the samples studied the content of acetic acid was a dominant VFA pollutant. The samples from animal farm contained significantly higher amounts of VFAs than those from wastewater treatment plants.

ESTIMATION OF THE LAKE WATER POLLUTION BY DETERMINATION OF 18 ELEMENTS USING ICP-MS METHOD AND THEIR STATISTICAL ANALYSIS

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Water is one of the most essential constituents of the human environment. The quality of water is predetermined by the intended uses and each of these uses affects, more or less, its quality. All natural water contains substances derived from the environment, both natural and antropogenic [1]. In order to investigate the pollution of the Malta Lake and characterize spatial distribution of the elements, 18 elements have been determined in water samples, taken from different parts of the lake. The levels present in water are typically in the $\mu g \cdot L^{-1}$ (ppb) to low $mg \cdot L^{-1}$ (ppm) range, requiring very sensitive analytical methodology to be used. Historically, flame atomic absorption spectrometry has been used for determining trace elements in water, however, it is traditionally a single-element technique which is fairly time consuming and prone to background correction interferences in some sample matrices [2]. The instrumental techniques available now for environmental analysis have reached a high degree of sensitivity for the most chemical elements. One of them is inductively coupled plasma mass spectrometry (ICP-MS). It have been proven to be reliable and applicable methods with the capability to determine simultaneously and accurately a wide range of elements at very low concentration levels [3]. Analyses of elements (Al, As, Ba, Ca, Cd, Co, Cr, Cu, K, Li, Mg, Mn, Na, Ni, Pb, Sb, Sr and Zn) were carried out using ICP-MS. Analytical quality control was verified by the analysis of certified reference material for water NIST 1643e. The search for the relationships between given elements may be a source of valuable information about their behaviour in the water environment. However, analysis of such comprehensive dataset is very difficult. For this reason, the obtained results of element concentrations in the Malta Lake were then submitted to the statistical analysis. The chemometric methods applied were factor analysis (FA) and principal component analysis (PCA).

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ANALYTICAL PROCEDURES IN DETERMINATION OF DRUGS FROM DIFFERENT THERAPEUTICAL GROUPS IN SURFACE WATERS

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Presence of pharmaceuticals in sewage water is caused by increasing consumption of drugs. This environmental pollution has been a deep problem for the analytical chemistry. New rapid and sensitive procedures should be proposed. A solid phase extraction (SPE) followed by liquid chromatography with diode array and fluorescence detection (HPLC-DAD-FL) was developed for analysis of 10 pharmaceutical residues in water samples. The compounds investigated are frequently used and belong to three different pharmaceutical groups: β-blockers (sotalol, metoprolol, propranolol, carvedilol), corticosteroids (prednisolone, dexamethasone), analgesic/non steroidal anti-inflammatory drugs (paracetamol, aspirin, dipyrone, ketoprofen). A solid-phase extraction using C_{18} and Oasis MCX cartridges to produce the best recoveries was developed. This method was verified by performing experiments in surface water. Literature survey reveals that many techniques have been reported for the determination of these drugs including HPLC, but for now no one have determined the procedure for all of this pharmaceuticals in one application.

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VOLTAMMETRIC DETERMINATION OF FUROSEMIDE, KETOPROFEN AND PROPRANOLOL IN WATER SAMPLES

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The expansion of pharmaceutical industry and growing use of medicines caused environmental problem as presence active compounds in surface and waste water. Various voltammetric techniques can be employed as simple and rapid methods to determination of pharmaceuticals belonging to different therapeutically groups in water samples. In the available literature only determination of propranolol in spiked river water samples by normal pulse voltammetry [1] can be found. The aim of this work was to investigated electrochemical behavior of furosemide, ketoprofen and propranolol by cyclic and differential pulse voltammetry. All researches in model solutions were made in Britton-Robinson buffer as electrolyte in pH range 1,81-9,36. Measurements were made in electrochemical cell equipped in three-electrode system with glassy carbon or gold electrode as working electrode. The spiked water samples were preconcentrated by solid-phase extraction on C_{18} cartridges. Next elaborated procedures were transferred to a *Speedisk* extraction. The proposed methods were applied to the preseparation of selected drugs from different water samples. The described procedures are suitable techniques for the determination such medicines as furosemide, ketoprofen or propranolol in environmental water samples.

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HPLC ANALYSIS OF SELECTED CARDIOLOGY DRUGS IN WATER SAMPLES

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Growing pharmaceutical environmental pollution has become a new analytical problem in few years. High consumption of drugs causes continous introduce of drugs and their metabolites to sawage waters. Therefore fast, rapid, sensitive and selective analytical methods should be proposed.

An analytical metod based on high performance liquid chromatography with DAD and fluorescence detection has been developed for determination of selected drugs in water samples. The investigated drugs were: sotalol, metoprolol and ketoprofen. Also a concentration of drug metabolites was investigated: a-hydroxymetoprolol (metoprolol metabolite) and salicylic acid (product of decomposition of acetylsalicylic acid). Enrichment of water samples was performed by solid phase extraction on C18 SPE cardriges and continously on Oasis MCX cartdriges. HPLC analysis of preconcentrated samples was carried on reversed phase C18e column with gradient elution. Worked out procedure of mentioned drugs simultaneous determination was not publicated in literature. Literature contains procedures of analysis, but different for each drug.This method was applied to real samples from surface waters of Poland.

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CHEMICAL AND PHYSICAL CHARACTERIZATION OF MARINE SEDIMENTS BY NIR DIFFUSE REFLECTANCE SPECTROSCOPY AND CHEMOMETRICS

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Near infrared (NIR) diffuse reflectance spectroscopy has been employed for a fast chemical and physical characterization of surface marine sediments through the estimation of properties like pH, Eh, elemental analysis and trace metal concentration, 81 samples, taken during different seasonal periods from 24 sampling locations across Ria de Arousa (North West of Spain).were employed to build calibration models and for their validation Sediment samples, contained into standard glass vials, used as measurement cell, were scanned from 833 to 2976 nm (12000 to 3360 cm^{-1}). Data of trace elements content were determined experimentally on samples by using reference procedures being found different ranges of concentration for trace metals under study: 3.5-26.2 $\mu g\ g^{-1}$ for Sn, 27.4-83.3 $\mu g\ g^{-1}$ for Pb, 0.13-0.97 $\mu g\ g^{-1}$ for Cd, 15.0-43.3 $\mu g\ g^{-1}$ for As, 1.5-5.3 $\mu g\ g^{-1}$ for Sb and 41.5-365 $\mu g\ g^{-1}$ for Cr. Concentration values found varied from high levels in the inner part of the Ria (near to the port and urban nucleus such as Vilagarcia or Rianxo), thus indicating industrial activity in the region, to natural background levels toward the mouth of the Ria. Carbon, nitrogen and hydrogen content were also experimentally determined, being found a variability range of 36.1-65.2, 7.2-15.75, 0.23-6.30 mg of C, N and H, respectively, per g of sediment fraction <63 µm. Physical parameters ranged between 7.41-8.48 and 267-408 for pH and redox potential (Eh) were experimentally measured in sediments fraction between 200 and 63 µm. Good residual prediction deviation (RPD) values (from 1.13 to 1.7) were obtained for all evaluated parameters being possible to considered NIR chemometrics combination an appropriate tool for screening and monitoring purposes. On the other hand, root mean square error of prediction values (RMSEP) were 0.13 units for pH, 30 mV for Eh, 4, 1.5 and 1.1 mg/g of sediment for C, N and H, respectively, thus indicating the excellent characteristics of the developed procedure for evaluation of the aforementioned parameters. For trace metal content, RMSEP values ranged from 0.15 to 45 µg/g and for Cr species the prediction values varied with quality coefficients from 50 to 500 %, thus indicating the strong limitation of the developed methodology for the estimation of acid, oxidable and reducible fractions of Cr in sediments but providing estimated errors of prediction for unknown samples equal or lower than 20% for Sn, Pb, As and Sb.

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DETERMINATION OF DIAZEPAM AND NORDIAZEPAM IN WASTEWATER BY SOLID PHASE EXTRACTION AND LIQUID CHROMATOGRAPHY COUPLED TO TANDEM MASS SPECTROMETRY

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During the last decades different analytical methods have been developed for about 150 pharmaceutical ingredients and related compounds in environmental matrixes [1]. Pharmaceuticals have been detected and quantified in different types of waters e.g. rivers [1], surface waters [2], sewage treatment plant influent and effluent waters [1], ground waters [3], and even in drinking water [1]. It is desirable to develop methods that focus on the metabolites which can be equally or even more potent than the parent compound. Herein we present a method for the determination of the benzodiazepine diazepam and its metabolite nordiazepam in wastewater. Centrifuged influent and effluent wastewater is successfully extracted with solid phase extraction with octadecyl extraction discs. All sample handling is performed in such way that the risk of sample contamination is minimized. Millipore water is used as procedural blanks and is extracted in parallel with samples to make sure that the analytes truly originates from the wastewater treatment plant and not from the laboratory. The procedural blanks is also integrated in the analyse process to avoid possible memory effects. Diazepam and nordiazepam are completely separated within 3.5 minutes with a Pro C_{18} column, 50×2.1mm (5 μm) from YMC and a C_8 SecurityGuard, 4×2 mm from Phenomenex®. Gradient elution is performed with formic acid in millipore water and formic acid in acetonitrile. Isotope-labelled internal standards, diazepam-$^2H_5$ and nor-diazepam-$^2H_5$, are used to compensate for ion suppression and matrix effects. The analytes are detected with tandem mass spectrometry in positive ion mode and by multiple reaction monitoring to achieve the required selectivity and sensitivity.

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VOLTAMMETRIC DETERMINATION OF SUBMICROMOLAR CONCENTRATIONS OF CARCINOGENIC 2,7-DINITROFLUORENE AT MENISCUS MODIFIED SILVER SOLID AMALGAM ELECTRODE

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The emissions of gasoline and diesel engines contribute significantly to the environmental pollution. Certain part of exhaust particulates consists of nitrated polycyclic aromatic hydrocarbons (NPAHs). NPAHs belong among the substances whose occurrence in the environment can be causally connected with an increased cancer rate [1]. Therefore, the sensitive and selective methods are necessary for the determination of these compounds in complicated environmental matrices. Due to the relatively easy reduction of nitro group at aromatic rings, NPAHs are suitable candidates for the application of modern voltammetric methods.

The studied compound 2,7-dinitrofluorene (2,7-DNF), known as proven carcinogen [2] and the component of exhaust gas [3], has been determined at meniscus modified silver solid amalgam electrode [4] (m-AgSAE) - a non-toxic alternative to traditional mercury electrodes. The stock solution was prepared in methanol due to the lower solubility of 2,7-DNF in water. Optimal conditions for 2,7-DNF determination have been investigated in buffered aqueous-methanolic solution. DC voltammetry (DCV) and differential pulse voltammetry (DPV) at m-AgSAE were used. The influence of pH at voltammetric behavior of 2,7-DNF was investigated in methanol - Britton-Robinson buffer solutions (1:1). The concentration dependences were measured under optimum conditions. Limit of determination was around 10^{-6} mol L^{-1} for DCV at m-AgSAE and 10^{-7} mol L^{-1} for DPV at m-AgSAE. Obtained results have been compared with previous determination of 2,7-DNF at mercury electrodes [5]. An attempt to increase sensitivity using adsorptive stripping voltammetry at m-AgSAE was made. Cyclic voltammetry at m-AgSAE was used to investigate mechanism of reduction of 2,7-DNF at m-AgSAE.

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DETERMINATION OF CHOSEN HEAVY METALS IN SEWAGE DEPOSITS AND ASHES FROM BURNING PLANT

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The sewage treatment plants are producing increasing amounts of sewage deposits. In Poland 42% of the total amount of sewage is being stored, 14 % is used in agriculture, and only 2% undergoes heat treatment. The last mentioned technology produces small amounts of waste and can greatly reduce the amount of the sewage deposits. In other countries in the UE the highest amounts of sewage is used in agriculture (32%), 25% is stored waste and up to 13% of average amounts is burned.

According to government order (*MOŚZNiL/*Polish government Ministry of Environmental Protection Natural Resources and Forestry/ from 11 October 1999) sewage deposits should contain determined amount of heavy metals. Heavy metals amounts allow to decide about agricultural or non agricultural usage of this waste (soil reclamation, destructed by industry; an industrial mineral waste stockpile; fixing of soils, exposed to wind and water erosion, with plants). Deposits with high amounts of heavy metals could be used in production of: wood and seedlings, inedible and non fodder plants (energy, cellulose-paper plants). The ashes from burned sewage deposits could be used as component of sett stone, building brick, for road building.

The aim of this study is analysis of chosen heavy metals content (Hg, Cu, Cr, Ni) in sewage deposits and ashes obtained as results of burning dry sewage deposits from one of Tri-City sewage plant.

This study was financial supported by Ministry of Science and Higher Education under grants: DS-8210-4-0086-8.

STUDY OF BIOACCUMULATION OF CADMIUM FROM AQUEOUS SOLUTIONS BY TWO STRAINS OF THE GENUS ASPERGILLUS NIGER BY FLAME ATOMIC ABSORPTION SPECTROMETRY

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In environmental sciences there is a need to develop technologies that can help by removal of toxic heavy metals found in natural waters and waste waters. Biological substrates such as bacteria, algae and fungus are materials able to accumulate metals from aqueous solutions through the biosorption process. The utilization of microbial cells with combination of sensitive and selective atomic spectrometry techniques used for metal determination is very important from the environmental analytical chemistry point of view for metal preconcentration purposes.

In the present work the removal of cadmium from aqueous solutions under laboratory conditions by fungal biomass of two strains of Aspergillus niger was investigated. Strain An1 was isolated from the Eutric Fluvisols FMm (pH H_2O/KCl 7.7/7.4). Strain An3 was isolated from the stream sediment (pH H_2O/KCl 5.27/4.8) from Pezinok region (Slovakia). Various parameters such as pH of the solutions, different initial cadmium concentrations, time of accumulation have been studied. In order to establish the effect of pH on the biosorption of cadmium ions, the batch equilibrium studies at different pH values were repeated in the range of 2.0-7.0. The optimal pH of cadmium accumulation by fungal mycelia of strains An1 and An3 was observed at pH 7.0 and 3.0 respectively. The relationship between the initial ion concentrations in the solution and cadmium ions accumulated in the biomass was studied. Some experiments were performed for comparison of batch and dynamic equilibrium studies for accumulation of cadmium from waters.

The digests of dry mycelium samples after microwave decomposition were used for determination of cadmium preconcentrated in biomass. The flame atomic absorption technique was used for the determination of cadmium concentration to study cadmium bioaccumulation.

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THE INFLUENCE OF K^+ IONS ON ARTIFICIAL GAMMA RADIONUCLIDE ^{137}Cs SORPTION IN THE SEDIMENT SAMPLES FROM THE DOBCZYCE RESERVOIR

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The influence of potassium ions on the sorption mechanism of artificial ^{137}Cs in sediments core samples taken at the Dobczyce drinking water reservoir was analyzed. Six measurement points, localized in two distinct regarding hydrological conditions parts of the reservoir (in Myślenicki Basin and Dobczycki Basin), were chosen (Fig. 1).

The values of selectivity coefficients for caesium ions sorption in the presence of potassium ions for the analyzed sediments are presented in Table 1.

Table 1. Changes of the selectivity coefficients for 137 Cs in the presence of potassium ions.

K M/dm^3	K_{sel} 1a	K_{sel} 2a	K_{sel} 3a	K_{sel} 4a	K_{sel} 5a	K_{sel} 6a
0,01	46,2	220,6	266,6	434,9	330,4	354,7
0,001	7,1	83,0	90,0	118,7	102,8	97,5
0,0001	2,3	17,7	27,2	39,0	25,8	35,5
0,00005	1,0	5,4	16,3	24,1	17,2	22,3
0,00001	0,2	1,7	3,5	5,0	3,2	3,9

High values of the selectivity coefficients (K_{sel}>100), for K concentrations higher than 10^{-4} M/dcm^3 indicate, that increase of potassium concentration influence the sorption mechanism of caesium. Our data illustrate that potassium is competitive towards caesium.

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APPLYING REFRESHABLE MERCURY FILM SILVER BASED ELECTRODE TO DETERMINATION OF Cr(VI) IN SOIL SAMPLES

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Two basic electrode systems, the mercury film electrode (MFE) and hanging mercury drop electrode (HMDE) are generally used for adsorptive stripping voltammetry (AdSV). However, MFEs are more suitable for field application and on-line measurements than the HMDEs because of the virtue of their robustness, mechanical stability, and simple maintenance. Another very interesting solving is the application of the refreshable mercury film silver based electrode for voltammetric determination [1]. The major advantages of this electrode is the possibility of exploiting it in environmental monitoring in a field measurements. In literature data numerous analytical methods have been described to identify and quantify Cr(VI) in environmental media. It is connected with the significant toxicity differences between Cr(III) and Cr(VI); hexavalent chromium is about 100-1000 times more toxic than the trivalent one. Determination of Cr(VI), especially in solid samples, is regarded as a one of the most challenging speciation tasks. Recently a new simple protocol for Cr(VI) determination in solid samples which allows for simultaneous extraction and determination of Cr(VI) in one step was described. However, in that procedure the HMDE was used as a working electrode, what causes some limitations of the procedure. In the present study, we used a refreshable mercury film silver based electrode (Hg(Ag)FE) for Cr(VI) determination in solid materials, with special respect to the soil samples. The whole procedure of extraction and than determination of Cr(VI) was applied on a single cell, which allowed for monitoring of the voltammetric scan. The application of the refreshable Hg(Ag)FE to measurements of Cr(VI) concentration in soil samples made it possible to perform field measurements. The optimization of conditions of the proposed procedure with regard to the influence of organic substances such as surfactants and humic substances (HS) always present in soil samples was performed. It was observed as it was predictable that the elevated concentrations of the organic matter caused decrease or total decay of Cr(VI) analytical response. Therefore to analysis of soil samples containing higher concentrations of organic matter the addition of Amberlite resin is recommended. The proposed procedure was tested by analyzing certified reference materials "Chromium (VI) in soil" with certified value of Cr(VI) 74.98 mg kg^{-1}.

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A NEW METHOD OF THE ENVIRONMENTAL SAMPLES PREPARATION FOR ASV ANALYSIS - APPLICATION OF TiO_2

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Most of natural samples contain surface active substances as well as humic and fulvic acids in concentrations which impede or sometimes even make reliable analysis impossible. It is especially noticeable in the case of stripping voltammetry measurements. Usually it is inevitable to eliminate those interfering compounds by means of application of microwave digestion or by UV decomposition of the sample in the presence of oxidating agents or photocatalysers [1]. The latter of mentioned methods is preferred due to its simplicity and low cost, but often the decomposition of organic matrices is not complete, especially if there are aromatic compounds present in the processed sample [2]. In such cases the application of fumed silica as organic compounds adsorbent was suggested [3]. However although fumed silica is efficient in elimination of surface active substances from the sample, only a small part of humic acids is adsorbed. The application of titanium oxide nanopowders as selective adsorbent of organic compounds and the agent promoting their UV decomposition is proposed herein.

The research were performed in standard conditions, i.e. three electrode voltammetric cell was used, the supporting electrolyte was deaerated prior to measurements, anodic stripping voltammetry (ASV) with differential method of measurements was applied as well as measurements of the double layer differential capacitance. 20 mg of the tested TiO_2 was added directly to the measuring cell containing 10 ml of the sample solution. The samples were than either sonificated or UV digested.

It was proved, that titanium oxides in acidified solutions of typical supporting electrolytes adsorb quickly and effectively humic acids and, even not so effectively but also other surface active substances, not affecting precision and accuracy of heavy metals (for example Pb and Cd) determination. The performance of the proposed method was illustrated by determination of metals concentrations in several synthetic and natural samples.

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DETERMINATION OF LEAD TRACES BY STRIPPING VOLTAMMETRY AT TITANIUM CARBIDE WORKING ELECTRODE

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The titanium carbide working electrode was tested as a novel, potential electrode for anodic stripping voltammetric determination of lead (II) ions traces. To demonstrate the practical applicability of the TiC electrode, an underpotential deposition/dissolution (UPD) phenomena system [1] in a electrolyte without removal of oxygen was tested. The UPD properties and, consequently, the ASV signals are strongly affected by the type and concentration of all the components of the measured electrolyte. The effects of dissolved oxygen, acids, anions and metal ions were investigated for the TiC electrode.The electrode was constructed be means of mounting a TiC disc (φ =3.5 mm) in a resin body. Titanium carbides used in presented herein research were obtained by means of self-propagating high temperature synthesis (SHS) [2]. Three compositions of TiC were tested differing in stoichiometry namely $TiC_{0.6}$, $TiC_{0.8}$ and $TiC_{1.0}$.

The TiC electrode was used for the determination of Pb^{2+} in concentrations ranging from 1 to 100 nM. The instrumental parameters, composition of supporting electrolyte and procedures of the electrode activation were optimized. The method enables determination of Pb^{2+} in the presence among others high excesses of Cd, Cu, In, Sb, Se, and Tl ions as well as surfactants, Triton X-100 and humic acids. The repeatability of DP ASV runs in synthetic solutions covering the entire concentration range is better than 3%. The calibration curve is characterized by a correlation coefficient of at least 0.999. The detection limit was 2 nM for an electrodeposition time of 30 s. For short-term reproducibility of the analytical response for the TiC1.0 electrode is very good (for 20 nM Pb^{2+} at 30 s electrodeposition time is 1-2%). The long-term stability (one week) of the TiC1.0 electrode is good. The sensitivity of the electrode over long periods of time and over a large amount of measurements may by about 10-20%. The TiC1.0 electrode used in synthetic solutions containing up to 100 nM of Pb^{2+} did not require mechanical pretreatment for over 100-200 measurements. The analysis of Pb^{2+} in synthetic solutions with and without surfactants, certified reference material and natural water samples have been performed.

The voltammetric data were associated with the structural characterization of the electrode surface using scanning electron microscopy (SEM) and X-ray fluorescence spectroscopy (XRF).

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EXTRACTION AND DETERMINATION OF TRINITROTOLUENES AND PRODUCTS OF THEIR BIOTRANFORMATIONS IN SOIL SAMPLES

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The worldwide mostly used highly energetic compounds like 2,4,6-trinitrotoluene (TNT) has been discharged into the environment since the WWI [1]. Considerable contamination of soil and water by these compounds is caused by various military activities [2]. Except 2,4,6-trinitrotoluene its constitutional isomers (2,3,5-trinitrotoluene and 2,3,4-trinitrotoluene) were distributed to the environment in wastewaters from 2,4,6-TNT production. These asymmetric trinitrotoluenes and other nitroaromatic compounds are relatively widespread and can be biotransformed or migrate in environment. TNTs and products of their degradation, aminodinitrotoluenes (ADNTs), diaminonitrotoluenes (DANTs) and triaminotoluenes (TATs) have been found to be cytotoxic presumably due to induced oxidative stress and demonstrated mutagenic capability. 2,4,6-TNT is classified as possible human carcinogen, where the evidence for human carcinogenicity is inadequate, and the animal carcinogenicity data are limited [1]. Major factors affecting fate and transport of 2,4,6-TNT in the environment are biotic and abiotic transformations, adsorption and irreversible bonding to soil organic matter [3]. Therefore both the knowledge of ecotoxicity of explosive compounds and their products of biodegradation, as well as content of these compounds in environmental is essential. HPLC with UV detection is commonly used method for the analysis of nitroaromatics due to its widespread availability. HPLC combined with MS or electrochemical detection (ED) are less frequently available methods of detection. The partial goal of the present study was to optimise properties for simultaneous HPLC/UV/MS determination of group of nitroaromatics compounds and products of their degradation (2,4,6-TNT, 2,3,5-TNT, 2,3,4-TNT, ADNTs and DANTs) in soil samples. Problems connected with extraction and isolation of compounds under investigation as the most important part of soil sample preparation are presented. Values of extraction efficiency for different extraction methods are compared in consideration of coextracted fractions of polar compounds. Extract treatment procedure eliminating negative effect of fractions coextracted from soil is proposed. The applicacation of proposed methods for determination of low levels of toluene nitroderivatives in soil samples is presented.

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ANALYSIS OF REGULATED PESTICIDES IN DRINKING WATER USING LARGE VOLUME INJECTIONS, ONLINE PRE-CONCENTRATION, AND FAST HPLC

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The Japanese Ministry of Health, Labour, and Welfare regulates certain pesticides. Sensitivity is paramount for the analysis and therefore a method for online sample preconcentration of drinking water is desirable. We describe a new method for this analysis using Ultra-HPLC, 2 C18 LC columns, and a LC-MS/MS instrument. Using this configuration, run times of 6 minutes are achieved for the analysis of a mixture of pesticides. For separation prior to analysis using a LC-MS/MS instrument, fast-HPLC is utilized allowing for short run times (ca. 6 minutes).

The SRM transitions are quantified and can be confirmed using the QED analysis. This method allows the direct injection of drinking water onto the loading column, with no sample preparation or offline concentration.

Bottled water was spiked with a commercially available mixture of pesticides ranging from 0.5 to 1000 pg/mL. 1 mL of the spiked water and blank samples of the water were injected directly onto a loading column. After approximately 1 minute, a multi port valve is switched to enable the load column to be back flushed onto the analytical column, where the compounds are separated by Ultra-HPLC prior to introduction into the mass spectrometer. After all of the compounds are eluted, the valve is switched back to the initial position, the loading column is cleaned with a high percentage organic phase and equilibrated, as is the analytical column.

In addition to the advantage of having an online sample preparation setup, the large injection volume allows for the pre-concentration of samples on the loading column, and the samples are then eluted onto the analytical column. This allows for excellent peak shapes for the analytes, which would not be attainable if the same injection volume was injected directly onto the analytical column due to overloading issues on the column. Furthermore, significant time savings are realized by this experimental setup versus off line SPE and concentration.

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SEPARATION OF INORGANIC AND LOW-MOLECULAR-MASS ORGANIC ANIONS IN ONE ION CHROMATOGRAPHIC RUN UNDER ISOCRATIC ELUTION

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So far the separation of inorganic and low-molecular-mass organic anions in a single run has been reported no to be possible under isocratic ion chromatography (IC) conditions, but only under gradient elution. However, for routine IC analysis, isocratic elution is the preferred separation mode and in many laboratories a gradient procedure is inadvisable. Therefore, in this work, a systematical investigation for the separation of low-molecular-mass organic anions (i.e., acetate and formate), and inorganic anions (i.e., F^-, Cl^-, NO_2^-, Br^-, NO_3^-, HPO_4^{2-}, and SO_4^{2-}) in one run was performed by means of isocratic IC.

Three different analytical anion-exchange columns were selected and studied: IonPac AS14 (9 µm particle size), Allsep A-2 (7 µm particle size) and IC SI-50 4E (5 µm particle size). The complete baseline separation in one run for all analyzed anions was achieved on the IC SI-50 4E column. In this case, an eluent containing a mixture of 3.2 mM Na_2CO_3 and 1.0 mM $NaHCO_3$ with a flow rate of 1.0 ml/min was applied and the separation was completed in less than 25 min. On the IonPac AS14 column, it was possible to separate acetate from inorganic anions in one run, but without formate, using the following conditions: 3.5 mM Na_2CO_3 plus 1.0 mM $NaHCO_3$ with a flow rate of 1.2 ml/min. Therefore, it was necessary to adapt a second run with a 2.0 mM $Na_2B_4O_7$ solution as an eluent under a flow rate of 1.0 ml/min for the separation of organic anions. In the case of the Allsep A-2 column, using an eluent containing a mixture of 1.2 mM Na_2CO_3 plus 1.5 mM $NaHCO_3$ with a flow rate of 1.6 ml/min, it was possible to separate almost all anions in one run, except the fluoride-acetate critical pair. When the concentration of fluoride was comparable, or higher than acetate, it was impossible to achieve a good separation of these two anions. All three columns were applied for the separation of concerned ions in precipitation samples, such as snow and rainwater. Additionally, a Certified Multianion Standard Solution PRIMUS for IC was used in order to make the validation of the analytical columns.

THE IMPACT OF AIR COMPOSITION RELATED TO CONSERVATION IN TWO EUROPEAN CHURCHES

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Preventive conservation is focused on the quality of atmospheric environment in order to control and retard eventual damage brought to our Cultural Heritage. Indoor air pollution, a consequence of both indoor and outdoor phenomena, can cause chemical damage and soiling of surfaces of artworks, through deposition of particulate matter or absorption of gases. In order to asses the role of air composition and its effect on the deterioration of historical churches and to preserve the monuments as long as possible, simultaneously studies have been carried out in two European churches.

Particulate and gaseous pollutants have been collected in order to achieve an integrated view of the environment and the possible threatening factors for the deterioration of works of art. Samples were taken in the Basilica Saint-Urbain in Troyes, France and in the church of Saint Michael Archangel in Szalowa, Poland. These two churches are important subject from the Cultural Heritage of the both countries.

Gaseous pollutants such as NO_2, SO_2 and O_3 were sampled by means of Radiello® diffusion tubes. The small size diffusive samplers allowed measuring the concentrations of gaseous pollutants, even in the less reachable locations. The analyses were performed by means of ion chromatography (IC) and UV/VIS spectrophotometry.

Particulate pollutants were collected with the use of a Berner cascade impactor on different substrates (Ag and Si) for size segregated single particles and a Plexiglass® filterholder unit on Nuclepore® membranes for bulk particles. The chemical composition and size characterization of atmospheric particulate pollutants nowadays is possible to be obtained by computer-controlled electron probe microanalysis (CC-EPMA) at the single particle level and energy-dispersive X-ray fluorescence (EDXRF) for bulk analysis.

The obtained results for the gaseous pollutants showed that outdoor generated gaseous pollutants had lower concentrations in both churches compared to the outdoor air. Suspended particulate matter inside the churches was strongly influenced by the activities taking place like heating, masses etc. High NO_2 concentrations sometimes related to candle burning led to the formation of nitrate containing particles. Some aggressive type of particles like nitrates and sulfates can lead to an acceleration of the deterioration processes at the investigated monuments.

DETERMINATION OF SEVERAL PESTICIDES AND METABOLITES IN WATER BY SOLID-PHASE EXTRACTION, LIQUID CHROMATOGRAPHY AND ELECTROSPRAY TANDEM MASS SPECTROMETRY

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The analysis of pesticides in water samples is a problem of primary concern for Quality Control Laboratories due to the toxicity level of these compounds and its public health risk. The Council Directive 98/83/EC of 3 November 1998 regarding the quality of water intended for human consumption states a parametric value of 0,10 µg/L for each individual pesticide and 0,50 µg/L for the sum of all pesticides monitored [1]. In order to evaluate the impact of pesticides and same metabolites in Lisbon drinking water supply system, we developed and validated an analytical method based on the on-line combination of liquid chromatography and tandem mass spectrometry after solid phase extraction (SPE-LC-ESI-MS/MS) [2,3].

In this work five pesticides had been studied: Bentazone, MCPA, 2,4-D, Chlorotoluron, and Propanil and three pesticide metabolites: Atrazine-desisopropyl, Atrazine-desethyl, and Terbuthylazine-desethyl.

Several parameters were optimized in order to get the best formation conditions of the precursor ion for each pesticide, using an electrospray source, namely capillary and extractor voltage, cone voltage, cone gas flow rate and desolvation gas flow rate. Two different precursor ion - product ion transitions were selected for each pesticide, one for quantification and one for qualification, and these ions were monitored under time scheduled multiple reaction monitoring (MRM) conditions, after optimization of the collision cell energy of the triple quadrupole. The selection of specific transitions for each pesticide guarantee a high degree of selectivity as well as additional sensitivity to quantify trace levels of these pesticides in water samples.

This method showed excellent linearity ranges for all pesticides (between 9,9 and 158 µg/L), with correlation coefficients greater than 0,9989. Recovery studies in several matrices with different fortification solution levels were performed using solid phase extraction with recoveries between 67% (Atrazine-desisopropyl) and 133% (Atrazine-desethyl) with RSD lower than 10,9% (Bentazone). The Determination Limits obtained for these compounds were between 0,020 µg/L (terbuthylazine-desethyl) and 0,075 µg/L (atrazine-desisopropyl). Interlaboratory studies showed good performance for this method with z-scores between -1,19 (2,4-D) and 0,66 (Chlorotoluron).

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HUMIC AND FULVIC ACIDS DETERMINATION IN SURFACE MARINE SEDIMENTS BY NIR DIFFUSE REFLECTANCE SPECTROSCOPY COMBINED WITH CHEMOMETRICS

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The term 'humic substances' is used in a generic sense to distinguish the naturally occurring material from the chemical extractions named humic acid and fulvic acid, which are defined "operationally" by their solubility in alkali or acid solutions. They are the most stable fraction of organic matter in soils and can persist for tens, hundreds or even thousands of years and moreover not only contribute to soil chemical and physical quality but are also precursors of some fossil fuels.

Conventional methods for Humic and Fulvic acid determination in solids generally involve extractions and precipitations using strong acids and alkalis and can be considered tedious, highly time-consuming and non-environmentally friendly procedures. For these reasons, it has been evaluated the potential of near diffuse reflectance infrared Fourier transform spectroscopy (near-DRIFTS) as a fast analytical methodology for non-destructive measurement of Humic and Fulvic acids in 41 surface marine sediment samples collected during two different seasonal periods from 24 different geographical places from Ria de Arousa (North West of Spain) with neither physical nor chemical pre-treatment. Predictive models were developed using partial least square (PLS) multivariate approaches based on raw and first-order derivative spectra.

Moreover, a critical comparison of both common spectral pre-treatments, multiplicative signal correction (MSC) and standard normal variate (SNV), was also evaluated. Results derived from this study showed that NIR diffuse reflectance spectroscopy combined with the appropriate chemometric tools could be considered as a useful screening technique for a rapid quantification of Humic and Fulvic acids in surface marine sediments.

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COMPARISON OF SOLID-PHASE EXTRACTION SORBENTS FOR CLEANUP IN POLYCHLORINATED BIPHENYLS AND PESTICIDE RESIDUES ANALYSIS

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Multiresidue procedures for the determination of polychlorinated biphenyls (PCBs) and pesticides in various food commodities typically require extraction with an organic solvent (or a mixture of solvents), removal of the co-extracted matrix interferents, and final determination using GC or HPLC with selective detector. Further cleanup of the organic solvent extract prior to final determination is commonly performed because sample matrix coextractants may have a destructive effect on the capillary column, interfere with the detection of analytes at trace levels and cause a sample matrix-induced enhancement effect [1].

Following many publications, solid-phase extraction (SPE) columns seem to provide a rapid extract cleanup to the determination of PCBs and pesticide residues in complex sample matrices. The types of SPE sorbents most commonly used for the cleanup of pesticides and PCBs in food commodities include unbonded normal phase sorbents such as *Alumina* and *Florisil*, bonded normal phase such as aminopropyl ($-NH_2$), reverse phase sorbents such as octadecylsilyl (C_{18}) and adsorbents such as carbon black (Envi-Carb). Many of published methods use combinations of two or three of the commercially available SPE columns [2, 3].

The main aim of this work was to find a sorbent (or a combination of sorbents) for the SPE technique that would permit the cleanup extract to the determination of pesticides and polychlorinated biphenyls. Octadecylsilyl (C_{18}), aminopropyl (NH_2), *Florisil*, *Alumina* and carbon black (Envi-Carb) SPE column were evaluated. In order to choose the best sorbent the model test was performed. The pesticides, PCBs and palmitic acid (as interfering compound) mixture in hexane was used. The relative sample cleanup provided by these SPE column was evaluated using gas chromatography with electron capture detection.

The $-NH_2$ and *Florisil* columns were found to provide the most effective cleanup, removing the greatest number of sample matrix interferences. Likewise, the C_{18} and Envi-Carb columns did little to eliminate matrix interferences (palmitic acid).

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OPTIMIZATION OF VETERINARY ANTIBIOTICS RESIDUES ANALYSIS BY LIQUID CHROMATOGRAPHY COUPLED TO THE TANDEM MASS SPECTROMETRY

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Veterinary antibiotics are widely used in many countries not only to treat disease and protect health of animals but also to improve growth rate and feed efficiency. As antibiotics do not undergo complete metabolism in animal organisms, the vast part of those is excreted unchanged in faeces and urine. Therefore, antibiotics as well as their metabolites are released either directly to the environment by pasture animals or indirectly during the application of manure or slurry as a fertilizer. The contaminated manure has been recognized as the main pathway of spreading the antibiotic agents, their corresponding resistance genes into the different environment compartments, food and plants. It is therefore of highest importance to develop easy and reproducible analytical methods for the determination of most important antibiotics in manure. Nowadays, the most widely used group of antibiotics in the European Union`s animal husbandry are tetracyclines, penicillins, sulphonamides, aminoglycosides and macrolides. The preferred analytical methodology for those analytes is liquid chromatography coupled with tandem mass spectrometry (LC-MS/MS). Moreover, a very common mode of LC-MS/MS experiments, a multiple reaction monitoring (MRM) is often used, which is the method with the highest sensitivity and selectivity. The aim of this project was to optimize the MS-MS parameters using ion trap mass spectrometry with electrospray ionization for the analysis of the most popular veterinary antibiotics (which belong to penicillins, tetracyclines and sulphonamides) and to select characteristic fragmentation ions of these compounds in order to work in MRM mode. For every compound a precursor ion and a minimum of two daughter ions were selected, which gives four identification points and makes the confirmation of analyzed compounds possible. Moreover, the optimization of chromatographic separation of these compounds has been done. Described method will be used in the future in the qualitative and quantitative analysis of veterinary antibiotics residues in the manure.

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EVALUATING THE MOBILITY OF HEAVY METALS IN INDUSTRIAL WASTEWATER SLUDGE USING SEQUENTIAL EXTRACTION PROCEDURES

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Proper evaluation of the effect of heavy metals on the natural environment is possible on the basis of knowledge about their forms and bindings with soil, sediment, sludge or solid waste components found. A sequential extraction could be the source of the above mentioned information, enabling identification and quantitative determination of various forms of the same chemical element. It is therefore widely used as a tool for the study of fate of metals in the environment [1-2].

The distribution of metals in galvanic wastewater sludge was investigated. Different extraction procedures comparison for the evaluation of metals mobility in industrial sludge were performed. A five- and free-stage fractionation schemes were used to partition the metals into: exchangeable, acid-soluble, reducible, organic matter and residual fractions [3-4].

The five-step sequential extraction of heavy metals from the industrial sludge used different extraction buffers: (i) CH_3COONH_4 (for the exchangeable fraction); 10ml of 1M CH_3COONH_4 for 1h in room temperature; (ii) CH_3COONH_4/CH_3COOH (for the acid-soluble fraction); 20 ml of 1M CH_3COONH_4 adjusted to pH = 5 with acetic acid for 5h in room temperature; (iii) $NH_2OH\cdot HCl$ and CH_3COOH (for the reducible fraction); 20 ml of 0,04M $NH_2OH\cdot HCl$ in 25% (v/v) CH_3COOH for 5h in 95°C; (iv) HNO_3, H_2O_2 and CH_3COONH_4 (for the organically bound fraction); 5 ml of 0,02M HNO_3 and 10 ml of 30% H_2O_2 adjusted to o pH = 2 with 65% HNO_3 for 5 h in 85°C and 10 ml of 3,2M CH_3COONH_4 in 20% (v/v) HNO_3 for 0.5 h in room temperature; and (v) HNO_3 and H_2O_2 (for the remaining metals); 3 ml HNO_3 and 6 ml 30% H_2O_2 for 1 h in boiling temperature and 10 ml H_2O for 0.5 h in boiling temperature. The free-stage fractionation was carried out according to the BCR procedure.

In experiments dewatered galvanic sludge from electroplating plant was used. Different chemical fractions of Cr, Cu, Ni, Pb, Fe and Zn were examined. Investigations were performed for air-dry weight of the sludge samples. The metal contents of the extracts were determined by flame atomic absorption spectrometry.

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DETERMINATION OF PHENOL OXIDATION PRODUCTS USING CHROMATOGRAPHIC TECHNIQUES

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Phenol is widely used in many industries, for example chemical, petrochemical or pharmaceutical industry. Waste waters from these industries often contain phenolic compounds and in this way the hazardous waste might be transported to the environment. Protection of water, air and soil against the penetration of this type of contaminants as well as the development of the appropriate degradation methods is of crucial importance. The most popular method of phenol degradation is its oxidation.

Generally, the phenol oxidation pathway consists of four main reactions:

1. the oxidation of phenol to hydroquinone, and benzoquinone;
2. the opening of aromatic ring to carboxylic acids;
3. the degradation of carboxylic acids;
4. complete mineralization to CO_2 and H_2O.

Phenol oxidation can be carried out in different ways: catalytic oxidation, electrochemical oxidation, photodegradation or sonoelectrochemical procedures.

The main products and by products are similar but these techniques differ in reaction speed and progress.

In this work chromatographic techniques were used to determine products and by-products formed during electrooxidation of phenol. SPE/GC/HPLC system was used for qualitative and quantitative analysis of water samples containing phenol, hydroquinone, benzoquinone and short chain mono- and dicarboxylic acids.

Analytical procedure consisted of SPE step followed by capillary GC-FID and RP-HPLC system was used for the determination of the content of phenol oxidation products. The sorption properties of polymeric sorbents based on styrene-divinylbenzene used in SPE were described basing on the breakthrough volume determined for individual compounds.

The LOD and LOQ of proposed analytical procedure were in the ranges: LOD: 0.042-23.83 μg/ml; LOQ: 0.128-72.21 μg/ml.

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PREPARATION AND PRESERVATION OF SALIVA SAMPLES FOR STATHERIN ASSAYS - A PRELIMINARY STUDY

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Statherin is a 43-amino acid residue peptide present in human saliva. It is known to restrain primary and secondary precipitation of calcium phosphate crystals, controls process of tooth enamel remineralization and affects bacteria adhesion to the surfaces of oral cavity. Furthermore there is the possibility of using statherin assays in determination of cancerous and precancerous alterations in oral cavity.

The aim of our study was to investigate optimal conditions to prepare and preserve the samples of saliva for further assays of statherin.

Samples of whole non-stimulated saliva were collected from six volunteers between 9.00 and 10 a.m. The two hours prior to saliva collection they refrained from eating, drinking, smoking, and oral hygiene activities. Saliva from each individual was collected over a 5 min period by spitting into chilled disposable polypropylene tubes. During the collection process, the samples were stored on ice.

The samples were treated separately, labelled A, B, C, D, E and F and prepared as follows.

To samples A, B, C and D 20% acetic acid was added in the ratio of 1 to 4. Than samples C and D were divided into two subsamples each (sample C into C1 and C2, and sample D into D1 and D2). Both subsamples C1 and D1 were centrifuged for 2 min at 14500 rpm and filtered (Titan Syringe Filter PTFE, 17 mm, 0,2 mm).

Sample E - 0,75 ml of saliva was taken and 0,4 mg synthetic solid statherin and 20 % acetic acid were added to the volume of 3,2 ml.

Sample F - 0,75 ml of saliva was taken and 0,4 mg of synthetic solid statherin, 2,5 ml of water were added. Just before the analysis 0,4 ml of the mixture was taken and 60 μl of 100% acetic acid was added.

Samples were stored at room temperature. All analysis were performed by reversed phase high performance liquid chromatography (RP HPLC) at the flow 1 ml/min, linear gradient 5-53% B (where B is 100% acetonitryle and A is 0,1% trifluoroacetic acid/water) for 40 min. HPLC analysis of samples C1 and D1 were performed directly from the solutions, whereas the analysis of other samples were performed after centrifugation and filtration (at conditions mentioned above).

Our results have shown that addition of 20% acetic acid considerably increases stability of both synthetic and native staterin in human saliva (native statherin in those samples is detectable even after 3 months). Furthermore, centrifugation and filtration of samples helps to prevent native statherin decomposition and in effect ensures better preservation of the sample for later assays.

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PRODUCTION OF NEW MATRIX-FREE REFERENCE MATERIAL OF ETHENE

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Every day, chemical and biological measurements are performed by a large number of analysts in laboratories throughout the world with the objective of studying the properties of matter and better describing and quantifying components of matter. Chemical and biological measurements are performed in all fields of human life, a major part of which within industry. They contribute, for example, to controlling the quality of raw materials, and intermediate and final products. They play also key roles in monitoring production processes, control of the potential impact of production on the environment or occupational health care, etc. [1]. One of the cornerstones in achieving verification of the accuracy of analytical measurements is the use of certified reference materials (CRMs) [2, 3].

The investigations over production of the new certified reference materials (matrix-free reference materials) are realize since a couple of years. The aluminum-coated glass fibers, which are carriers of ethene, can be classified to the above mentioned types of materials. The bottles of 1500 of 3 cm length of glass fibres have been prepared. The five pieces of glass fibres are packed into bottle. Analysis were performed by (between-bottle and within-bottle) have been done by GC-TD techniques. The next steps of the production of new certified reference materials will be to more the certification study by means interlaboratory comparison.

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GEOCHEMICAL CHARACTERIZATION OF A POLLUTED AQUATIC SITE CLOSE TO A FORMER Pb-Zn SMELTING FACTORY: METALEUROP (NORTHERN FRANCE)

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Metal contamination from metallurgical and mining industries can have significant environmental and geochemical impacts on surrounding river systems, where large amounts of ores, dusts and/or slags are extracted or produced [1]. In this presentation, the behaviour of metals in the Deule aquatic system (Northern France) in the vicinity of a former plant (Metaleurop) that had produced zinc and lead during more than one century, will be presented and discussed.

First of all, concentrations of metals have been examined in ores, sediments, and suspended particulate matters (SPM). High concentrations of lead and zinc have been detected in these samples but other elements, generally found at low levels in natural environments have also been found here at high concentration like thallium and indium [2]. In a second step, sequential extractions have been carried out on sediments and SPM and they have revealed an important lability of most of the metal pollutants considered (excepted for Sn, which is quite exclusively associated to the residual fraction).

This overview deals also with the repartition of metal pollutants between the water and the particles. It has been shown that most of the metals are located in particles with relatively low dissolved concentration compared to the high and historical pollution of the whole aquatic ecosystem.

Finally analyses of particles by using X-ray diffraction and an environmental scanning electron microscopy equipped with an energy dispersive X-ray spectrometer (ESEM/EDS) on crude sediments and heavy minerals show unambiguously anthropogenic inputs of lead and zinc under several forms [2, 3].

The whole behaviour of metal pollutants in this aquatic system still needs to further investigations, that are in progress: (i) speciation of metals in waters and porewaters; (ii) metal exchanges at the water-sediment interface; and (iii) in situ remobilisation kinetic study due to daily surface sediment disturbance by barge traffic.

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APPLICATION OF NEUTRON ACTIVATION ANALYSIS IN ESTIMATION OF SELENIUM STATUS IN HUMAN

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Within the frame of recent years, selenium has became as an objective of intensive scientific researches. Nowadays, it is generally recognized that insufficient selenium consumption with reference to nutrition needs, can results in etiology of disease processes or, in some cases, in the intensification of an existing disease. Numerous epidemiological studies have demonstrated an inverse relation between low Se intake and the development of so-called civilization diseases, among others, some types of cancer. Considering the possible risks associated with sub-optimal selenium intake, the monitoring of Se content in the human organism need to be conducted.

The goal of this study was to evaluate the selenium status in Pomeranian inhabitants relative to cancer mortality in Pomeranian District. To accomplish this aim, the study included the investigation of the selenium mass fraction in toenail clippings taken from 111 random inhabitants of various areas of the Pomeranian District. In addition, 85 nail clippings were collected from healthy persons in Lubuski voivodeship in Poland. Toenail specimens were analyzed by Instrumental Neutron Activation Analysis giving means of 0.59 ± 0.10 and 0.64 ± 0.16 mg kg^{-1} Se, respectively. It has been confirmed that the concentration of selenium in toenail samples indicates significant differences among healthy residents of Lubuski district and people living in northern Poland.

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INTER-INDIVIDUAL DISTRIBUTION OF METAL CONCENTRATION IN FOUR BIOINDICATOR ORGANISMS AND ITS USE FOR OPTIMAL SAMPLING DESIGN OF A MONITORING SYSTEM

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The monitoring of heavy metals in the marine environment is often carried out by using bioindicator organisms. In most cases metal concentrations in an area are evaluated using pooled samples from a single sampling site. Thus, a large number of individuals are analyzed per site, but neither the statistical distribution of the data nor the intrasite variability are known. In order to optimize the monitoring of heavy metals using this kind of samples, some authors have suggested that the variability among individuals should be studied at least in one site. This work was designed to know the frequency distribution and the interindividual variability of Hg, Cd, Pb, Cr, Ni, As, Ag, Cu and Zn in four bioindicator organisms (the blue mussel *Mytilus galloprovincialis*, the clam *Venerupis pullastra*, the king scallop *Pecten maximus* and the cockle *Cerastoderma edule*). In most cases metals in one-individual samples where shown to follow a log-normal distribution. As the pooled samples included more individuals they approached the normal distribution but still being closer to the log-normal one, suggesting that, in all cases, a logarithmic transformation should be used to normalize the data.

The interindividual variability observed indicated that at least two pooled samples of thirty individuals (a hundred in few cases) must be analyzed to detect differences of 25% (both between sites and with time).

DETERMINATION OF HETEROCYCLIC AMINES AND CHOLESTEROL OXIDATION PRODUCTS IN THERMALLY TREATED MEAT WITH ADDITION OF VEGETABLES BY LIQUID CHROMATOGRAPHIC METHODS (HPLC AND TLC)

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Certain meat-cooking practices are connected with producing of several types of mutagens and carcinogens such as polycyclic aromatic hydrocarbons or heterocyclic amines (HAs, aminoazaarenes). Additionally, thermal treating of high fat and protein containing food may cause oxidation of cholesterol, ubiquitously present in mammalian tissues, leading to formation of products (oxycholesterols) which have atherogenic and carcinogenic properties. Nowadays some investigations are designed to reduce human exposure to harmful food contaminants. Because onion and garlic contain potentially biological active components, including antioxidants, we have started investigations on influence of these vegetables on formation of potentially atherogenic and carcinogenic compounds in thermally treated meat, which is still the main source of amino acids for humans.

Pork collars and chops as well as the pan residues formed during frying of the meats, prepared with and without additives (garlic and onion), were investigated for contents of aminoazaarenes and oxycholesterols.

The application of tandem solid phase extraction (SPE) with the use of columns filled with Extrelut - diatomaceous earth (Merck), propylsulphonic acid (PRS) and C-18 phase (Bakerbond) enabled selective isolation of HAs fractions from the meat matrix. To obtain oxycholesterols fraction, a multistage clean-up procedure based on liquid extraction with Folch's solution and solid phase extraction was used. For SPE Mega Bond Elut columns (Varian) containing 10 g of silica gel and florisil, as well as 500 mg of SiOH (Bakerbond) columns were used.

Aminoazaarenes (DMIP, IQ, MeIQ, MeIQx, 4,8-DiMeIQx, PhIP) were determined with high performance liquid chromatography method with diode array detection (HPLC/DAD). Concentrations of oxycholesterols: 7-ketocholesterol and 7-hydroxycholesterol were determined by TLC/densitometry method. Silica gel and chloroform-acetone (9:1, v/v) as stationary and mobile phases were used. Quantitation of 7-ketocholesterol was carried out directly after TLC separation and for 7-hydroxycholesterol- after Liebermann-Burchard reaction.

Concentrations of the two determined oxycholesterols in the meat dishes prepared without vegetables were at the level of some hundreds ng in 1 g of thermally treated meat. Addition of onion and garlic induced decrease of these concentrations. The total content of the determined HAs was lower (from 0 to tens ng/g of meat). The vegetables did not influence the formation of aminoazaarenes as significantly as in the case of oxycholesterols, moreover an increasing of the concentration of some HAs was observed in the samples prepared with garlic. The concentration of oxycholesterols in pan residues was several times lower than those in meat, while the concentration of HAs was at the same level in meat and in pan residue.

ANALYTICAL STUDY OF ISOPROTURON PHOTODEGRADATION IN AQUEOUS SOLUTION

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Isoproturon (IPU) is a selective, systemic herbicide used in the control of annual grasses and broad- leaved weeds in cereals [1]. It is used, especially in Europe, at a maximum application rate of 1.5 kg active ingredient per hectare. Particular attention should be given to the potential for groundwater contamination by IPU leaching and to the protection of aquatic organisms in surface water [2] because of its toxicity to fish and plants. In addition, a study indicated that the degradation products of IPU were more toxic on *Daphnia magna* than the parent compound [3]. Therefore, the analysis of IPU and its degradation products in water samples is a problem of primary concern [4].

Concentrations of IPU and its degradation products by several photochemical advanced oxidation processes (AOPs) were determined in this work by large volume injection micro- liquid chromatography with UV detection at 244 nm. The identification of secondary products was done by μ-LC-MS and μ-LC-UV. The degradation experiments were carried out in a cylindrical quarz glass vessel, stirred with a magnetic bar, using a UV lamp with an incident photonic flux of $5x10^{-6}$ Es/s. Most of the intermediary products identified by μ-LC-MS, μ-LC-UV, and GC-MS have been previously found at the monuron degradation by the same processes [5]. A degradation scheme of IPU by AOPs is proposed in this work, based on the identified intermediary products and the photo degradation kinetics of an IPU aqueous solution of 0.05 mM. The conclusion is that IPU is faster degraded than monuron in identical conditions. The results must be confirmed by toxicity tests on the degradation products.

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CONTAMINATION LEVELS AND PRELIMINARY ASSESSMENT OF GROUNDWATER VULNERABILITY BY LEACHING PROCESSES IN SOILS

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The impact of industrial activities on soil and underground water was evaluated in this study, with a particular focus on some traces and heavy metal accumulation, leaching processes and possible contamination of the underground water.

Leaching refers to the removal of soluble materials by water passing through soil. Naturally occurring salts, chemical fertilizers, and pesticides are subject to leaching. Whether leaching actually occurs depends on the amount of water passing through the soil and the rate of water movement. Leaching potential refers to the risk that soluble contaminants will be transmitted through the soil to the groundwater reservoir.

This methodology will be applied for a soil characterisation study in the zone of Campana, Argentina. Campana is a city located along the Paraná River at about 90 km northwest of the Buenos Aires City, the Capital of Argentina. This region holds a considerable industrial activity that includes two oil refineries, a steelwork, petrochemical plants and paper industries. These heavy industries are located very close to urban and residential areas. In addition, emissions originated from the river harbour, the ship traffic and the frequent wood fires as well agriculture and waste burning must be considered.

Data were evaluated by a high-energy polarizing beam energy dispersive X-ray fluorescence spectrometry (EDXRF) for soil samples and total reflection X ray spectrometer (TXRF) for leaching solution samples [1,2].

The study showed no obvious adverse impact of the industrial activities on underground water quality, but contamination by Cr, Pb and Cu is possible in the future.

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DIRECT ANALYSIS OF POLYCHLOROBIPHENYLS IN FISH AND SEAFOOD BY PRESSURED SOLVENT EXTRACTION WITH IN-CELL CLEANUP AND GC-MS

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Polychlorobiphenyls (PCBs) have been widely used during the last century in a broad range of applications, including heat transfer or dielectric fluids. Despite their banishment in the mid-eighties, PCBs remain micro-pollutants of great concern in the whole environment, due to their high toxicity, endocrine disrupting properties, and long-term persistence. In addition, like other lipid-soluble xenobiotics, they are known to accumulate in organisms, especially in species at the top of the food chain. Consequently, organisms living in polluted waters can irreversibly store PCBs in their fatty tissues, which may constitute pollution archives, but also represent a risk for human consumption. Therefore, the objective of this study was to quantify selected PCBs in fish and seafood products relevant from both environmental and food safety points of view.

PCBs can be detected and quantified by gas chromatography with electron-capture detection (GC-ECD) or mass spectrometry (GC-MS). However, extreme care has to be taken during the sample preparation to obtain reliable results. Factually, during the extraction of PCBs from fatty samples, which is usually performed by soxhlet, ultrasonic or pressured fluid extraction, a wide range of organic compounds are co-extracted. Prior to GC-ECD or GC-MS analysis, this fatty matrix has to be eliminated by successive purification steps, to avoid an excessive background noise in chromatograms and to prevent column contamination. These treatments are very time-consuming, especially with a high number of samples, and thus constitute the main limiting step within the analytical throughput. With the aim of reducing the time needed for sample preparation, a new protocol using pressured solvent extraction has been developed. This procedure is based on the addition of successive layers of silica and acid-impregnated silica in the extraction cell, which actively retains matrix compounds. This "in-cell cleanup" allows the simultaneous extraction and purification of samples, so that the obtained extracts can be directly analysed by GC-MS without additional treatments, reducing the time needed for sample preparation.

This one-step extraction and purification procedure was applied to a number of seafood samples (prawns, mussels etc.), as well as fish (e.g. trouts, eels) caught in rivers presumably polluted by PCBs. The results pointed out that the concentrations of PCBs may vary considerably in fish and seafood samples, depending most likely on the fat content, size, and eating habits of the fish (i.e. being carnivorous vs. herbivorous). Among the 14 monitored PCBs, the congeners 153 and 138 were largely prominent in all the analysed samples.

THE CONTENT OF BUTYL- AND PHENYLTIN DERIVATIVES IN THE SEDIMENT FROM THE PORT OF GDANSK

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Harbor sediments containing large deposits of organotin compounds constitute a potential threat to the marine environment. Sediment dredged from the bottom of port canals is dumped at sea in the designated areas. Because of that there is a necessity to continually monitor and analyze the dredged spoils.

Samples of harbor sediments were collected twice in the years 2003 and 2005 from the following locations: Ziółkowskiego, Siarkowe, Wiślane, Węglowe, Chemików and Paliw Płynnych Quays. The cores of 25 cm length sliced into 2- and 5-cm segments were analyzed. After drying and homogenization, samples were split into two granulometric fractions, i.e. <2.00 and <0.063 mm. It has been established that sediment samples from the Port of Gdansk area mainly consist of fine and medium-fine sands with a small admixture of silty-clay, stones and gravel. The dominant fraction in whole sediment, i.e. fraction grain diameter <2.00 mm, was sand (grain diameter 2.00-0.063 mm). However, the highest concentrations of butyl- and phenyltin compounds were found in the fine sediment fraction. The content ratio of phenyltin to butyltin derivatives was 1:53 and 1:79 for fraction sizes <2.00 and <0.063 mm, respectively. The contents of TBT, DBT and MBT in the analyzed samples in the <2.00 mm fraction were 2144.9, 434.7 and 148.1 $\mathrm{ngSn \cdot g^{-1}}$d.w, respectively, while the corresponding values in the <0.063 mm fraction were 6556.4, 1593.7 and 450.0 $\mathrm{ngSn \cdot g^{-1}}$d.w. The mean MPhT concentrations have been estimated at 29.0 and 49.9 $\mathrm{ngSn \cdot g^{-1}}$d.w for the <2.00 and <0.063 mm fraction size, respectively. The estimated content levels of DPhT and TPhT were in most cases below the detection limit of the applied method. The sediment cores collected from the locations characterized by high industrialization and intense exploitation (Wiślane, Węglowe and Chemików Quays) contained the higfhest concentrations of BT and PT. The share of the determined compounds in the samples from the remaining quays (i.e. Paliw Płynnych, Ziółkowskiego and Siarkowe Quays) was many-fold lower.

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A SANITARY SURVEY ON COMMUNITY DRINKING WATER SUPPLIES IN COASTAL AREAS OF SRI LANKA

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A sanitary survey on community drinking water supplies was carried out in Sri Lanka on 158 dug wells - rarely connected to simple distribution systems - used for drinking purposes within households sited in coastal areas of the districts of Kalutara, Galle and Matara.

The survey consisted of sanitary inspection and water quality analyses. *In-situ* inspections aiming to achieve a comprehensive assessment of sanitary conditions of water sources were performed according to a new sanitary report form developed on the basis of WHO guidelines. Physico-chemical analyses (*i.e.* temperature, pH, electrical conductivity, salinity, redox potential, chlorophyll, cyanobacterial cells, dissolved oxygen, chlorine residue, total chloride) were performed through rapid validated tests using a multi-parameter *in-situ* probe monitoring instrument, reagent kits and *in-situ* assays based on photometric response.

Water samples were collected during the inspections and analysed according to EU standards to assess chemical and microbiological water quality. Laboratory chemical analyses performed within the NWS&DB laboratory of Colombo included measures of turbidity, ammonium, nitrate, nitrite, fluoride, total organic carbon and total phosphorus. Microbiological analyses were performed through conventional routine methods according to international and EU standards on the following parameters: Enterococci, *Escherichia coli*, Colony count at 37°C, total Coliforms and Enteric pathogens (*Salmonella spp.*).

Information gathered during sanitary inspection, combined with the results of the in situ and laboratory tests were reported in a web-shared database.

Significant hazards and critical points were identified in almost all the investigated water supplies. On the other hand, an altered water quality resulted from analytical results due to parameters of health and aesthetic concern. Only 13.3% of the examined sites fully complied with the chemical requirements of the current Drinking Water Directive 98/83/EC, as regards of the investigated parameters. Non-compliances were especially due to chemical indicator parameters (84.0%) and often associated to low pH values and/or high water turbidity. The water of only 4 wells was found in compliance with the standard values of the EU regulation (*i.e.* absence of *E. coli* and Enterococci - indicator of faecal contamination - in 100 ml). Furthermore, a risk assessment directly linked to the presence of pathogens in water used as a drinking water was performed, involving investigation of *Salmonella spp.*, the more common pathogen in water. A total of 59 samples (48.8%) out of the 121 investigated presented a contamination due to the occurrence of *Salmonella spp.*, with positive samples distributed within the 3 districts. The overall results showed a significant level of risk associated with drinking water consumption within the investigated areas, calling for an urgent improvement of water management particularly focused on source protection and disinfection practices.

FORMS OF HEAVY METALS IN THE SEDIMENTS OF THE CHOSEN STREAMS IN THE SWIETOKRZYSKI NATIONAL PARK, POLAND

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This article presents the results of a geochemical investigation of sediments from the chosen streams in the Świętokrzyski National Park (southern Poland). The sediment samples were analysed for pH and grain size distribution. The grain size fraction $< 2\,\mu$m was used for chemical analysis: total element content (Al, Ca, Fe, K, Mn, Cd, Ni, Pb, Zn), total inorganic and organic C, and bonding form fractionation with a five-step sequential chemical extraction by Tessier et al. method [1]. Each of the chemical fractions is operationally defined as follows: (1) exchangeable; (2) bound to carbonates or specifically adsorbed; (3) bound to Fe-Mn-oxides; (4) bound to organic matter and sulphides; and (5) residual. Residues after sequential extraction were mineralised in concentrated nitric acid in order to check if applied sequential extraction procedures allowed to extract total amount of metals from bottom deposits. Metal contents were determined with F-AAS technique in particular extracts.

Bottom deposits of tested watercourses are characterized by high diversity of occurrence and content of individual fractions of analysed heavy metals. Among others it is a result of different land development, plants and possibility for inflow of pollutants from flow down. Moreover diversified surface features and lithology of catchment significantly contributes to permeability of surface deposits and water quality. The multielement measurements gave useful information to assist in the interpretation of the possible geochemical forms and sources of the trace elements in sediments of the streams in the Świętokrzyski National Park.

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THE APPLICATION OF THE DIFFERENTIAL PULSE VOLTAMPEROMETRY TO DETERMINE THE DEGREE OF ZINC COMPLEXATION BY CHELATING AGENTS

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Substances, which are complexing microelements in fertilizers should carry off cations in solutions, independent of other fertilizer compounds and at the wide range of pH [1]. Plant should take microelement in time which is correlated with the biodegradation time of chelating agents used in liquid fertilizers production [2]. The degree of micronutrient complexation in liquid fertilizers should be 80% or more [3].

Both natural and synthetic compounds are used for complexing fertilizer microelements. The most commonly used synthetic complexing agents are ethylenediaminetetraacetic acid (EDTA), diethylenetriaminepentaacetic acid (DTPA), N-(hydroxyethyl)-ethylenodiaminotriacetic acid (HEEDTA) and their salts [2]. But the biodegradation degree of this compounds is too small. For this reason it is important to search for substances which will have similar complexing properties but higher biodegradation's degree. Among substances, which are characterized by these properties, we can distinguish: S,S-ethylenediaminedisuccinic acid (S,S-EDDS), methylglycinediacetic acid (MGDA) and dicarboxymethylglutamic acid (GLDA) [4].

The aim of researches was to determine of degree of zinc complexation by different chelating agents in aqueous solution in the presence of basic electrolyte and at different pH values.

The degree of zinc complexation by chelating compounds (EDTA, DTPA, HEEDTA, NTA, S,S-EDDS, MGDA, GLDA) was determined by the differential pulse voltametric with dropping mercury electrode working in SMDE mode. Reference electrode was silver chloride electrode and auxiliary electrode was glassy carbon electrode. Voltametric researches were carried out on the AUTOLAB PGSTAT 12 (Eco Chemie - The Netherlandes) with GPES software with the use of mercury electrode 663 VA Stand (Metrohm - Swiss).

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THE POSSIBILITY OF THE APPLICATION OF ACTIVATED SLUDGE FROM MUNICIPAL WASTEWATER TREATMENT PLANT IN BIODEGRADATION OF CHELATING AGENTS

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In the present work, the chemical analysis of activated sludge and influence of chemical parameters on the activated sludge from municipal wastewater treatment plant destined for biodegradation test is discussed.

Activated sludge is a biocenosis of different microorganisms, for example bacteries, microscoped fungis, ciliata or rotatoria. In traditional terminology activated sludge is decribed as mixed microorganisms cultures, which take of an active participation in wastewater treatment [1].

The aim of researches was to assess the chemical parameters and their influence on the activated sludge cultivated under laboratory conditions destined for biodegradation tests. This assessment was made by the determination of total nitrogen content with distillation method, chemical oxygen demand (COD) by dichromate method, total suspended matters by gravimetric method and pH measurement. These parameters were determined on activated sludge samples and waste in three intervals of time: t=0 days, after 7 days and after 14 days. First experiments (t=0) were performed immediately after sampling the activated sludge from municipal wastewater treatment plant.

Researches were carried in three reactors of 3.5 dm^3 capacity. Every day, after 24 hours, synthetic sewage was taken for analysis, and the same volume was added to the reactor to keep the age of activated sludge. As a inoculum activated sludge from municipal wastewater treatment plant was used. It is mechanical - biological wastewater treatment plant with chemical support of phosphorus compounds removal and about 70,000 m^3 of wastes are cleaned per day.

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ISOTOPES OF URANIUM ^{234}U AND ^{238}U FOR INDUSTRIALIZED AREAS (WISLINKA)

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Amongst natural radionuclides, alpha emitters play a significant role in state radiological effects connected with accumulation of these radionuclides in organisms. Uranium occurs naturally in the Earths crust and is present in much higher concentration (more than 10%), along within thorium and other rare-earth elements. Naturally occurring uranium contains three alpha emitting radionuclides ^{234}U, ^{235}U and ^{238}U. The ^{234}U isotope belongs to the radioactive decay series of ^{238}U. Natural concentration of uranium in environment is increased by results of activity - industry, fossil fuel combustion, phosphate fertilizers in agriculture, domestic and industrial sewage.

One of significant components of Vistula river delta is phosphogypsum waste dump near Martwa Wisła in Wiślinka. Phosphogypsum waste heap in Wiślinka was started 30 years ago. Phosphorites, the main ingredient of phosphogypsum is imported from Africa North (Morocco) to Poland. Waste heap is forty meters high, several million tons weight and covers over 85 hectares of land.

Samples of water were collected in November 2006 from area around the phosphogypsum waste dump. The activities of uranium were measured using the alpha spectrometry. The highest concentrations of uranium were observed in the nearest area of waste heap. Isotopes of uranium ^{234}U and ^{238}U are not in the radioactive state equilibrium. Higher disequilibrium has been noticed rather in water samples close to dump, than in ones from bigger distance.

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DETERMINATION OF ANIONS AND CATIONS IN AEROSOLS BY ION CHROMATOGRAPHY

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The determination of anions and cations in atmospheric aerosols yields essential information concerning transport and atmospheric transformation processes as well as emission sources. Up to now these determinations have been carried out using filters that collect the aerosol particles over a long period of time, usually 24 hours. Prior to ion chromatographic analysis, the particles are removed from the filters and taken up in water. However, this batch method only allows to determine averages over a time span of 24 hours or more. Additionally, this method is very labour-intensive, temporal resolution is poor and semi-continuous on-line measurements are not possible. On top of this, the results can be falsified by desorption processes and chemical reactions. The reliability of the results thus obtained is therefore questionable.

In contrast to the above, the particle sampler to be described allows continuous sampling of aerosols. Changes in the ionic composition of the aerosols are monitored. The sampling system is coupled to an 850 Professional IC for anions and cations, which allows quasi-continuous measurements. The temporal resolution is 5 to 15 minutes. Rapid changes can thus be recorded immediately and correlated with meteorological and other data.

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ON-LINE HIGH-PERFORMANCE LIQUID CHROMATOGRAPHIC SEPARATION AND COLD VAPOR ATOMIC FLUORESCENCE SPECTROMETRIC DETERMINATION OF METHYLMERCURY AND INORGANIC MERCURY

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A reversed-phase high-performance liquid chromatography-ultraviolet-post-column oxidation-cold vapor-atomic fluorescence spectrometry (HPLC-UV-PCO-CV-AFS) is developed for mercury speciation. In this studies, the efficiency of different complexing reagent (e.g. 2-mercaptoethanol, cysteine, EDTA) in a methanol-water mixture as mobile phase is evaluated for HPLC separation of methylmercury and inorganic mercury coupled with on-line CV-AFS determination. Different reversed-phase columns (C_{18}) were also studied for the efficiency of separation. Several parameters (e.g. composition and flow-rate of mobile phase) are investigated for the optimization of HPLC separations. The efficiency of post-column oxidation was also studied (length of the UV coil, bromate/bromide concentration in oxidizing agent, oxidizing agent flow-rate). CV-AFS technique parameters are also studied for their effect on sensitivity (tin (II) chloride and hydrochloric acid concentrations in the reducing agent, reducing agent flow-rate, length of the reduction coil and argon flow-rate). Quantitative recoveries for both inorganic mercury and methylmercury are obtained from a spiked natural water sample.

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MERCURY IN THE GROUNDWATER OF THE NEOGENE LAYER OF POZNAN CITY, POLAND

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The aim of this study was to determine a distribution of mercury in ground waters from Tertiary sediments of the Poznań city. Total mercury concentrations have been determined in samples collected from 37 sites in 2006. Mercury was determined using the cold vapor atomic fluorescence spectrometry method (CV-AFS). The median of total mercury concentration in ground water was 7.9 ng dm^{-3} (range 3.3-48). Higher mercury concentrations were in samples collected from sediments of Lower Miocene 15 ng dm^{-3} (range 6-48), lower in sediments of Middle Miocene 7.3 ng dm^{-3} (range 4-29) and the lowest in sediments of Upper Miocene 4.5 ng dm^{-3} (range 3-12). The total mercury concentration in ground water from Tertiary sediments was not correlated ($p > 0.05$) with conductivity acidity and total organic carbon. Obtained results of this study showed that direct leaching from Quaternary sediments is not main source of mercury in ground water from Tertiary sediments.

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THE DEVELOPMENT OF SOLID PHASE MICROEXTRACTION AS THE PASSIVE SAMPLER FOR THE DETERMINATION OF GASEOUS PESTICIDES IN AIR

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Air quality is very important to human health. Pesticides belong to a family of semi-volatile organic compounds that have been observed in the atmosphere. Many samplers, including active samplers and passive samplers, have been developed for the analysis of the gaseous pesticides. Solid phase microextraction (SPME) has the advantages of solvent-free, convenient coupling with field analytical instruments, cost effectiveness and simplicity of operation. It has been described as an innovative, power free, multi task passive air sampler providing both peak and time weighted average concentrations [1].

Herein, solid phase microextraction (SPME) was experimented for pesticide air sampling. Active " low volume sampling " with Polyurethane foam (PUF) was also performed to calculate the sampling rates of pesticides using SPME fibers. The analysis of the target analytes were performed by GC-MS/MS.

A standard gas generating system was developed in the present study. In this system, the concentration, temperature, and air velocities could be controlled and modified. 11 target pesticides (powder or liquid) were put in a section of Teflon tube and then the tubes were put into two ovens of the standard gas generating system according to the boiling points of the pesticides. All the pesticides were detected by SPME from the outlet of the ovens. To transfer the pesticides from the oven to the gas sampling bulb, a dilution loop was added and the exit of the transfer line was connected to a glass sampling bulb. After dilution by a factor 30 by the dilution gas, 10 pesticides could be detected by low volume sampling with PUF (flow rate of 1.5 l min^{-1} for 4 h and 10 h). The concentrations ranged from 84 to 4061 ng m^{-3}. 6 pesticides were detected by SPME after the fiber was exposed to the air in the sampling bulb for 30 min. From the SPME extraction profile, the uptake rates (n/t) could be obtained. Using Fick's law of diffusion, the sampling rates (SRs) could be calculated using the equation $SR=n/Ct$, where n is the amount of analyte on the fiber, C is the gaseous concentration of pesticides, and t is the sampling time [2]. The SRs for 6 pesticides were 20.4-48.3 ml min^{-1} for the exposed fiber and 0.166-0.929 ml min^{-1} for the retracted fiber. Once the SRs were known, SPME could be applied to determine the unknown concentrations of pesticides in greenhouses air samples.

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AIR CONTAMINATION AND THE INHALATION EXPOSURE IN AGRICULTURAL GREENHOUSES: SAMPLING AND ANALYSIS OF GASEOUS PESTICIDES BY SPME-GAS CHROMATOGRAPHY-TANDEM MASS SPECTROMETRY

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The warm and humid conditions often encountered inside greenhouses cause high pest and disease pressure and lead to intensive pesticide use. To estimate the exposure of the pesticides for the greenhouse workers, the concentrations of pesticides in the air are required. The conventional method for the determination of the concentration of pesticides in air is active sampling method. The method draws air at constant flow rates through solid sorbents using a pump and the analyte sorbed on the sorbents is desorbed and analyzed. To overcome the limitations inherent to active sampling, such as the high cost of the pump, frequent calibration routines, and the requirement of chemical desorption with toxic solvents, passive air sampling tools and methods have been developed as a versatile and cheap alternative to the active methods. Passive sampling can be defined as any sampling technique based on free flow of analytes from the sampled medium to a collection medium, as a result of the difference in chemical potential of the analytes between the two media.

Solid phase microextraction (SPME) is one of the most attractive passive sampling techniques developed recently [1]. In the present study, solid phase microextraction (SPME) was applied to the determination of the concentration of pesticides in the air. Sampling time with SPME ranged from 30 min for exposed fiber to 8 h for retracted fiber for assessment of short-term and long-term exposures, respectively. Using Fick's law of diffusion, the concentration of pesticides on the SPME fiber can be calibrated using the sampling rates (SRs). The sampling rates (SRs) of two modes of SPME in the field were determined. In field sampling, two pesticides, dichlorvos and cyprodinil were detected by exposed SPME and SRs were 32.4 ml min^{-1} and 18.4 ml min^{-1}, respectively. With retracted SPME, only cyprodinil was determined and the SR was 1.55 ml min-1. During the sampling period, the concentrations of cyprodinil increased from 0.08 μg m^{-3} to 0.59 μg m^{-3} during the first sampling day. And it decreased rapidly from 0.59 μg m^{-3} to 0.07 μg m^{-3} in the next day and then remained the similar level. For dichlorvos, the concentration increased from 0.15 μg m^{-3} to 0.36 μg m^{-3} during the first sampling day (5 days after spraying). In the following day, the concentration decreased slightly to 0.34 μg m^{-3} in the morning. Then the concentration decreased rapidly from 0.34 μg m^{-3} to 0.07 μg m^{-3} during the second day. From the data, it could be concluded that the concentration of cyprodinil decreased faster than dichlorvos. Calculated from the 8 h average concentration of cyprodinil, the daily exposures of cyprodinil were 174 ng d^{-1} on the second day.

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DIFFERENT WATER SAMPLING TECHNIQUES FOR MONITORING OF TRACE METALS CONCENTRATIONS IN THE MORAVA RIVER

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The concentrations of Cd, Cu, Ni, Pb were monitored using different sampling method in Morava River (Czech Republic, South Moravia). Unfiltered and filtered samples of water were taken to assessment of total metal and total dissolved metal concentrations. Available concentrations of trace metals for aquatic organisms were monitored by deployment of aquatic moss species *Fontinalis Antipyretica*. The Diffusive gradient in thin films technique (DGT) [1] was used for determination of kinetically labile metal species which are able to diffuse through the diffusive gel and which are accumulated in resin gel that contains Chelex 100 Resin. The *Fontinalis Antipyretica* and DGT sampling units were deployed together in Morava River for 28 days intervals from August 2007 to April 2008.

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FRACTIONATION AND SPECIATION ANALYSIS OF ALUMINIUM AND THALLIUM AFTER BIOACCUMULATION AND BIOSORPTION THEIR LABILE SPECIES BY MICROSCOPIC FILAMENTOUS FUNGI AND COMPUTER MODELING

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From the distribution of Al(III) species results that only Al^{3+} aqua ions and their some cationic and anionic hydroxocomplexes are presented in aqueous solution. The sulphates, fluorides and some organic complexes of Al are common soluble species. The Al labile cationic monomeric aqua-, hydroxo- and probably sulphato- complexes, and some polymeric species of Al (e.g. Al_{13}) are considered to be most toxic. Thallium has two important oxidation states, Tl(I) and Tl(III). The Tl(I) (thallous) compounds behave like alkali metals, whereas Tl(III) (thallic) compounds are less basic, resembling aluminum. The Tl(I) forms (relatively weak neutral or anionic complexes) are the dominant species in natural environment. They are somewhat more toxic than Tl(III) species which form much stronger complexes. The labile, more water-soluble, Tl species (e.g. sulphate, acetate, carbonate) have been found to be more toxic. Bioaccumulation and biosorption of Al and Tl labile species by different kinds of microbial fungi (*Neosartorya fischeri, Aspergillus niger, Aspergillus clavatus*) were used as the bioseparator-based tool for operationally and/or functionally defined fractionation of both metals in synthetic solutions and polluted natural waters. The speciation of both metals in synthetic solutions was calculated by computer modelling. The concentrations of Al and Tl were measured by FAAS, ETAAS, HG AAS and ICP OES. The obtained results show that only soluble inorganic momomers of Al(III) and Tl(I) are presented in the water synthetic solutions at given pH values. The labile aqua cations Al^{3+}, $Al(OH)^{2+}$ and $Al(OH)_2{}^{+}$ are the prevailing species below pH 5.0, between pH 5.0 and 6.2 there is a mixture of these cations and $Al(OH)_3$ species and above pH 6.2 the dominant species is $Al(OH)_4{}^{-}$. The labile cations Tl^{+} and relatively weak neutral complexes (TlOH) are the prevailing species at given conditions. It is assumed that dimethylthallium ($Me2Tl^{+}$) is the main Tl chemical form biovolatilized by fungal biomass of *Neosartorya fischeri*. The used approach can be useful for *in-situ* bioseparation of toxic Al and Tl species directly in the ecosystem and also for biotechnological application of the remediation techniques based on the long-term bioaccumulation of both metals by studied fungi.

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THORACIC, FINE THORACIC, SUB-MICROMETER ATMOSPHERIC PARTICULATES AND BTEX IN THE OFFICE ENVIRONMENT

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Since people in moderate-temperature developed countries spend more than 90% of their time indoors, the quality of indoor air has received growing attention from many environmental scientists. Quite often office workers complain about health problems which seem to be related to the indoor air quality at the workplace environment.

In total, ten offices were selected for closer inspection in the city centre of Antwerp, Belgium. The selection was made along the same main street, in order to ensure a comparable outdoor influence. Each office was sampled for thoracic (PM_{10}), fine thoracic ($PM_{2.5}$) and sub-micron (PM_1) atmospheric suspended particulate matter during three working days and two nights. PM samples were analysed gravimetrically and subsequently the chemical composition was determined by energy dispersive X-ray fluorescence spectroscopy and ion chromatography. The black carbon content was monitored continuously (every 5 minutes) during the whole sampling week. Additionally, benzene, toluene, ethyl benzene and the xylene-isomers (BTEX) were sampled passively for five working days (8h/day).

The experimental design described above allowed to assess the levels of PM and BTEX to which the office workers were exposed. These levels were compared to the amount of PM and BTEX collected during night and weekends, respectively, in order to determine the amount of anthropogenic pollutants emitted indoors.

The variation of the PM levels among the different offices was explained by some office characteristics. For example, offices equipped with a mechanical system for ventilation were shown to have substantially lower levels of coarse particulates, while the finer particles weren't affected too much. The BTEX levels, and especially the finer PM levels, were significantly enriched during working hours so that emissions by human activities could not be ruled out. Nevertheless, it should be stressed that also the ambient pollution had a great impact on the air quality at the office environment.

MONITORING OF INORGANIC GASEOUS POLLUTANTS IN THE POLISH REGION OF THE BLACK TRIANGLE

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In the late 70's, the triangular border area between Germany's Southern Saxony, Poland's Lower Silesia and the Czech Republic's Northern Bohemia gained its ominous fame as one of the most polluted area in Europe. This is the reason, why it got a shameful nick name "The Black Triangle". Its location in the old and geologically diverse mountains makes it rich with various natural resources and therefore rapid and intensive development of heavy industry, which generated high concentrations of SO_2, NO_2 and other air pollutants. The acres of dead forests due to extremely acidic rains created a gloomy landscape. Since 1991, Poland, Czech Republic and Germany have been working together to reverse the trend in air pollution by reducing pollution by using desulphurisation equipment, electrostatic precipitator, modern combustion techniques and fuel with small amounts of sulphur and nitrogen. However, the monitoring of gaseous pollutants related to a human health is still important and necessary. The aim of presented work was to monitor the level of inorganic polluting gases as NO_2, SO_2 and O_3 within the Polish part of the Black Triangle. The area of Lowest Silesia is very famous for its health resorts offering mineral waters and being very attractive for tourists. The investigation was focused on the Kotlina Jeleniogórska region with the health resorts: Świeradów, Czerniawa, Rozdroże Izerskie, Szklarska Poręba, and Cieplice. Samples were collected during four campaigns with passive diffusion tubes exposed to ambient air for seven days. Afterwards, adsorbed amounts of gases was analyzed by ion chromatography. The sampling was organized seasonally in July 2006, February 2007, July 2007, and February 2008. During the 1st and the 3rd campaign, the measured levels of NO_2 (mean values: 6 $\mu g/m^3$ and 4 $\mu g/m^3$, respectively), SO_2 (0.8 $\mu g/m^3$ and 0.9 $\mu g/m^3$) and O_3 (115 $\mu g/m^3$ and 77 $\mu g/m^3$) were similar between different sites, except Cieplice with a higher concentration of NO_2 (below 12 $\mu g/m^3$ and 11 $\mu g/m^3$), and a lower concentration of O_3 (77 $\mu g/m^3$ and 48 $\mu g/m^3$). However, during the 2nd and the 4th campaign, no significant differences of NO_2 (around 16 $\mu g/m^3$), SO_2 (2 $\mu g/m^3$) and O_3 (30 $\mu g/m^3$) levels between five sampling locations were found. As expected, a continuous trend of the changes of the gaseous pollution in summer and winter was observed. The seasonal changes of the atmospheric pollutants are linked to domestic heating (during the cold season), which has a meaning in terms of the recognition and share of different sources of pollutants (fossil fuel combustion). The concentration of O_3 was much higher in summer than in winter, while the concentration of NO_2 and SO_2 much lower. To estimate the influence on the level of gaseous pollutants from the local sources or from the surrounding countries sources, the backward air masses trajectories were used.

IMPACT OF OUTDOOR HIGH AIR POLLUTION EPISODES ON INDOOR AIR QUALITY IN NURSING HOMES FOR THE ELDERLY - CASE STUDY IN BELGIUM

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Belgium is known as a region with the highest annual mean mass particulate matter (PM) concentrations in Europe, and also represents a country of a very high percentage of elderly population. Numerous studies have shown a strong association between daily mortality and fine PM in ambient air; especially this is pronounced for elderly people who represent a population group, which is susceptible to the short-term effects of air pollution [1, 2].

The aim of this study was to asses the indoor air pollution in nursing homes for the elderly, e.g. in Ranst (Belgium) and to gain improved knowledge on which chemical compounds are associated with the adverse health effects. Since this specific group of people spend the major part of the day indoors, the air quality inside the buildings seems to be of great importance. The size fractions of PM_1 and $PM_{2.5}$ (PM smaller than 1 μm and 2.5 μm, respectively) were collected indoors and outdoors of the building, during a two week sampling campaign in February 2008. This period was selected on the base of an air pollution model, which forecasted an episode of high PM pollution. Harvard-type impactors (MS&T Area Samplers, Air Diagnostics and Engineering, Inc., Harrison, ME, USA) equipped with a very quiet low-volume oil-free pumping unit (flow rate about 23 and 10 l/min for PM_1 and $PM_{2.5}$, respectively) were used for PM collection. Samples were collected on Teflon membrane filters during 24 hours. The collected bulk PM samples were analysed gravimetrically to determine the total mass concentration. The elemental composition of the dust was determined with energy-dispersive X-ray Fluorescence analysis (EDXRF). Elements, such as Si, K, Ca, Ti, V, Fe, Al, S, Cl, Se, Sr, Cr, Ni, Mn, Cu, Zn, As, Pb were detected. Selected gaseous compounds, both organic (BTEX) and inorganic (NO_x, O_3 and SO_2), were sampled by means of Radiello® (Fondazione Salvatore Maugeri, Padova, Italy) passive diffusive samplers.

During the first week, the outdoor concentrations of PM_1 and $PM_{2.5}$ did not exceed a value of 26 $\mu g/m^3$ and 53 $\mu g/m^3$, respectively. In second week, however, the values were significantly higher with a maximum of 46 $\mu g/m^3$ for PM_1 and 100 $\mu g/m^3$ for $PM_{2.5}$, which reached already smog concentrations. In general, all indoor/outdoor ratios for both PM_1 and $PM_{2.5}$ were lower than 1; they oscillated around 0.5. It should be stressed that in the second week the value of 50 $\mu g/m^3$ was extended indoors. The contribution of PM_1 in the $PM_{2.5}$ fraction was 60-70% and was significantly higher in the first week. Ozone and SO_2 concentrations were relatively low and did not exceed the EU outdoor limits. The values for NO_x were higher and they were in some cases close to the EU restrictions. The levels of BTEX were significant; especially benzene approximated the limit value of 5 $\mu g/m^3$.

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APPLICATION OF CLOUD POINT EXTRACTION FOR SELECTIVE SEPARATION AND PRECONCENTRATION OF ANTIMONY(III) IN NATURAL WATERS

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In this work, cloud point extraction (CPE) was applied for selective separation and preconcentration of Sb(III) prior its determination by electrothermal atomic absorption spectrometrometry (ETAAS). After complexation of Sb(III) with ammonium pyrrolidine dithiocarbamate (APDC) in mildly acidic medium, the analyte was quantitatively extracted to the phase rich in the non-ionic surfactant octyl phenoxy polyethoxy ethanol (Triton X-114) after centrifugation. Then, the mixture was cooled in an ice-bath to increase the viscosity of the surfactant-rich phase and the bulk aqueous phase was decanted. Finally, the surfactant-rich phase was diluted by 0.20 mol l^{-1} HNO_3 in methanol and the concentrated analyte was introduced into ETAAS. Potential factors affecting the CPE separation/preconcentration of Sb(III) were investigated in detail. Under optimal conditions, the relative standard deviation (RSD) for ten replicate measurements at 0.40 $\mu g\ l^{-1}$ Sb(III) level was 6.5% and the enrichment factor for this determination was 28. The linear concentration range was from 0.10 to 3.50 $\mu g\ l^{-1}$ Sb(III). The detection limit of 0.03 $\mu g\ l^{-1}$ Sb(III) was achieved. The optimized method was applied to the determination of Sb(III) in natural waters.

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SEPARATION, PRECONCENTRATION AND DETERMINATION OF THALLOUS AND THALLIC SPECIES IN WATER SAMPLES BY SOLID PHASE EXTRACTION AND ETAAS

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In natural waters, thallium exists as either Tl(I) (thallous) or Tl(III) (thallic) species. The oxidation state of Tl affects its complexation and subsequent bioavailability and toxicity in the environment. Thallium content in surface waters is within the range 1-82 ng l^{-1}. Due to this low contents of thallium in water samples, it is necessary to combine the laboratory separation, preconcentration and determination techniques for the purpose of Tl speciation analysis [1]. The scope of the presented work was to use an solid phase extraction for the separation and preconcentration of thallium species in water samples followed by electrothermal atomic absorption spectrometry (ETAAS) determination. In this method, Tl(III) was stabilized by formation of a Tl(III)-DTPA complex. Tl(I) species remained in its original form. These two species were then separated by using a strongly acidic, gel-type cation exchange resin Amberlite IR120 and nitric acid as the eluent in a batch solid phase extraction protocol. The potential interferences of Fe(III), Al, Ca, Mg and other metals were investigated. The optimized experimental conditions for separation/preconcentration step (pH 2-3, time 15 min, temperature 60°C) and Zeeman ETAAS determination (chemical modifier Pd + ascorbic acid, atomization temperature 2100°C [2]) were used for the speciation analysis of thallium in filtered acid water samples from open quartzite mine in the Banská Štiavnica - Šobov region (Slovakia) where an acid mine drainage is present mainly as a product of pyrite oxidation [2]. For both Tl species the preconcentration factor about 40 was achieved, then LOD and LOQ were 25 ng l^{-1} and 90 ng l^{-1}, the calibration curve was linear from 75 ng l^{-1} to 25 μg l^{-1}, the precision expressed by a RSD ranged from 3 to 19%. The accuracy of analytical results was checked by the analyte addition technique and by analysis of water CRM samples.

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CHROMATOGRAPHIC EVALUATION OF SOME CARBOHYDRATES FROM ROMANIAN WINES

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Sugars play a decisive role in the wine formation through alcoholic fermentation and in the establishment of wine type regarding the sweet taste. Romanian wines are of a large variety: white, rose, red, dry, demi-dry, demi-sweet and sweet.

The best choice for analysis of the complex mixtures of sugars is the chromatographic separation.

In this paper are presented some chromatographic (HPLC, TLC) studies regarding the natural carbohydrates (glucose, fructose, sucrose) occurring in wines on natural way or by addition.

The identification and quantification by HPLC method of some studied carbohydrates from different wine samples was done using a Jasco-980 liquid chromatograph and different conditions in isocratic elution (Hamilton PRP-200 column with 0.5 mM H_2SO_4 mobile phase at a flow rate of 0.5 mL/min; refractive index detector).

The TLC method for the separation of the mentioned compounds was performed on plates of silica gel 60 Merck on aluminium support, in normal saturated chamber, developed three successive times by the mobile phase of ethyl acetate/2-propanol/water (6:3:3, v/v) mixture. The sugars spots were visualized by spraying the plates with a solution of thymol in acetone, the spots being well separated. The densitograms were registered on a Desaga CD-60 densitometer.

The studied wines were purchased from the market covering the whole range of white wines with different degrees of sweetness from different Romanian vineyards.

The chromatographic results were compared with that obtained by mass spectrometry.

Our analyses demonstrated the natural content in carbohydrates (fructose and glucose) of the studied white wines.

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THE OPLC CONTROL OF NATURAL CARBOHYDRATES FROM ROMANIAN WINES

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The OPLC method [1] has not yet been used for analysis of natural carbohydrates (fructose, glucose, sucrose) from wines [2,3]. Taking into consideration the well-known advantages of the OPLC method (elution short time, a better resolution, small sample quantities), we applied this method to control the wine quality.

In the present work we analyzed by this technique the sugar content of some Romanian wines because sugar, as it is well-known, play a decisive roll in the wine formation, (alcoholic fermentation) and the establishment of the wine type (dry, demi-dry, demi- sweet or sweet). The measurements were carried out on a Personal OPLC 50 Chromatograph. Best results were obtained on silica gel OPLC plates, with the isopropanol-ethyl acetate-water or acetonitrile-water as mobile phases. The spots were visualized by spraying with a thymol solution. The densitograms were registered on a Desaga CD-60 densitometer.

The experimental results obtained studying 30 types of wines from the market indicated their natural origin concerning the carbohydrate content.

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CHROMATOGRAPHIC STUDIES REGARDING THE COLORANTS FROM ROMANIAN WINES

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The natural colour of red wines is due to the phenolic compounds (antocyanines and tanins) and that of the white wines to the flavones, catechins and leucoantocyanines. The colour of wines defines their type and quality, gives information about the aspect, taste and composition and allows their classification (white, rose, red).

The chromatographic methods are suitable for the analysis of both natural and synthetic colorants [1,2]. If the synthetic colorants from the suspect wines can be easy identified by the empirical method of wool impregnation, the natural colorants others than those original from grapes can be identified only by analytical methods.

This paper presents some chromatographic (HPLC, TLC) studies regarding the food colorants (natural and synthetic) that could be used for wine adulteration.

The experiments were performed on different natural extracts (beetroot, red grapes, bilberries, Enocolor (trademark skin grape extract).

The HPLC determinations of studied colorants were performed with a Jasco-980 liquid chromatograph on Nucleosil 120 C18 columns, with gradient elution and UV-Vis detection.

The TLC experiments for the separation and identification of analyzed colorants were carried out on RP-C18/UV_{254} plates eluted with an acetone-water buffer solution in a saturated chamber with two deepings. The densitograms were registered on a Desaga CD-60 densitometer.

The studied wines were purchased from the market covering a large range of wines (white, rose and red) from different Romanian vineyards.

The chromatographic results were compared with that obtained by mass spectrometry and UV-Vis spectroscopy.

The results obtained from this study of food colorants (natural and synthetic) could be used to enhance the control of quality and of authenticity of Romanian wines.

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PCBS SORPTION ON RIVER SEDIMENTS

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The sorption process may significantly influence the chemical and biological transformation or degradation of chemicals in the aquatic environment [1-4]. Hydrophobic chloroorganic compounds are generally resistant to degradation and even at very low concentrations they have an impact on biota health. In aquatic systems, sorption of hydrophobic chloroorganic compounds runs on the abiotic particles (e.g. dissolved organic compounds, suspended matter and sediments) as well as on water organisms [4-10].

The sorption of 8 PCBs (IUPAC No 28, 52, 101, 118, 153, 138, 180, 189) on three river sediments conducted on bath-type experiments were studied. The sediments were taken from river mouth cross-sections of the Warta and Olawa Rivers and from the Odra River in Opole town. The sediments were characterized by the TOC content from 1 to 9%. After 30 minutes of sorption experiments in temp. 20°C 90% PCBs from a water phase were sorbed on the sediments. The sediment-water partition coefficients (Kp [L/kg d.m.]) and organic carbon normalized sediment-water partition coefficients (Koc [L/kg TOC]) were calculated. The log Kp values varied from 2,66 to 4,27 while the log Koc values varied from 4,36 to 5,31. With increasing the TOC contents in the sediments log Kp values increased, and square of correlation coefficients (R^2) for linear relationship between log Kp as well as TOC contents changed from 0,67 to 0,99. As far as sediment characterized by TOC content equal 9% is concerned, the log Koc values increased with increasing of PCBs hydrophobicity (octanol-water partition coefficient, Kow), ($R^2 = 0,84$). There were no linear correlation for the PCBs log Koc and Kow values for the sediments with TOC contents less than 9%. It was found that temperature had a certain influence on the PCBs sorption. In case of the PCBs sorption on sediments characterized by the TOC equal 1% the content of the sorbed PCBs in 4°C was slightly higher than in 20°C. As far as the sediments with a higher TOC content (TOC > 4%) are concerned, there was no temperature influence on PCBs sorption.

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CRITICAL COMPARISON OF ANALYTICAL PERFORMANCE OF CVAAS AND ICP-MS FOR THE DETERMINATION OF MERCURY IN ENVIRONMENTAL SAMPLES

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Mercury is a toxic element of widespread environmental and clinical importance. The monitoring of the presence of mercury and its compounds requires the use of valid analytical methods, which offer accurate and precise results, independently of the chemical form of the interest element. Cold vapour atomic absorption spectrometry (CVAAS) and inductively coupled plasma mass spectrometry (ICP-MS) has been most widely used for the detection of mercury. The aim of presented work was to evaluate and compare the analytical performance of CVAAS and ICP-MS for the determination of mercury under the conditions of using single-compound calibration. The investigations were carried out using mercury in the form of inorganic as Hg(II) or organic as phenylmercury (PhHg(I)) ions. Preliminary experiments were focused on the evaluation of the analytical figures of merit for the determination of mercury being present in defined chemical form. Besides the measurement techniques being used, the sensitivity was always higher, when mercury was present as inorganic Hg(II) ions. In the case of CVAAS sensitivity was three times higher for Hg(II) than for PhHg(I) and limits of detection were 27 ng L^{-1} and 75 ng L^{-1}, respectively. With the use of ICP-MS sensitivity for Hg(II) was two times higher than for PhHg(I) and limits of detection 15 ng L^{-1} and 42 ng L^{-1} were obtained, respectively. It could be therefore concluded that in both techniques analytical parameters depend on chemical form of mercury. Thus, the measured total concentration of mercury in natural samples may not reflect the real content of mercury, if the calibration has been made with the use of standard solutions containing single mercury species. This hypothesis was confirmed by the recovery studies, which were performed for the determination of mercury species in various water samples. It was found, that in any of used analytical technique, it was not possible to obtain accurate results for Hg(II) with the use of calibration curve made for PhHg(I), and for PhHg(I) with the use of calibration curve made for Hg(II). Therefore, the effort was done towards optimization of the measurement conditions as to obtain the uniform response, independently on the mercury species being present in the sample solution.

METHYL- TERT- BUTYL - ETHER ANALYSIS IN SOME SITES AND RIVERS IN ROMANIA

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MTBE (Methyl-tert-butyl-ether) is a chemical of high production volume used worldwide with an amount of about 20 Mt/year [1]. The by far major use of MTBE is its blending into gasoline as octane enhancer and/or as oxygenate additive. The use of gasoline oxygenated with MTBE resulted in 16- 23% lower emissions in CO and 18% lower emissions in unburned hydrocarbons. The main production capacities of MTBE in Europe are located in Netherlands (1.123 Mt), France (0.831 Mt), Germany (0.652 Mt), Spain (0.42 Mt), Belgium (0.387 Mt), Italy (0.352 Mt), United Kingdom (0.304 Mt), Romania (0.22 Mt, at Onesti, Ploiesti, Midia, Pitesti).

MTBE can be emitted into aquatic environment through a variety of sources. Point source releases are mainly related to: leaking underground storage tanks (LUSTs); at MTBE production/ formulation sites; to leaking pipelines; to gasoline stations. If only one litter of gasoline containing 11% w/w MTBE is mixed with 4000 m^3 of water the resulting concentration is 20 μg MTBE/L. With this MTBE concentration the water gas unpleasant taste and odour of terebentine. It is not drinkable. So, large amounts of water can be contaminated with small quantities of Euro Super gasoline. USEPA proposed a maximum concentration of **20- 40 μg/L** in 1997 [2]. This limit, 20 000-100 000 times inferior than the concentration with toxically effects on rats, was fixed as a taste and odour threshold for humans.

Systematic monitoring studies have been done in Germany [3] where maximum concentration of MTBE was found in a contaminated site in Duesseldorf (41.9 mg/L). Other maxima: 0.608 μg/L in drinking water, at Spergau; 5.42 μg/L in river water (Rhine); 0.631 μg/L in snow (at Smucke); 28.42 μg/L in industrial effluents (Leuna).

This study presents MTBE analysis results in several contaminated sites and two rivers in Romania, using the method recommended by Schmidt [4].The samples were stored in 100 mL brown glass vials, acidified with HCl to pH 2; stored and transported at maximum 277 K and analysed within 3 weeks. The analysis methods consist of three steps: enrichment, separation and detection of MTBE. The enrichment step is generally seen as the most critical step in all methods. The enrichment is done by the Head Space Solid Phase Micro Extraction (**HS- SPME**) method. The maximum concentration was of 37 mg/L in some contaminated sites near gasoline stations, and 6.2 μg/L in Arges River.

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DETERMINATION OF FLUORINE IN SELECTED CERAMIC MATERIALS

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Fluorine belongs to the group of the most dangerous elements for the environment. Among all elements it is characterized by the highest reactivity, so in natural environment fluorine exists always in compounds. It is estimated, the Earth's crust contains 0,06 - 0,07% of fluorine. It is present in mineral deposits (fluorspar, apatite, and cryolite), coal and oil. In living organisms fluorine affects metabolism. Within last several years the concentration of fluorine in environment considerably increased. The biggest quantity of fluorine is emitted by aluminum industry, iron and steel industry and phosphorus industry.

Monitoring of fluorine concentration and its emission to the environment are necessary. European committee in cooperation with EIPPCB (European Integrated Pollution Prevention and Control Bureau) issued the document entitled "Reference Document on Best Available Techniques in the Ceramic Manufacturing Industry", according to which the control of fluorine emission is key issue.

Majority of ceramic manufacturing conditions are sufficient for decomposition of fluorine compounds, present in used raw materials. The quantity of raw materials used annually by ceramic industry is so big, that fluorine emitted in gaseous phase should not be ignored.

Existing methods of fluorine determination are not appropriate to ceramic raw materials. Polish standard PN-79/C-04531 which describes the fluorine determination in inorganic materials does not guarantee the correct results, the values obtained according its procedure are significantly lower than the expected values. The necessity of emitted fluorine control and the lack of correct analytical procedures induce us to develop the correct analytical methods. In different kinds of raw materials the fluorine is bounded in various structures, so application of the same method of fluorine determination for different kinds of raw materials is difficult.

The methods of fluorine determination in selected raw ceramic materials were investigated. The method of fluorine determination in cements and aluminosilicate material has been developed. The correctness of method was verified on certified reference materials. The fluorine in zircon silicate structure pigments has been analyzed, and the results corresponded well with expectations.

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EMIM CATION AS A NEW TERMINATING ELECTROLYTE IN ISOTACHOPHORESIS

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Room-temperature ionic liquids (RTIL), salts that are liquid at ambient temperature, are normally composed of relatively large organic cations and inorganic or organic anions. Unlike molecular liquids, ionic liquids, which are polar solvents, are environmentally benign, nonvolatile, nonflammable; most of them have good solubility in water and are stable in air. In addition, by varying the lengths and branching of alkyl chains of the anionic core and the cationic precursor, it is possible to design solvents for specific applications. Because of these characteristic properties, ionic liquids are widely used as new solvent media in heterogeneous catalysis, synthesis, electrochemistry, sensors, battery applications, analysis and separation. Typical ionic liquids consist of an organic cation with delocalized charges and a small inorganic anion, most often weakly coordinating fluorocations such as BF_4 or PF_6. Millions of possible cation and anion combinations offer their widely tunable properties with regard to polarity, hydrophobicity and solvent miscibility behavior.

Currently, scientists are interested in the applications of ionic liquids in separation and analysis. Reports on ionic liquids used as running electrolytes in capillary electrophoresis (CE) appeared frequently. Other scientists systematically studied the stationary phase of gas chromatography based on ionic liquids. Ionic liquids were used as additives in eluents to separate in high performance liquid chromatography (HPLC) and countercurrent chromatography (CCC).

Results of application of selected imidazolium ionic liquids (especially EMIM (1-ethyl-3-methyl-imidazolium) cation) as a new type of terminating electrolyte (TE) in isotachophoresis (ITP) with conductometric detection are presented. In experiments seven different types of leading electrolyte (LE) with new terminating electrolyte (in different concentrations) were studied. After optimization, proposed buffers were successfully used in control of qualitative and quantitative analysis (sodium, potassium, calcium and magnesium) of different type of waters. The new ITP methods was satisfying and basic validation parameters were assigned. Thanks to its low cost and high rate the presented method can be used in qualitative routine analysis as an alternative technique to ion chromatography.

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ELECTROOSMOTIC FLOW IN NON-CHARGED MONOLITHIC POLYSTYRENE-DIVINYLBENZENE CAPILLARY COLUMN

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Electrochromatography (CEC) is a separation technique, which is regarded as a hybrid of liquid chromatography and capillary electrophoresis. In CEC, liquid chromatographic stationary phases can be used together with the electroosmotic flow generated in capillary columns. Flat profile of the EOF makes the electrochromatographic separations more efficient comparing to pressure-driven systems.

The electroosmotic flow is a phenomenon that makes electrochromatographic separation possible to perform. From this point of view the knowledge on the linear velocity (or electroosmotic mobility, μEOF) of the mobile phase that can be generated in a packed capillary is necessary. In our previous work we reported that EOF can be observed in DVB-modified capillaries which were used for electrophoretic separation of bacteria. This made us interest in application of uncharged polystyrene-based phases in CEC.

In this work we present the results of our study on the electroosmotic flow generated in uncharged monolithic columns based on copolymer of styrene and divinylbenzene. The μ_{EOF} vs pH profiles are presented for unmodified PS-DVB phase as well as for PS-DVB alkylated with octadecyl chains using Friedel-Crafts reaction and grafting. Molecular modeling results are presented for explanation of the observed phenomena

EXTRACTION OF XENOESTROGENS FROM WATER AND TISSUE USING A MOLECULARLY IMPRINTING POLYMER FOLLOWED BY QUANTIFICATION BY HIGH PERFORMANCE LIQUID CHROMATOGRAPHY

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Molecularly imprinted polymers are synthetic crosslinked polymers with strategically positioned binding sites for a selected analyte, creating the potential for MIPs to function as selective solid phase extraction (SPE) sorbents. Molecularly imprinted polymers (MIPs) can mimic the recognition and binding capabilities of natural biomolecules. The template, monomer(s), cross-linker and solvent (porogen) used during the synthesis are key parameters in successful obtaining of a selective MIP. Since all the above-mentioned parameters have a strong influence on the overall performance of MIPs in terms of affinity, selectivity, loading capacity, etc., their proper selection will ensure that polymers with the appropriate properties are obtained for a particular application.

Non-covalent imprinting is one of the most convenient way of synthesis of MIPs. In such an approach the monomers should form the complex with the template at the early stage of polymerization. The interactions (of different nature) between the molecules involved in the formation of such a complex will have the great influence on the shape of the cavity created during the polymerization process. Hence, the mechanisms by which the resulted polymers can specifically bind the imprinted or similar molecules are attributed to the specific arrangement of the functional groups within the polymer that corresponds to the print molecule and to the presence of shape-selective cavities. Except the purely chromatographic applications molecularly imprinted polymers were also used as specific binding matrices for the solid phase extraction and cleanup of biological sample extracts.

The aim of this study was develop 4-nonylphenol, zearalenone and estradiol MIP to be used as a specific sorbent for solid phase extraction of xsenoestrogens from different samples (water, tissue). Using non-covalent and semi-covalent approaches, molecularly imprinted polymers have been synthesized using 1-allylpiperazine, TRIM and methacrylic acid (MAA) as monomes, and cyclododecanyl-2,4-dihydroxybenzoate (CHDB - ZON-mimicking molecule) and ß-estradiol as the template.

The polymers were evaluated from the point of view of their selectivity in solid-phase extraction (SPE) coupled to liquid chromatography. The solid-phase extraction procedure using MIPs, including the clean-up step to remove any interferences, was optimized. The MIPs were applied for selective extraction of estradiol, 4-nonylphenol and zearalenone from biological and water samples.

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AN APPROACH TO THE RISK ASSESSMENT OF ORGANIC POLLUTANTS IN TERRESTRIAL ECOSYSTEMS: THE CASE OF A CHEMICAL COMPLEX IN NORTH-WEST PORTUGAL

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Organic pollutants (OPs) can be highly persistent in the environment, easily adsorbed to surfaces and accumulate through the food chain [1]. Concentrations of OPs in soils are not predictive of their risk, as they can differ from the bioavailable fraction.

The aim of this study is to understand the link between OPs in soil and adverse effects on the ecosystem, since some of them are known or suspected to be carcinogenic and/or mutagenic. In this work it is suggested an approach to perform a risk assessment of the terrestrial ecosystem surrounding a chemical complex, by integrating chemical and biological tools. The study site is a chemical complex that includes, among others, the production of aniline, nitrobenzene, PVC, isocyanide polymers of aromatic base and polystyrene polymers.

A comprehensive preliminary characterization of the ecosystem is carried out to identify potential exposures, sampling sites, define the set of soil properties to be assessed and establish sampling analytical procedures. Therefore, at this stage it is delineated the assessment design, data needs, measures and methods for conducting the analysis phase of risk assessment process. A conceptual model to identify sources and ecological receptors to predict the potential exposure pathways is created.

A screening of contamination is then performed by sampling and analysing soils (0-15 cm) in potential contaminated sites. This includes the *in situ* evaluation of bioavailability, bioaccessibility and bioaccumulation of OPs. This is assessed through different extraction procedures, evaluation of bioaccessibility and bioaccumulation of contaminants in soil and plants collected from the selected areas. The assessment of the toxicity of soil is carried out by using indicators for effects. At this stage bioavailability of contaminants in selected soils and their potential to cause toxic effects is assessed through laboratory and in situ ecotoxicological assays with edaphic species such as Microtox^{Ň} avoidance assays, elutriate assays and the Ames test.

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EVALUATION OF RECOVERY OF β-BLOCKERS FROM FILTERPLATES WITH ANALYSIS BY LIQUID CHROMATOGRAPHY COUPLED WITH TANDEM MASS SPECTROMETRY (LC-MS/MS)

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Filtration can be one of the most important steps in sample preparation, and can help eliminate large particles that may block or damage chromatography systems. Many types of products are available on the market, which are easy to use and allow high sample recovery with good repeatability. The majority of filtration devices deal with a minimum sample volume of 1 ml. However, there is a problem with how to deal with smaller sample volumes, particularly with an increased use of plate wells for high throughput analysis. The use of 96-well filterplates may offer a solution for dealing with sample volumes of lower than 1 ml.

At Brixham Environmental Laboratory an evaluation of sample recovery from two commonly available 350 μL well filterplates was conducted (Pall AcroPrep 1.2 μm Supor; Millipore 0.45 μm hydrophobic PTFE). β-blockers were prepared at concentrations of 1.0 μg l^{-1} and 100 μg l^{-1} in HPLC water, *Daphnia* medium, and freshwater algal medium. Samples were filtered through the filterplates into collection plates using a vacuum manifold and were then transferred to vials prior to analysis.

Analyte separation was performed using a Waters Xbridge C18 HPLC column (50 mm x 1.0 mm I.D., 3.5 μm particle size). The mobile phase was MeOH : LC-MS grade water with 0.1% ammonium hydroxide. For quantitative analysis a triple quadrupole mass spectrometer (TSQ Quantum Access, ThermoFisher) was used with an electrospray in positive ionization mode ((+) ESI). For increased sensitivity, selected reaction monitoring (SRM) was used with the ion transitions monitored. LCQuan™ (ThermoFisher) software was used for data acquisition and processing.

Findings from preliminary work will be presented.

DETERMINATION OF ORGANOCHLORINE PESTICIDES IN WATER SAMPLES USING DISPERSIVE LIQUID-LIQUID MICROEXTRACTION PRIOR TO GAS CHROMATOGRAPHY-MASS SPECTROMETRY

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Sample preparation is one of the most important steps in the total analytical procedure (TAP) and liquid-liquid extraction is one of the oldest techniques used for this aim. However, it tends to be replaced nowadays by new modes of handling much more rapid, clean, simple, easy and ecological, using small amounts of organic solvents or even being eliminated.

Single drop microextraction (SDME) is a new extraction mode, and it is a miniaturization of the traditional liquid-liquid extraction technique. This mode extracts compounds in a droplet of an extractant phase which complies with the ecological criterion, obtaining also good analytical figures of merit. However, SDME presents sometimes some operational difficulties, such as the droplet is likely to break during the extraction process, there is a possibility of air bubbles formation and it also requires a relatively large time of equilibrium and in many cases the equilibrium is not reached. Dispersive liquid-liquid microextraction (DLLME) appears as a recent alternative to SDME [1,2]. This new microextraction mode uses the extractant phase directly dispersed in the sample instead of a droplet hanging from a syringe. The DLLME mode not only presents all the advantages of SDME but also eliminates the droplet instability problems and the equilibrium is instantly reached.

The DLLME uses a dispersant, acetone is usually used for featuring very low toxicity, together with a few microlitres of an extractant solvent in small volume of liquid sample. The dispersant produces the dispersion of the extractant solvent in the sample forming a great number of microdroplets, what means that the surface of contact between the solvent and the sample is significantly increased. After centrifuging, the small droplets of the extractant solvent are deposited at the bottom of the conical tube and part of them are directly taken and injected into a gas or liquid chromatograph.

In this work DLLME-GC-MS is used to determine 18 organochlorine pesticides in water samples. 10 μl of tetrachloroethene as extractant solvent and 1 mL of acetone as dispersant solvent are used. After the extraction the sample is centrifuged for 3 minutes at 2300 rpm and 2 μl of the extraction solvent are injected in a high-resolution gas chromatograph equipped with a mass spectrometer. The method is validated and applied to "real world" water samples.

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DEVELOPMENT OF A NOVEL ANALYTICAL METHOD FOR THE DETERMINATION OF UV FILTERS IN SURFACE WATER SAMPLES USING SINGLE-DROP MICROEXTRACTION PRIOR TO LIQUID CHROMATOGRAPHY ANALYSIS

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For many years, the main concern regarding the use of UV filters in sunscreen cosmetic products was their efficacy in attenuating the negative effects that sunlight exposure could cause on human health. Nevertheless, another important aspect has recently emerged related with studies showing evidence that UV filters are present in the aquatic environment. Although the use of UV filters is limited compared to other chemicals (e.g., soaps and detergents), their environmental consequences may still be significant, because of the potential direct input to surface waters through bathing activities and the fact that they can be accumulated by living organisms [1]. So, the development of sensitive analytical methodologies is necessary to determine UV filters in water samples in order to monitor these compounds. Liquid-phase microextraction (LPME), and especially single-drop microextraction (SDME), is a promising technique for extracting and concentrating organic compounds.

Ionic liquids (ILs) are a group of new organic salts consisting of a combination of organic cations and various anions that are liquids at room temperature. Important features of ILs include their immeasurably low vapour pressure, high stability, large viscosity, moderate dissolvability of organic compounds as well as adjustable miscibility and polarity. The main advantages of ILs when used for single-drop microextraction (SDME) are the possibility of using longer sampling time as well as larger droplet volume [2].

The purpose of this work is to develop a sensitive ionic-liquid single-drop microextraction (IL-SDME) methodology for the determination of different UV filters in surface water samples. For this goal 1-hexyl-3-methylimidazolium hexaflurophosphate has been used as acceptor phase in SDME. After the extraction is accomplished, liquid chromatography (LC) is used for the determination of the target UV filters. Experimental design is used to obtain the optimum conditions for the main experimental parameters involved in SDME (i.e., droplet volume, sample volume, extraction time, ionic strength, stirring speed and ethanol percentage).

The proposed IL-SDME method has proved to be rapid, inexpensive, simple, precise, virtually solventless, sensitive and environmental friendly for the analysis of the target UV filters in water samples, representing an excellent alternative to traditional and other recently introduced methods.

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METAL-CONTAMINATED SOIL REMEDIATION USING MARBLE INDUSTRY SLUDGE AND ORGANIC MATTER AS SOIL AMENDMENTS

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Mining activities often generate high amounts of wastes with high environmental impacts. These wastes are usually placed on the ground forming tailings which are characterized by low pH, high concentration of heavy metals, lack of nutrients, low water retention capacity and high electrical conductivity [1]. These factors convert tailings in adverse environments to plant establishment and, as a consequence, their surfaces usually remain bare and completely exposed to weathering and erosion agents. In this way, tailings may be a potential source of contamination to water and soil of their surroundings. In the case of the nearby urban or agricultural areas these effects may reach regional scales and affect the human health [1].

Many techniques are available in remediation of metal polluted soils (i.e. soil washing, vitrification, soil flushing, etc.) but the most of them are expensive and environmentally invasive. The establishment of a stable plant cover is considered a suitable option to get long term reclamation. Plant species which may be considered for phytostabilization purposes should be metal tolerant and with low ability for metal uptake in order to prevent risks in food chain. Selected plant species should have fast growth and spread, and be able to get an effective soil cover [2]. In some cases, amendments (e.g., fertilizer, lime, organic matter) may favour the plant establishment [1]. The plant species selection to carry out the phytostabilization of mining wastes must be site specific since besides being tolerant to metal pollution, must be adapted to local climate. In this sense, it is useful to search plants that have spontaneously colonized mining sites from ancient times and therefore are completely adapted to these polluted environments. The natural colonization of mine sites is slow since the physicochemical characteristics of these sites are not suitable for the most of plant species. In this study the phytoestabilization and phytoextraction potential capacity of *Solanum nigrum* L., *Piptatherum miliaceum* (L.) Cosson, *Brassica juncea* (L.) Czern. and *Spergularia purpurea* (Persl) G. Don. fil. was studied. A 90 days-pot experiment was carried out to evaluate the effects of marble sludges and municipal biosolids addition on the growth and metal accumulation of the plants studied, grown in a mixture soil: tailing 1:1. The soils and tailings were collected at the abandoned copper mine of Tinoca in Southeast Portugal. The carbonate content seems to play a significant role in chemical stabilisation of metals and in a decrease of toxicity of soil: tailing mixtures. This effect might contribute to the higher plant biomass productions observed compared with the control. The capacity of the cutting marble sludges to modify the pH probably leads to the adsorption and precipitation of the metals present in solution, minimising their mobility, bioavailability and phytotoxicity.

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POLYCYCLIC AROMATIC HYDROCARBONS (PAHS) IN SEDIMENTS: MONITORING THE EVOLUTION OF THE SHORE APPROACH AREA OF THE GULF OF GELA (ITALY)

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According to the permits granted by the competent authorities, to make a sealine connecting Lybia to Sicilian coast, a marine environment periodical monitoring of the Italian shore approach in Gela had to be set up.

The purpose of this study was to determine the concentration and distribution of PAHs in the sediments of the Gela area (Italy) to provide data for Environmental Impact Assessment. Sediments are composite materials consisting of inorganic components, mineral particulates and organic matter in various stages of decomposition. It is well known that they are sensitive indicators between natural and anthropogenic variables. Sediments therefore represent the most important reservoir of PAHs in the marine environment. Another purpose is to establish the sources of PAHs.

The first survey was carried out in June 2003 before the laying activities. By autumn 2006 other four survey was performed, the first of which just after the sealine installation to assess the impact of laying and of dredging operations. Purpose of such campaign is to qualify by comparison the trend of environmental status.

Investigations were carried out into the sixteen PAHs identified by the US-EPA as requiring priority monitoring action within the framework of environmental quality control. Other non-US-EPA listed PAHs, namely perylene, was also investigated in order to obtain further information on their origins. Perylene is usually considered a marker of the terrestrial origin of organic matter in the sediments. Together with PAHs, we analyzed water and organic contents because it has been demonstrated that the concentrations of PAHs in sediments were affected by chemical composition of the samples such organic matter and water content.

From a comparison among the results of the pre-lay survey and those of the other surveys performed after the pipeline installation, a modification in the time of the concentrations of PAHs can be observed. In the first post lay survey we measured highest PAHs concentrations than that of pre-lay survey. During the other surveys we observe a progressive decrease of the total PAHs concentrations.

ANALYSIS OF POLYCHLORINATED BIPHENYLS IN MUSSEL SAMPLES BY MICROWAVE ASSISTED EXTRACTION, MEMBRANE ASSISTED SOLVENT EXTRACTION AND HIGH RESOLUTION GAS CHROMATOGRAPHY

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Galicia is an important shellfish-producing region in northwest Spain. The contamination of the production zones and the marine water in Galicia is controlled by a wide monitoring activity at regional level. Experience indicates that mussel are the best indicators of coastal pollution because they accumulate certain contaminants, including PCBs, to much higher levels than those found in water. PCBs are substances of low biological degradability and high lipophilicity, they tend to accumulate throughout trophic levels of the food net.

Analysis of PCBs in biota is performed by conventional and recent methods like Soxhlet, microwave assisted extraction and accelerated solvent extraction, combined with tedious "clean up" techniques. The dense polypropylene membranes have been used as extraction technique. Membrane assisted solvent extraction combined with large volume injection with gas chromatography and mass spectrometric detection have been developed by Pop et al. [1,2].

The purpose of this work is to optimise the use of membrane in the "clean up" step after PCBs microwave extraction. Because of the high number of variables that potentially affect membrane assisted solvent extraction, an experimental design has been used to simultaneously optimise the operational parameters and to establish their possible interactions. With this purpose, Plackett-Burman 2^5 type III resolution factorial design (Minitab 15 statistical package) have been applied on a microwave extract of freeze-dried mussel spiked with a mixture of PCBs (IUPAC number, CBs 31, 28, 52, 101, 118, 153, 105, 138, 156 and 180). Five experimental variables possibly affecting membrane assisted extraction have been optimised (methanol content of sample extract, extraction time, extraction temperature, stirring rate and extraction solvent volume). It involved 13 randomized runs. Each factor is tested at both a high and low level.

The numerical analysis of the results shows that CBs 31, 28, 118 and 180 extractions appeared affected by one statistically significant factor, extraction time, and CBs 153, 138 and 156 by agitation rates. These two factors, extraction time and agitation rates, have a positive sign, it suggests that they facilitate the extraction on increasing their value. Of all the studied factors only methanol content has a negative influence on extraction. Any interactions were not statistically significant. Further experiments were performed in order to fine tune the main factors.The performance of the optimised analytical method was compared with that of Microwave Assisted Extraction and purification on adsorbent columns. The optimised method offers high efficiencies when operating at their optimal conditions. In addition, compared to conventional purification is significantly less time-and solvent-consuming.

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REMOVAL OF IBUPROFEN FROM WATER BY *Typha* spp.

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In recent years, the occurrence and fate of pharmaceuticals in the aquatic environment has been recognized as one of the emerging issues in environmental chemistry. Several routes have been identified for the entrance of pharmaceuticals into the environment, being the wastewater treatment plants (WTP) one of the most significant sources [1]. Ibuprofen is one of the pharmaceuticals most frequently found in water resources. This is due to its high load in WTP influents and, despite the also high removal rates in WTPs (up to 90%), still results in the discharge of contaminated effluents [1]. As a polishing step which can significantly improve WTPs efficiency in removing this type of trace organics, constructed wetlands systems (CWS) are an increasingly used form of tertiary treatment. CWS are low-cost and low-maintenance wastewater treatment systems which explore the long known ability of natural wetlands to depurate water. In these engineered systems, wastewater treatment is achieved by the concerted action between plant rhizomes, microorganisms and the support matrix components. A CWS efficiency can be significantly improved by the careful design and the optimization of the operation conditions which is achieved by careful selection of the support matrices, plants and microorganisms used. In order to evaluate the possibility of using CWS to remove Ibuprofen from contaminated effluents two studies were conducted: (i) *Typha* spp., a macrophyte plant commonly used in CWS, was grown under hydroponic conditions with and without exposure to Ibuprofen in concentrations at environmental levels, in order to test for its ability to tolerate and remove Ibuprofen from water; (ii) a CWS microcosm using clay aggregates (LECA) as substrate and planted with *Typha* spp. was used to evaluate its efficiency in removing Ibuprofen from contaminated wastewater. The wastewater samples were collected from a WTP located in a small village near Évora. These assays were performed using wastewater doped with Ibuprofen at environmental concentration levels. The quantification of Ibuprofen was achieved using HPLC-DAD with a reversed phase column and triple quadrupole LC-MS-MS in the negative mode [2]. *Typha* spp. has shown a good removal capacity for Ibuprofen. This pharmaceutical exhibited an apparent innocuity towards *Typha* spp. which lead us to investigate the biochemical mechanisms involving the elimination of the oxidative stress induced by the presence of the xenobiotic. The CWS microcosm planted with *Typha* spp. showed a good removal efficiency of Ibuprofen from contaminated wastewaters.

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REMOVAL OF THE β-BLOCKER ATENOLOL FROM WATERS USING A LECA BED PLANTED WITH *PHRAGMITES AUSTRALIS*

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In the modern society, an ever increasing number of pharmaceutical active compounds (PhACs) is used for the treatment and prevention of various diseases. Ingested drugs are only partially absorbed by the organisms and studies have shown that the excreted compounds are only partially removed in the sewage treatment plants (STPs) [1].

β-Blockers are used in treatment of high blood pressure (hypertension) as well as in patients recovering from heart attacks. In several studies, they were detected in surface water, thus indicating incomplete degradability of these substances in STPs. Despite the low concentrations detected (ng/L - μg/L), those studies have shown damaging effects of these compounds on the aquatic ecosystems [2].

Subsurface flow constructed wetland systems (SSFs) are low cost wastewater treatment systems usually used to provide a form of secondary or tertiary treatment for wastewaters. Depuration in SSFs is achieved by the concerted action between plant rhizomes, microorganisms and the support matrix components. SSFs' efficiency can be significantly improved by optimization of the operation conditions which is achieved by careful selection of the support matrices, plants and microorganisms used.

The aim of the present work was to evaluate the efficiency of a SSF microcosm, using Light Expanded Clay Aggregates (LECA) as the substrate and planted with *Phragmites australis* plants, to remove atenonol from contaminated water. The wastewater samples were collected from a STP located in a small village of Alentejo-Portugal. Assays were performed using wastewater doped at two different concentration levels, to evaluate both the toxicity to plants and the removal rates at environmental concentration levels. The quantification of atenolol was achieved using HPLC-DAD with a reversed phase column, and triple quadrupole LC-MS-MS in the positive mode [3].

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PLUTONIUM ISOPTOPES ^{241}PU AND $^{240/239}$PU ACTIVITY RATIO IN ATMOSPHERIC FALL OUT AFTER CHERNOBYL ACCIDENT

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The principal source of plutonium radionuclides in the Baltic Sea is the atmospheric fallout from nuclear weapon tests. Other sources such as releases from nuclear power plants and the European nuclear reprocessing facilities at Sellafield and Cap de la Hague are often considered less important. Since 26th April 1986 another source of plutonium isotopes, that is the Chernobyl-originated radioactive debris, has had to be taken into account.

Activity of ^{241}Pu in atmospheric fallout in 1986 was calculated using indirect method. The measurements of β-emitting ^{241}Pu were done through the measurements of its decay product - α-emitting ^{241}Am. $^{240/239}$Pu activity ratios were measured using accelerator mass spectrometry (AMS).

Plutonium released in the moment of reactor explosion existed as insoluble PuO_2, and almost whole amount fell as dry atmospheric fallout or with the wet fallout. Air filter analysis indicates after Chernobyl accident ^{241}Pu concentration increased suddenly over 3500 times and was decreasing slowly. In November 1986 got the level before the accident.

The nuclide compositions of plutonium in filter samples correspond to their means of production. AMS measurements of atmospheric fallout collected in April showed sufficient increase of ^{240}Pu/^{239}Pu atomic ratio from 0.28 from March to 0.47. Also such high increase of ^{240}Pu/^{239}Pu atomic ratio, cose to reactor core ^{240}Pu/^{239}Pu atomic ratio, was observed in September and equaled 0.54.

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CANISTER SAMPLING AND GAS CHROMATOGRAPHY (GC-FID/MS) DETERMINATION OF C_2-C_{10} ALDEHYDES, ALCOHOLS AND KETONES IN AMBIENT AIR

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A new analytical method is designed, developed and tested for determining 26 polar compounds (C_2-C_{10} aldehydes, alcohols, ketones) in the ppmv-ppbv range collected into canisters and analyzed using gas chromatography (GC). Dual columns, RTX 502.2 and CP-WAX, coupled to dual detectors, mass spectrometer (MS) and flame ionization detector (FID), respectively, are used. The CP-WAX column determined acetone and propanal while other compounds are determined using RTX 502.2 column. The precision, accuracy, method detection limit (MDL) and average recovery of the developed technique is in the range of ±20%, 30%, 20 ppbv and 70~130%, respectively. Also, the effect of presence of ozone and humidity in gas standard on the system response was evaluated. Efficiency of this optimized method is demonstrated and successfully applied to characterize ambient air samples in an industrial zone of Hsinchu county in Taiwan.

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MULTIELEMENTAL ANALYSIS OF THE BIOMASS OF MACROALGAE FROM THE BALTIC SEA BY ICP-OES

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Marine green macroalgae are considered as a very good biomonitor of pollution with metal ions in aqueous environment, because they can easily accumulate mineral ions from water, in which they grow. This process - called bioaccumulation, depends on the cellular metabolism and involves binding of inorganic species to the cell wall, their transport into cellular interior and finally deposition in sub-cellular organelles [1]. In the literature it is reported, that green macroalgae were used in the past as biomonitors of metal contamination in many coastal waters [2, 3, 4, 5]. It was indicated that metal concentration in seaweed was correlated to the metal ions concentration in the water [3]. On the other hand, a special attention should be paid to the content of heavy metals in marine macroalgae, because they are the basis of the trophic chain and can be responsible for metals biomagnification through the food web, which can result in severe health risks [5].

The major goal of this paper was to discuss the mineral composition of the biomass of marine edible macroalga *Enteromorpha sp.*, with the consideration of its use both as biomonitor and also as a future feed for animals and food for people. For the experiments, Enteromorpha sp. was chosen, since it is the most abundant macroalga in the macrophytobenthos on the Polish coast of the southern Baltic [6]. The mineral content of Baltic seaweeds was determined by the multielemental analysis by the Inductively Coupled Plasma-Optical Emission Spectrometer -Varian VISTA-MPX ICP-OES (Victoria, Australia). Samples of *Enteromorpha* sp. were collected from the coast of the Gulf of Gdańsk (Gdańsk-Brzeźno) in April 2007 and from the open Baltic Sea (Niechorze - Poland) in July 2006 and in August 2007. The mineral composition of examined macroalgae was compared with the results reported by other authors for *Enteromorpha* sp. from the Baltic Sea and also from various areas of the world and from different time periods. The mineral content of alga was also related to the composition of water from the Baltic Sea. Obtained results showed, that mineral content of *Enteromorpha* sp. did not significantly varied according to place of harvest in the Baltic Sea (with exception of Pb, which was 8.5 times higher in alga from the Gulf of Gdańsk than in alga from the open Baltic) and similar time sampling, but when compared with mineral content of algae from another time periods [9, 10] and from another world regions [7, 8], the differences were noticeable. It was observed, that the concentration of toxic elements (Cd, Ni and Pb) in examined algae was lower than in algae collected from the Baltic Sea several years ago.

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STATISTICAL ASSESMENT OF THE CONCENTRATION DATA FOR 46 CHEMICAL ELEMENTS IN THE THREE-SPINED STICKLEBACK WITH RESPECT TO THEIR SPATIAL VARIATIONS

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The three-spined stickleback is widely distributed in the aquatic environment. It inhabits streams, rock pools, estuarine waters and seas. Gasterosteus aculeatus occurs numerously and is of negligible economic value. It is also robust and can withstand handling and transport, and is easily caught with the minimum of equipment and resources (hand-net). Because of it the three-spined stickleback may be a good biological candidate for environmental monitoring.

The aim of this study was to evaluate the suitability of the three-spined stickleback as biomonitor of chemical elements content (Ag, Al, As, Ba, Bi, Ca, Cd, Ce, Cl, Co, Cr, Cs, Cu, Fe, Ge, Hg, I, K, La, Lu, Mg, Mn, Mo, Na, Nb, Ni, P, Pb, Pr, Rb, Ru, S, Sb, Se, Sm, Sn, Sr, Te, Th, Tl, U, V, W, Y, Yb, Zn) in Baltic waters in comparison with Norwegian location of sampling.

The three-spined stickleback was collected from the six locations: Koszwalski Canal, Wiślinka (both in the vicinity of mouth of Vistula River), yacht port in Gdynia, Puck, Hel and Norwegian Lake. The fish were caught by hand-net. The samples were weighed and their total length was measured. The fish age was determined using sagittal otoliths. Dried and homogenized samples were digested in Milestone UltraCLAVE using concentrated nitric acid. The levels of selected trace elements in *Gasterosteus aculeatus* were determined by High Resolution Inductively Coupled Plasma Mass Spectrometry HR-ICP-MS (Finnigan™ ELEMENT2).

U Mann-Whitney's test shows significant differences in Rb, Th, Tl and Sm concentrations in samples belonging to different sex group (higher levels are noted for female). Spearman's rank correlations indicates relationships between elements concentrations and age, i.e. negative for Ge, Mo, Ni, Sb and W whilst positive for P ($P<0.05$).

Based on the results of both the U Mann-Whitney's test and Spearman's rank correlations it seems that the stickleback could be useful tool for monitoring because of a lack of the sex- and age-dependent variations in concentration of most trace elements in the fish analysed.

The results of statistical analyses confirm geographical differences between concentrations of some elements found in specimens from the Gulf of Gdańsk and Norwegian waters. Distribution pattern of chemical elements varied notably depending on the location of the sampling sites. The fish levels of Ba, Co, Cr, Ge, Hg, K, Rb, Te, Tl and V were generally higher in Norwegian waters in view of ANOVA (Kruskal-Wallis test) in comparison with samples originated from the Gulf of Gdańsk.

The observed distribution pattern of the chemical elements content in the three-spined stickleback may reflect possible influence of environmental conditions on their bioaccumulation. The preliminary data obtained advocate the use of *Gasterosteus aculeatus* as an appropriate monitor-organism for assessing some trace elements levels in the aquatic environment.

CHEMICAL ELEMENTS RELATIONSHIPS IN THE THREE-SPINED STICKLEBACK FROM THE DIFFERENT GEOGRAPHICAL REGIONS IN VIEW OF FACTOR ANALYSIS DATA

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Concentrations of 46 elements was determined in the three spined-sticklebacks from the area influenced by anthropogenic activity in the Gulf of Gdańsk and neighborhood of Trondheim (Norway). Trace elements tend to accumulate in marine organisms and then they can also be transferred along the sequential levels of the food chain.

The three-spined stickleback was collected from the six locations: Koszwalski Canal, Wiślinka (both in the vicinity of mouth of Vistula River), yacht port in Gdynia, Puck, Hel and Norwegian Lake. The fish were caught by hand-net. The samples were weighed and their total length was measured. Dried and homogenized samples were digested in Milestone UltraCLAVE using concentrated nitric acid. The levels of selected trace elements in *Gasterosteus aculeatus* were determined by High Resolution Inductively Coupled Plasma Mass Spectrometry HR-ICP-MS (Finnigan™ ELEMENT2). The complete data sets concerning the distribution and coassociations of elements content (Ag, Al, As, Ba, Bi, Ca, Cd, Ce, Cl, Co, Cr, Cs, Cu, Fe, Ge, Hg, I, K, La, Lu, Mg, Mn, Mo, Na, Nb, Ni, P, Pb, Pr, Rb, Ru, S, Sb, Se, Sm, Sn, Sr, Te, Th, Tl, U, V, W, Y, Yb, Zn) in *Gasterosteus aculeatus* were processed statistically in STATISTICA for Windows (Release 7.1, Copyright© Statsoft, Inc.).

The results of comprehensive factor analysis (FA) confirm geographical, geological and anthropogenical differences between concentrations of elements in the specimens from the Gulf of Gdańsk and Norwegian waters. F1 achieves the highest loadings for Ca, Cl, Mg, Mn, Na, P, Sr, U, Zn. These loadings are responsible for identification of samples originated from the Hel and Wiślinka (Gulf of Gdansk), what is attributable to individual tendency of the fish to accumulate these elements. Factor 2 is responsible for the discrimination of one specimen originated from Puck. The highest levels of Al, Ce, Cs, Lu, Pr, Sm, Th and Y are associated to this object. The samples from Norwegian waters are clearly characterized by higher levels of Ge, Hg, Rb, Te and Co, what is shown by the lowest values of factor 3. The samples from Gdynia are distinguished from the others by F4. The levels of Bi, Cr, Sb, Ni, Pb and Sn are responsible for this distinction what may attest to the local anthropogenic contamination.

The applied chemometric analysis was useful in our monitoring studies and the presented results show that the three-spined stickleback tends to be valuable biomonitor of elements content in waters.

SYNTHESIS AND CHARACTERIZATION OF COMPLEX COMBINATIONS OF NI(II) WITH NEW ALIPHATIC ASYMMETRICAL DIOXIMES

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The dioximic structures make up the subject of study of many researches as regard their analytic capacity of application, a very interesting and also a very thoroughly examinated field. The increasing interest in this class of compounds goes by itself, taking into account the broad variety of possibilities and purposes these organic binders and the metallic complexes they build may be used under. This paper presents the preparation of the nickel (II) chelates with asymmetric a-dioximes and both the chemical and physico-chemical characterization with TG, DTA, and DTG measurements studies the thermal behavior of these compounds. These complexes have a great importance from the analytical methods for determining the metal mentioned under this form. The synthesis of aliphatic asymmetric dioximes offers to the chemistry analysts the possibility of increase of sensibility and of selectivity of color and precipitation reactions of them with the transitional metals, especially with Ni(II), reason for why there was elaborated a series of method for dosing it under dioximats form.

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INTERACTION OF ARSENATE AND CYANOBACTERIAL BIOMASS (*MICROCYSTIS SP.*) - INVESTIGATION OF METABOLITES

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Sorption and biotransformation of arsenate by water bloom forming cyanobacterial biomass (predominantly *Microcystis sp.*) has been studied in this work. Biomass coming from Brno dam reservoir was cultivated in river water enriched by arsenate for 6 days. Water and aqueous extracts of biomass were subjected to anion exchange chromatographic analysis (Hamilton PRP X-100 column, ammonium acetate mobile phase pH 6.0) with ICP-MS detection. Quantitative reduction of arsenate to arsenite was observed followed by biomethylation mainly to dimethylarsinate (DMA). Monomethylarsonate (MMA), DMA and both inorganic species were determined in biomass extract and water. Up to 56% of the original arsenate content in water has been methylated by cyanobacterial biomass. In addition to these species, some unknown As species were found in biomass. For identification of these species several methods based on chemical reactivity were applied. Anion exchange chromatography - pH-specific hydride generation - ICP-MS revealed possible occurrence of MMA(III) in biomass as a semi-product of biomethylation [1]. Another species were borohydride-reducible however not hydride-forming neither under neutral nor acidic conditions. Alkaline hydrolysis of the extract resulted in increased DMA peak in chromatogram coming from dimethylarsinoyl group in the molecule [2]. Two unknown species were identified likely as arsenoribosides based on these information. Natural biomass contains up to 40% As in form of arsenoriboside.

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DIFFERENTIAL MERCURY ACCUMULATION AND DISTRIBUTION IN SALT MARSH PLANTS AND SEAGRASSES FROM A CONTAMINATED TEMPERATE COASTAL LAGOON

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Taking advantage of a well defined environmental contamination gradient present in the Ria de Aveiro coastal lagoon (Portugal), resulting from 50 years of continuous mercury discharges originating from a chloro-alkali industry, we studied the mercury accumulation and distribution between the aboveground and belowground biomass of several salt marsh plants (*Halimione portucaloides, Juncus maritimus, Scirpus maritimus* and *Arthrocnemum fruticosum*) and the dominant seagrass species *Zostera noltii.*

Due to an ongoing eutrophication process and a progressive substitution of rooted primary producers for macroalgae, our results are compared with previous work focusing on the dominant seaweed species (*Enteromorpha intestinalis, Fucus vesiculosus* and *Gracilaria verrucosa*)[1], and put into perspective in terms of the estuarine mercury cycle and transport from the contaminated area.

All salt marsh plants accumulated mercury essentially in the root system, with *H. portucaloides* presenting the highest levels, up to 1.3 mg kg^{-1} in the most contaminated area. Belowground/aboveground ratios were generally below 0.4, suggesting that salt marsh plants are efficient mercury immobilization agents. Moreover, due to their sediment accretion capacities, salt marsh plants seem to play an important role in the sequestration of mercury in estuarine sediments.

Seagrasses, on the other hand, accumulated considerable amounts of mercury in the aboveground biomass with belowground/aboveground ratios reaching as high as 1.4. These results may probably be a result of their different uptake routes (roots and foliar uptake), and suggest seagrass meadows can play an important role in the export of mercury from contaminated areas, considering the high aboveground biomass replacement rates.

Comparing our results with previous work on seaweed species in the same location [1], it was evident that rooted macrophytes accumulate less mercury in their aboveground biomass than macroalgae. The change of primary producer dominance due to eutrophication may hence originate significant changes in mercury export rates and also bioavailability to estuarine food webs, since macroalgae associated mercury will be more readily available to organisms through the detritus pathway, and stress the need to reverse the systems eutrophic status.

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DETERMINATION OF MERCURY IN HORSE MACKEREL BY HYDRIDE GENERATION AND COLD VAPOUR ATOMIC ABSORPTION SPECTROMETRY

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In recent years, and based on the importance of fish as a part of healthy diet, there has been a notable promotion of fish consumption. However, the balance between health benefits and risks, due the intake of chemical contaminants, is not well characterized. The nutritional benefits of fish are mainly due to the content of high-quality protein, vitamins and other essential nutrients. Moreover, fishes are rich in two kinds of omega-3 polyunsaturated fatty acids (PUFAs): eicosapentaenoic acid (EPA) and docosahexaenoic acid (DHA) [1].

Natural and anthropogenic pollution provoked by heavy metal discharges to the marine environment is of great concern all over the world due to the toxicity and accumulative behaviour of heavy metals [2]. With the exception of occupational exposure, fish is considered the single largest source of mercury to man [3]. To evaluate the fish safety in what concerns heavy metals, it is indispensable to analyze the muscles, since they are the edible parts. According to European Community Regulation, the maximum allowed value of mercury in fish is 0.5 mg/kg wet weight.

In the present study, fresh samples of Horse mackerel (*Trachurus trachurus*; a highly appreciated fish in Portugal) were purchased from different local markets in Oporto region (NW Portugal) and were characterized concerning their mercury content. Samples were digested using ultrapure nitric acid (65%) by microwave-assisted digestion. The operational parameters for sensitive and accurate determination of mercury in edible fish tissues by hydride generation and cold vapour atomic absorption spectrometry analysis were carefully optimized and will be discussed. All the results obtained were below the maximum level established by the European Commission Regulation.

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OPTIMISATION OF PROGRAMMED TEMPERATURE VAPORIZATION (PTV) INJECTION FOR THE ANALYSIS OF THE 15 + 1 EU POLYCYCLIC AROMATIC HYDROCARBONS (PAHS)

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Traditionally, split-splitless injection has been the most frequently used injection mode in the analysis of polycyclic aromatic hydrocarbons (PAHs) by gas chromatography. However, the use of large-volume injection techniques such as on-column injection and above all programmed temperature vaporization (PTV) recently has gained importance. The use of the PTV technique provides several advantages compared to the traditional split-splitless injection mode. These are manifested in the analysis of the 15 +1 EU priority PAHs [1,2], by a lower discrimination of the heaviest target compounds, the dibenzopyrenes (molecular weight is 302 atom mass units), leading to an improvement in sensitivity and better peak shapes. This poster reports on the influence of several PTV parameters (injection volume, initial temperature (without using cryogenic liquids), vent pressure, respectively vent flow) on the analysis of the 15 +1 EU priority PAHs.

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COMBINATION OF MICROWAVE ASSISTED MICELLAR EXTRACTION AND SOLID PHASE EXTRACTION (MAME-SPE) FOR THE EXTRACTION OF PHARMACEUTICALS COMPOUNDS IN MOLLUSC SAMPLES PRIOR THEIR DETERMINATION BY HPLC-DAD

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Several pharmaceuticals, widely used for human and veterinary medicine, are excreted unchanged as active metabolites in high percentage in the environment. They are continually introduced into the aquatic environment as complex mixtures via a number of routes but primarily by both untreated and treated sewage.

Bivalves are important members of aquatic ecosystems and markedly interact with water and sediment. These sessile and long-lived organisms filter large quantities of surface water for feeding and respiration. They are therefore particularly susceptible to environmental stressors, including point-source and diffuse contamination, water-level variations and climatic changes. Studies on the effects of different pharmaceuticals in different aquatic species revealed significant differences in toxicity for each compound depending on the nature of the test organism [1-2].

Different methods of extraction for pharmaceutical compounds have been described. Microwave assisted micellar extraction (MAME) has been developed for the extraction of different pollutants from solid matrices [3] owing to its simplicity, low cost, easy handling and non-toxic solvent use. Mollusc samples need to combine an additional clean up step after the extraction due their complexity [4].

The combination of microwave assisted micellar extraction and solid phase extraction (SPE) using a non ionic surfactant, Polyoxyethylene 10 lauryl ether (POLE), has been implemented for the simultaneous determination of a group of pharmaceuticals such as carbamazepine, clorfibric acid, ketoprofen, naproxen, bezafibrate and ibuprofen prior to their determination by liquid chromatography with UV-diode array detector (DAD), in mollusc samples.

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ANALYTICAL METHOD FOR METAL DISTRIBUTION IN THE ORGANIC AND INORGANIC FRACTIONS OF SEDIMENT: A CASE-STUDY ON SEDIMENT OF GANZIRRI MARINE COASTAL LAGOON IN MESSINA (ITALY). EXTRACTION AND ICP-MS ANALYSIS

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The content of As, Be, Cd, Co, Cr, Cu, Mo, Ni, Pb, Sb, Se, Tl, V and Zn, has been determined in the organic and inorganic fraction of sediments samples from Sicily. A modified type-Tessier sequential extraction procedure has been used to recognize metals in five different fractions categorized as follows: a) exchangeable metals, b) metals bound to carbonates, c) metals bound to iron and manganese oxides, d) metals bound to organic matter, and e) metals in residual fraction. To reduce the extraction time of the Tessier method [1], the last step of speciation was carried out by mineralization in a microwave oven. The metals were analyzed by means ICP-MS.

To compare the total metals content at the different sampling sites, the metal pollution index (MPI) was used. The values ranged from 1.5 to 3.0. Generally, the metal content in the labile fraction of sediments is rather low and representing from 1.4 to 2.0% of the sum of four fractions. In all the sediments investigated in the present study, Fe-Mn oxides play a major role in binding As, Cu, Mo, Ni and Zn sometimes reaching about 80% of the total metals. Most of the metals (Be, Co, Tl, V, Zn) occur in the form of sulphur and/or of organic complexes that can strongly influence their mobility and availability in the environment and to a minor extent are bound to carbonates and Fe and Mn oxides [2].

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DETERMINATION OF SELECTED PERFLUORINATED CARBOXYLIC ACIDS BY GAS LIQUID CHROMATOGRAPHY - MASS SPECTROMETRY IN NATURAL AND TECHNOLOGICAL MATRICES

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Perfluorocarboxylic acids (PFCAs) have been extensively used for 50 years in many technological applications, individually or as composites in manufactured products, such as surfactants, food containers, in leather and carpet technology, as upholstery and fabrics. Nowadays PFCAs are found widely in various compartments of the environment where they are recognized as highly stable, toxic and persistent chemicals. For these reasons their toxicological activity is studied through several in vitro test systems of different biological complexity. Moreover, methods for the enhanced treatment and degradation including abiotic and biological systems are also under extensive investigation. These type of studies require good and reproducible analytical methods enabling determination of PFCAs in various matrices. In this project we have used gas chromatography coupled with mass spectrometry (GLC-MS) to determine selected PFCAs in natural and technological matrices. Determination of perfluorocarboxylic acids was carried out using an *in situ* derativatization method [2,3]. The sample reacted with 2,4-difluoroaniline using dicyclohexylcarbodiimide as catalyst to produce the acid anilide. Quantitation utilizes gas chromatography with mass selective detector in the selected ion monitoring mode. In this work, we have shown that the GLC-MS method is a viable procedure for the analysis of the PFCAs in matrices of different origin.

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EXAMINATION OF CADMIUM AND MCPA INFLUENCE ON NUTRIENT AVAILABILITY IN SOIL

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Heavy metals and organic compounds including pesticides are most common additives and contaminants of soil. Among heavy metals cadmium is an element of significant environmental concern due to both its high loading input to soil, toxicity to plants and cumulative effect in animals. MCPA, a slightly toxic phenoxy herbicide in EPA toxicity class III, is a General Use Pesticide (GUP). It is a component of many herbicides produced also in Poland and is widely used in many orchards and fruit and vegetable plantations. When xenobiotics are introduced to soil they affects soil microbiological, physicochemical and biochemical processes. Introduction of MCPA and cadmium to soil may result in changing soil microorganism community and thus it may also affect the solubility and availability of nutrients.

The aim of the study was to examine the influence of cadmium and MCPA on availability of nutrients and to evaluate water contamination risks resulting from changes in their mobility in soil.

TRACE AND ULTRA-TRACE ELEMENTS IN SURFACE WATERS OF THE TATRA MOUNTAINS

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The Tatra Mountains are alpine type mountains located in south Poland. The Eastern (High) and Western Tatras are build of different type of rocks and soil. The High Tatras are build mainly with magma type rocks (granites) and the Western Tatras with sediment rocks (dolomite). Consequently, the composition of surface as well as underground waters in both parts of the Tatras differ significantly. The present investigations were aimed mainly in finding the differences in trace and ultra-trace components of waters.

The examination covered 4 sampling points in the High Tatras and 14 in the Western Tatras. ICP-Q-MS, ICP-ToF-MS and ICP-AES techniques were applied in the investigations of elemental (isotope) analysis of waters. Other water physicochemical parameters including temperature, pH, dissolved O_2 and conductivity were measured *in situ* with the use of a portable Multiline F/SET-3 system.

The obtained profiles (mass spectra) of trace elements in water samples collected from different places in the Tatra Mountains were compared using correlation coefficients between the profiles as a similarity parameter. Significant differences were detected not only between the waters of the High and Western Tatras but also between waters in the brooks flowing along the neighbouring mountain valleys. Particularly interesting results obtained in the present investigations concern White Valley (Dolina Białego) where in 50's of the XX century uranium ore was output but then gave up because of low uranium concentration and small stock. Still two drifts, upper and lower, have remained which are not available to the tourists. It was found that the concentration of uranium (238) in water collected from the bottom of the upper drift significantly exceeds (by more than ten times) concentration of the element in the White Brook (Biały Potok) flowing down along the valley. It may be concluded that uranium is continuously washed out from the rocks but when it reaches the bottom of the valley it is diluted by water of the main brook flowing through the valley.

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THE EFFECT OF CIGARETTE BRANDS AND SMOKING TOPOGRAPHY ON HYDROGEN SULFIDE LEVELS IN TOBACCO SMOKE

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Hydrogen sulfide (H_2S) is a toxic compound that might influence respiratory system, as well as cardiovascular and central nervous systems. Tobacco smoke is one of the environmental sources of the compound. The exposure to secondhand smoke states a significant hazard for so-called passive smokers.

The aim of the study was to determine levels of hydrogen sulfide in tobacco smoke generated from various cigarettes brands and in various smoking conditions (smoking topography). Levels of hydrogen sulfide were determined in mainstream smoke (MS, smoke inhaled by active smoker) as well as in sidestream smoke (SS, smoke emitted to the indoor air to which passive smokers are involuntary exposed).

Fifteen commercially available brands of cigarettes were smoked with smoking machine using international laboratory standards (ISO 3308). Hydrogen sulfide was absorbed from MS and SS in sodium hydroxide solution (1 M). Then, sulfide ions were determined with ion selective electrode (ISE) (precision of the method 2.14%, repeatability 3.15%). Moreover levels of hydrogen sulfide were determined using the same analytical method in tobacco smoke generated from two commercial cigarettes' brands and two types of reference cigarettes (1R5F, 3R4F, University of Kentucky, USA) in modified smoking conditions. Puff volume and its duration, intervals between puffs were modified in order to simulate real-life smoking topography (how smokers smoke cigarettes indeed). The obtained results were analyzed using ANOVA analysis (Statsoft, Poland).

Hydrogen sulfide levels in MS varied from 14.98 to 48.57 μg/cigarette (mean 24.37±9.05) and in SS from 33.05 to 55.31 μg/cigarette (mean 39.33±9.28). Distribution ratio of hydrogen sulfide between SS and MS varied form 1.10 to 2.17 (mean 1.71). The results of ANOVA analysis indicated that there is significant difference ($p<0.05$) of hydrogen sulfide levels between examined brands of cigarettes. The distribution ratios SS/MS were similar for all examined cigarette brands. The obtained results showed that smoking topography also significantly ($p<0.05$) influenced levels of hydrogen sulfide in both main- and sidestream smoke. For example, during short-lasting puffs higher levels of hydrogen sulfide were generated than during long-lasting puffs ones of the same puff volume.

Cigarette brands as well as smoking topography influence levels of hydrogen sulfide in MS and SS. Thus, they are significant factors that might impact exposure of active and passive smokers to hydrogen sulfide from tobacco smoke.

AUTOMATED INTELLIGENT DILUTION FOR ION CHROMATOGRAPHIC DETERMINATIONS

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The setup consisting of 850 Professional IC, 858 Professional Sample Processor and MagIC Net™ software offers a variety of sophisticated sample preparation options. One of these is automated intelligent dilution.

In order to perform automated dilutions the above-mentioned instrument setup is additionally equipped with a magnetic stirrer and an 800 Dosino. The latter aspirates a defined volume of a concentrated sample and transfers it to the mixing vessel. Subsequently, the dilution medium, generally ultrapure water, is dosed into the mixing vessel. After intensive stirring, the peristaltic pump of the sample changer transfers the sample to the injection valve of the ion chromatograph where the sample constituents are separated and detected. Alternatively, the sample can be injected directly. After the quantitation of the sample's constituents, the software verifies whether the concentrations lie within the calibration range. If this is the case, the next sample will be analyzed. If not, the software, after calculating the dilution factor, reanalyzes the sample after applying the appropriate dilution.

This paper will give a description of the straightforward analytical setup and demonstrate the usefulness of automated intelligent dilution applied to cation and anion determinations.

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DEVELOPMENT OF THE PROCEDURE FOR THE ESTRADIOL DETERMINATION IN ENVIRONMENTAL WATER SAMPLES BY USING CLINICAL ELISA KITS

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Steroid hormones are naturally synthesized by both humans and animals and are released into environment. Significant levels of these hormones have been detected in sewage all over the world. Estrogens, such as 17β-estradiol (E2), estron (E1) and estriol (E3), have been often identified as the major contributors to the endocrine-disrupting activity of environmental waters. However, their analysis in environmental water samples is still a challenge due to a great complexity of matrices and very low concentrations at which they are physiologically active. So analytical procedure must be characterized by very low detection limits and the selectivity required for reliable determination of these compounds.

The aim of our work was to develop the procedure for the rapid screening of 17β-estradiol (E2) concentrations in environmental water samples by using commercially available enzyme-linked immunosorbent assay (ELISA) kits being applied for clinical diagnostics.

As pre-treatment method for E2 determination by ELISA kits a solid-phase extraction (SPE) was used. We tested the efficiency of extraction on three different phases (Isolute ENV+, Oasis HLB, C_{18}-Bakerbond) applying three different water matrices. Efficiency was studied by using tritiated estradiol. On the basis of the obtained results the extraction on Isolute ENV+ (hydroxylated polystyrene-divinylbenzene copolimer) was selected. Next, we tested usefulness of three commercially available clinical ELISA kits: Estradiol EIA Kit (Cayman Chem. Comp. ANN Arbor, USA), Ferit Igenix-E2-EASIA (BioSource Europe S.A.) and Salivary Estradiol ELISA (DRG Instruments GmbH, Marburg, Germany) for E2 determination in water. Because ELISA kits studied by us had been worked out by the manufacturer for the determination of E2 concentrations in systemic fluids, so we tested an influence of dissimilar matrices on the shape of calibration curves and we matched suitable matrix making E2 determination possible in extracts of environmental water samples. On the basis of the obtained results for the determination of E2 concentrations in environmental water samples Estradiol EIA Kit by Cayman was selected. The calculation of recoveries for three different concentrations of hormone in three different water matrices (redestilated water, surface water and sewage effluent) was made for the selected ELISA kit. The recoveries of spiked water samples were between 32% and 137%. Also a working range of the kit and a detection limit were determined. Using this ELISA kit the E2 concentrations in different environmental water samples like river water, lake water and sewage effluent were determined. The E2 concentrations in examined water samples were in the range from 0.2 to 8.8 ng/L.

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DETERMINATION OF URANIUM AND THORIUM IN NATURAL WATERS BY ICP-OES AFTER ON-LINE SOLID PHASE EXTRACTION AND PRECONCENTRATION IN THE PRESENCE OF 2, 3-DIHYDRO 9, 10-DIHYDROXY 1, 4 ANTHRACENE DION

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Determinations of uranium and thorium are important from the point of view of their technological applications especially in metallurgy, ceramic and nuclear industry [1-5]. SPE is the most preferred preconcentration technique, not only for enriching uranium and thorium but also for other inorganics.

An on-line solid phase extraction method, linked to inductively coupled plasma optical emission spectrometry (ICP-OES) has been examined using octadecyl-bonded silica cartridge for determination of low levels of uranium and thorium in aqueous samples. 2,3-dihydro 9,10-dihydroxy 1,4-anthracene dion forms an hydrophobic complex with the cations and resulted complex was retained on SPE. Retained complex was washed using acidic solution and introduced in to ICP for determination. Various effective parameters and chemical variables such as sample pH, amount of ligand (as a complexing agent), sampling and eluting flow rates and concentration of the eluent were optimized. Under optimal conditions, calibration curves with dynamic linear ranges of 0.5-200 μg L^{-1} ($r^2 = 0.9999$) and 0.5-500 μg L^{-1} ($r^2 = 0.9994$) for U and Th were obtained respectively. Limits detection 0.69 μg L^{-1} and 0.84 μg L^{-1} were obtained for U and Th respectively. Sample throughput was 10 samples h^{-1}.The interference effects of several metal ions on percentage of recovery of U and Th were also studied. The method was applied to the recovery and sequential determination of these actinide elements in different water samples.

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HEAVY MINERAL SANDS FROM THE POLISH COSTAL ZONE

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The main aim of our investigations was to describe the heavy mineral sands from the Polish costal zone and to determine activity concentrations of radionuclides and heavy metals concentrations found in these sands.

The beach sands are mainly composed of quartz with a pale beige colour, however sometimes dark patches can be found on the beaches. The darkness of the patches is related to the presence of heavy mineral sands that are a class of an ore deposit. The higher density of dark sands and consequently the gravity of mineral grains are responsible for the formation of patches. The dark sands could be an important source of zirconium, titanium, thorium, tungsten, and many others elements and minerals. The dark sands composition depends on the source rocks.

Our samples of heavy mineral sands were taken from the open seashore and from the beach located in the Puck Bay area. The densities of the initial (mixed) samples were determined. They were 2.52 g cm^{-3} and 2.38 g cm^{-3} for open sea and the Puck Bay shore areas, respectively. Obtained values were compared with density of light sand, which was 1.55 g cm^{-3}.

Each initial sample was divided in two phases: magnetic and the remaining phase. Then samples (initials, magnetic phase, and the remaining phase) were taken for analysis.

Measurements of the radionuclides activity concentrations were carried out using gamma spectrometry method. Heavy metals after mineralization were determined using atomic absorption spectroscopy (AAS).

The spectrum of naturally occurring radionuclides found in the heavy sands was wide and activities of isotopes exceed few times the values found in the light sand. Additionally, in the samples from the Puck Bay region the anthropogenic isotope of caesium 137 originated mainly from the Chernobyl accident was found. Heavy metals concentrations were also higher.

VOLATILE ORGANIC COMPOUNDS EMISSIONS OF SEWAGE SLUDGE FRY DRYING PROCESS. QUALITATIVE AND QUANTITATIVE APPROACHES

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Considering the practical difficulties for the disposal of two wastes (sewage sludge and recycled cooking oils), an innovative thermal drying process called fry-drying has been developed [1]. Dewatered sludge is directly contacted in the dryer with hot recycled cooking oils as the heat medium. Fry-drying presents a potentially convenient method for their combined elimination by incineration of the final fry-dried sludge.

The objective of this work consists in participating in environmental impact assessment of the process. In this context, an experimental device was established to study the atmospheric emissions. Volatile Organic Compounds (VOCs) were collected on adsorption traps (Carbotrap 300 and Tenax TA) for gaseous phase and by SPME for the atmospheric incondensable phase. Samples were analysed by gas chromatography coupled to mass spectrometry and flame ionization detector.

About fifty VOCs were identified. They belong to different chemical families (alcanes, aldehydes, carboxylic acids, aromatic compounds…). Concentrations in the gaseous phase vary between 0.01 and 16 mg/L according to considered VOC.

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LOW ENERGY, PORTABLE ION CHROMATOGRAPH FOR ON-SITE ENVIRONMENTAL ANALYSIS AND MONITORING

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The need for on-site analysis has become important in diverse areas, from pristine national parks to hazardous waste disposal sites, and has led to a considerable interest in the development of self-contained field-portable instrumentation. In this paper, we present a low energy, low cost, fully computer controlled, field portable capillary IC system. The IC system is based on open tubular ion chromatographic capillary columns that provide only a minimum flow resistance - gravity or very low pressure pumping principles can be applied, off-the shelf conductometric detection based on a capacitance measurement and manual valve or timer-controlled electrokinetic injection. The principles of column construction and characterization, evaluation of various injection principles and some aspects on the detection will be presented. The prototype of the instrument that fits into a 15x15x5 cm box, requires only set of AA batteries to power the EK injection part can be constructed with a price tag below USD 300.

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ANALYSIS OF CHOSEN XENOBIOTICS BIOMARKERS EXPOSURE IN URINE AND LIFE STYLE OF MEDICINE STUDENTS

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Although medical students express positive attitudes toward providing lifestyle counseling, they require more instruction in the areas of weight screening, nutrition, other health behaviors (smoking) and physical activity recommendations in order to be helpful to their patients.

The study included the students' questionnaires analysis regarding their life style and knowledge concerning xenobiotics as well as collection of urine, blood and saliva samples to examine students' exposure to chosen xenobiotics biomarkers. Data obtained from questionnaires (describing the life style, eating habits, environmental exposure to xenobiotics) were compared with the results of chosen biomarkers determination.

Among the investigated students group (n=133), in 48% of examined population urine samples nicotine metabolites were detected. The analyses were carried out with use of ELISA technique.

The study analyses included determination of main nicotine metabolites by means of ELISA, mean concentration in urine samples=265.65±875.81μmol cotinine/mol creatinine, as well as TLC technique coupled with densitometric analysis, mean concentration in urine samples for cotinine=127.43±269.15 and for trans-3'hydroxycotinine= 197.51±251.24 μmol cotinine/mol creatinine. The correlation coefficients for nicotine metabolites determination results obtained by ELISA and TLC technique with densitometry were calculated.

Apart from nicotine metabolites the study research included determination of aldehydes like malondialdehyde (MDA) and 1-hydroxypyrene, biomarker of PAHs exposure as well as less specific biomarker of tobacco smoke exposure.

The average age of first cigarette smoking was 15.3±2.5 years. Nearly the half of investigate group declared active smoking (44.8%, where 44.7% are women and 45.6 are men); 10 % of examined population declared smoking more than 10 cigarettes per day. According to the data obtained from questionnaires, every third examined student (31.3%) was exposed to passive smoking. Almost all interviewed students (96.4%) were aware of harmful influence of cigarettes smoking and in most cases this knowledge was based on information obtained at school (93.4%).

Percentage of investigated medicine students who are expose to tobacco smoke are comparable to the results obtained in similar researches carried out in Albania (43.3%) and Croatia (36.6%) (*CDC, MMWR 2005, 54(20):505-09*).

The study was as a part of project 0152/PO1/2007/32 financed in 2007-2009 by the Polish Ministry of Science.

NEW ELECTROCHEMICAL SENSORS BASED ON SYNTHETIC AND NATURAL RECEPTOR FOR DETERMINATION OF ACRYLAMIDE AND ACRYLIC ACID

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The presence of toxic acrylamide in wide range of food products such as potato crisps, French fries or bread was confirmed by Swedish scientists from the Stockholm University. The neurotoxity, and possible carcinogenicity, of this compound and its metabolites imposes a duty to control them by quantitative and qualitative assays. Exposing acrylamide to pH extremes result in its hydrolysis to acrylic acid.

The main objective of the work presented is the development of the new electrochemical method for the determination of acrylamide and acrylic acid - product of acrylamide hydro-lysis in food samples.

The sensors studied are based on synthetic receptor bistetralactam and neutral receptor hemoglobin.

Synthetic ionophore has been applied for chemical modification of gold electrodes by covalent method. This method assumed covalent binding the macrocycle to the electrode surface. Modification consisted of one step in which disulfide group containing macromolecules spontaneously formed SAM. These electrodes have been used for determination of acrylic acid in aqueous solutions.

Hemoglobin has been applied for modification of glassy carbon electrodes through the carbon nanotubes. Formal potential obtained for $Fe^{2+}/^{3+}$ redox center of hemoglobin was 46 mV. These electrodes have been used for determination of acrylic acid in aqueous solutions.

Interactions with analytes were confirmed by Osteryoung square wave voltammetry (OSWV).

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ATMOSPHERIC POLYCYCLIC AROMATIC HYDROCARBONS IN SOUTH FRANCE: A SPRING-TIME STUDY

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There is an increasing concern about the occurrence of polycyclic aromatic hydrocarbons (PAHs) in the environment as they are ubiquitous in ambient air and some of them are among the strongest known carcinogens. PAHs and their derivatives are produced by the incomplete combustion of organic material arising, partly, from natural combustion such as forest and volcanic eruption, but with the majority due to anthropogenic emissions. The PAH concentration varies significantly in various rural and urban environments and is mainly influenced by vehicular and domestic emissions.

The purpose of this research was to optimize an analytical method to determine background PAH average concentrations over the urban agglomeration of Toulouse during spring 2006 for various types of sites (traffic, urban, industrial). To this aim, the 16 recommended as priority pollutants by the Environmental Protection Agency (EPA) were analyzed. Atmospheric samples were collected using two air samplers (Partisol Plus, Ecomesure and DA80, Megatec) equipped with quartz fiber filters and polyurethane foams. Particles with a diameter $<10\ \mu$m (PM10) were collected. The analyses have been performed by gas chromatography coupled to mass spectrometry (GC-MS) in selected ion monitoring (SIM) mode. For all the sites, concentrations obtained from DA80 sampler were less than those obtained from Partisol Plus. For this last one and for the two urban sites, total atmospheric concentrations between 12 and 20 ng/m^3 have been obtained, whereas for the industrial site the values averaged 22 ng/m^3. In addition, and regardless of site, the average concentrations of Benzo[a]pyrene, at present the only regulated PAH, were always less than the 1 ng/m^3 limit.

ASSESSMENT OF POLYCYCLIC AROMATIC HYDROCARBONS IN SARDINE SAMPLES BY THE QuEChERS METHOD

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Polycyclic aromatic hydrocarbons (PAHs) are a group of contaminants that are widely distributed in the environment and known to be cancer causing agents: several are classified by the International Agency of Research on Cancer (IARC) in group 2A and 2B [1]. Exposure to PAHs can be due to occupational, environmental and dietary sources. The general population is exposed to PAHs through polluted air, drinking water and predominantly food. A number of studies revealed the contamination of the aquatic environment with PAHs [2]. They become concentrated in marine sediments, especially in coastal waters, where bottom-feeding fish and filter-feeding invertebrates are particularly prone to exposure and accumulation of such compounds [2].

A large number of papers have been published on PAHs extraction from fish material using mainly Soxhlet based procedures, batch extraction enhanced by sonication, supercritical fluid extraction, matrix solid-phase dispersion and microwave-assisted extraction [3]. Actually, the "Quick, Easy, Cheap, Effective, Rugged and Safe" (QuEChERS) method, described by Anastassiades et al. [4] and based on liquid-liquid partitioning with acetonitrile followed by a clean-up step with dispersive SPE, is being explored for the analyses of pesticides and non-pesticide food contaminants.

The goal of this work was to study and adapt the QuEChERS method to the extraction of 16 PAHs from Sardine (*Sardina pilchardus*) samples. Liquid chromatography (LC) with a fluorescence detector was used for the efficient determination of the selected group of PAHs. The optimized protocol was applied for quality control of fresh Sardine samples sold at the Metropolitan Oporto Area (Portugal). Fishes were also characterized relatively to their weight, length, gender, water and fat content. The humidity percentage of the fresh fishes was evaluated gravimetrically and the lipid content was quantified by microwave-assisted extraction using a mixture of petroleum ether and acetone (2:1, v/v).

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APPLICATION OF ION CHROMATOGRAPHY FOR DETERMINATION OF THIOCYANATE IONS AS BIOMARKERS OF ENVIRONMENTAL TOBACCO SMOKE EXPOSURE

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Tobacco smoking constitutes a significant source of indoor air pollution. Some research centers conduct studies on the tobacco burning process, the composition of tobacco smoke and on how it affects the bodies of active and passive smokers. The analysis of human biological fluids (urine, whole blood, blood serum and plasma, saliva, breast milk) can be a valuable source of information about the risk level for humans from environmental tobacco smoke.

One of the biomarkers of environmental tobacco smoke exposure are thiocyanate ions. The thiocyanate ion is usually present in low concentrations in biological fluids as a result of digestion of some vegetables or by intake of thiocyanate-containing foods such as milk and cheese. Higher concentration of this ion, which is a metabolic product of cyanide, arises from tobacco smoke. The level of thiocyanate is thus considered a good probe for distinguishing between smokers and non-smokers and its determination is useful for the evaluation of smoking behaviour.

Although some methods have been reported for individual determination of thiocyanates in saliva samples (capillary electrophoresis, capillary isotachophoresis, spectrophotometry), rather limited attempts have been made for determination of ions, which are constituents of natural saliva (Na^+, K^+, Mg^{2+}, Ca^{2+}, Cl^-, PO_4^{3-}) and interpretation of the obtained results in the context of tobacco smoking.

The goal of this study was to present the effectiveness of the proposed sample preparation procedure combined with ion chromatography technique for determination of inorganic ions, especially thiocyanates (as biomarkers of environmental tobacco smoke exposure) in human saliva samples collected from passive, moderate and heavy smokers. The correlations between tobacco consumption and the level of thiocyanate ion were also ascertained. The experimental data were put to the data handling in order to obtain maximum possible information concerning both concentration levels and correlations between determined ions.

STUDY ON THE RELATIONSHIP BETWEEN INDOOR AND OUTDOOR LEVELS OF PARTICULATE POLLUTANTS IN TWO MUSEUMS IN THE HAGUE, THE NETHERLANDS

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Non-destructive research techniques are a powerful tool to monitor the deterioration processes affecting Cultural Heritage (CH) objects.

Particulate pollutants have been sampled in two Dutch museums in order to achieve an integrated view of the environment and the possible threatening factors for the deterioration of works of art. The investigated museums were the Museum Gevangenpoort (GP) and the Gallery Prince Willem V (GW) in The Hague, The Netherlands. The samplings were carried out before and during reconstruction works taking place in the direct neighbourhood of the museums, in order to assess the influence of these works on the air quality in the two museums. Samples of indoor and outdoor particulate pollutants were taken for bulk and single particle analysis during a period of several months at each museum. Whereas the GP remained open to the public during the construction works, the GW was closed in this period.

Particulate pollutants were taken with the use of a Berner impactor on different substrates (Ag and Si) for size segregated single particles and a Plexiglass® filterholder unit on Nuclepore® membranes for bulk particles.

The chemical composition and size characterization of atmospheric particulate pollutants was carried out by using computer-controlled electron probe microanalysis (CC-EPMA) at the single particle level and energy-dispersive X-ray fluorescence (EDXRF) for bulk analysis.

Elemental concentrations in the bulk aerosol samples were clearly higher in the GP. The main reasons for this observation are that the museum is not very well isolated from the outdoor air (e.g. open chimney of the hearth, doors etc.) and that the museum stayed open for visitors during the construction works on the building behind the museum. The highest concentrations in both museums were observed during the last sampling campaign when the works were in a progress stage. This observation is certainly related to the construction works, especially as elements like Si, Ca, Fe and Cr showed increasing concentrations with the advance of the construction works.

A COMPARISON BETWEEN METAL FRACTIONS, OBTAINED FROM SEQUENTIAL EXTRACTION METHOD AND SINGLE EXTRACTIONS IN SOILS OF CENTRAL GREECE

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In studies of heavy metal pollution in soils, the use of sequential extraction schemes to determine metal partitioning has experienced increased attention, because it has been recognized that the chemical form of the metal in soil determines its behaviour in the environment [1, 2]. The purpose of this study was to compare soil fractions of Cd, Cu, Pb and Zn determined by the modified BCR sequential extraction method, with the results, obtained from single extractions employing reagents and reacting conditions similar to these of sequential extraction method steps. For this scope, two soil samples were collected from an agricultural and two from an industrial area of central Greece. The soil samples had different pH values, CEC, buffering capacities and different heavy metals content.

Heavy metals were determined after division into four fractions by sequential extraction with (a) acetic acid (exchangeable and specifically adsorbed metals), (b) a reducing agent (bound to Fe/Mn hydroxides), (c) an oxidizing agent (bound to soil organic matter), and (d) aqua regia (bound to mineral structures, residual). Aliquots of the sample were subjected to single extractions using similar reacting conditions as the steps of the sequential extraction. Metal concentrations in the supernatant solution were determined with flame or Graphite furnace atomic absorption. For each extract, external standards, prepared in the corresponding extraction solution, were used for calibration. All extraction sequences were replicated four times. The estimation of the exchangeable, bound to carbonates and reducible steps from single extractions on separate subsamples was equivalent to performing the sequential extraction.

The extractability of Cd, Cu, Pb and Zn in the soils samples was, also, compared by single extraction ($CaCl_2$, DTPA, NH_4Cl, 0.1M HCl and 1M HCl) and sequential extraction procedures. Among the extractants, 1 M HCl extracted the largest proportion of Cd (75 to 95% of total), Cu (69 to 89%), Pb (47 to 92%) and Zn (31 to 61%) from soils followed by 0.1M HCl, NH_4Cl, DTPA and $CaCl_2$. In all the extractants, the proportion of extractability of metals was higher in the industrial than the agricultural soils. Regardless of soils and extractants, relative extractability was higher for Cd as compared to other three metals. The use of 1M HCl may be recommended for first-level screening of soil contamination with heavy metals. The other four weak extractants are believed to provide a better assessment of bioavailable/mobile metals content in soils than 1M HCl extractant. The single extraction procedures are simple and easy to perform and obtained results are comparable with sequential extraction procedure.

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EFFECT OF SOIL MOISTURE CONTENT ON THE METAL CONCENTRATION MEASURED BY DIFFUSIVE GRADIENTS IN THIN FILMS TECHNIQUE (DGT)

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In situ measurement were performed by means of the diffusive gradients in thin films technique in order to characterize the sewage sludge amended soil from one representative sampling site in the Czech Republic, included in the monitoring investigations. This technique reflects actual metal ion concentrations in soil solution, the rate of metal re-supply from soil solids to soil solution, and the transport rate of metal ions through the soil. The DGT technique is likely to provide a good surrogate for a metal pool in contaminated soils, which might be available for a metal uptake by a plant root system.

Impact of soil moisture content on the DGT metal uptake of cadmium, copper, nickel and lead was studied in this work. The DGT devises were deployed in the soil aliquots with various moisture content from 33% to 100% and fluxes of individual selected metals were measured. Results of the mathematical method of regression used for calculation of distribution coefficient K_d, which is in this instance a ratio of the equilibrium concentration of metal ion in the soil pore water solution and the equilibrium concentration of the same metal in soil together with the calculation of the pool concentration of the metal in soil are discussed in the contribution.

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NEW RESIN GEL FOR DIFFUSIVE GRADIENTS IN THIN FILM (DGT) TECHNIQUE BASED ON SPHERON-OXIN ION-EXCHANGER

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The diffusive gradients in thin film technique (DGT) represent a relatively new approach to in situ determination of labile metal-species in aquatic systems. The DGT device accumulates labile species from the solution while deployed in situ and therefore contamination problems associated with conventional collection and filtration procedures are eliminated. The technique employs a hydrogel layer to control the diffusive transport of metals to a cation-exchange resin, usually Chelex 100, which is selective to free or weakly complexed metal ion species. For the determination of a metal ion of interest, the prerequisite of using DGT technique is to find out suitable binding phases and diffusion layers [1].

This study deals with a new resin gel based on Spheron-Oxin® (5-sulphophenyl-azo-8-hydroxychinoline) [2] ion exchanger for DGT technique. This new binding phase with a higher selectivity for trace metal species than Chelex 100 could potentially provide more information on metals speciation in aquatic systems. The performance of this new binding phase was tested for the determination of Cd, Cu, Ni, Pb and U under laboratory conditions. Resin gel based on Spheron-Oxin® appears to be a new useful resin gel for speciation analysis of uranium in natural waters.

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MERCURY AND METHYLMERCURY IN SEDIMENTS OF THE DEULE RIVER, NORTHERN FRANCE

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The Deule River in France has been polluted by important industrial metallurgical activities during all the XXth century, which result in historical pollution of sediments by metallic pollutants. Our study is focused on the river sediments close to the former Zn-Pb smelting factory (Metaleurop) located near the city of Douai. Because of natural high concentrations of mercury present in the ores used by this factory, its production processes and its waste-water management, the mercury has been progressively introduced in the whole aquatic ecosystem, and finally massively accumulated in the sediments.

Two sediment cores have been sampled from Deule River in November 2003: the first one upstream and the second one downstream the factory. Both cores were sliced each centimetre, dried at room temperature for 48 hours and finally sieved at 63 μm before analyses.

Total mercury (HgT) and monomethyl mercury (MeHg) species have been quantified for each sediment sample. For the HgT analysis an advanced mercury analyser instrument (AMA 254) was used. Determination of methylmercury compounds in sediment was undertaken using headspace gas chromatography with atomic fluorescence detection after aqueous ethylation with sodium tetraethylborate [1].

Total mercury concentrations in the both sediment cores ranged from 10.9 to 127 mg.kg^{-1} and methylmercury levels in sediments ranged from 2.3 to 82.6 μg.kg^{-1}. These profiles do not indicate any significant evolution of HgT and MeHg concentrations over the first ten centimetres and any consistent gradient with increasing depth. This is not uncommon [2] and may partly be explained by bioturbation and boat traffic which tend to mix sediment level. In the downstream sediment (under 12 cm), concentrations of HgT and MeHg increase up to ten times, that means higher concentrations should be present in the past times. In addition, the methylation rate does not seem highest in the upper sediment layers as observed by Mikac and co-workers [3]. Finally, methylmercury concentrations depend on a lot of environmental variables (such as pH, temperature, complexing agent, biological activities) and are consequently not directly bound to total mercury concentrations. Indeed, no relevant correlation coefficient values between HgT and MeHg has been found.

In future, the influence of external environmental factors on methylmercury production as well as methylation and dimethylation degree by using mercury isotopes will be studied to provide better understanding of the mercury cycle in the River Deule.

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DETERMINATION OF LINURON AND CARBENDAZIM IN CROPS FROM WESTERN POLAND USING HIGH PERFORMANCE LIQUID CHROMATOGRAPHY

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Pesticides are used by farmers to prevent damages to the crops caused by various pest such as weeds, insects, fungi and microorganisms. The use of pesticides thereby increases crop yields and maintains crop quality. However, pesticides may be hazardous for the environment and the food consumers' health in used improperly or too frequently. Therefore, monitoring the occurrence of these substances is very important. The aim of this work is to demonstrate the applicability of a reverse phase high performance liquid chromatography (HPLC)-based method for the determination of linuron and carbendazim in matrices such as fruits, vegetables and cereals. In the developed method, the residues of both pesticides were extracted with acetone followed by a solid phase extraction (SPE) clean-up step. The pesticides were then separated on a RP C_{18} (150 mm Î 4.6 mm, 3 μm) column using a gradient of acetonitrile-water (from 30:70 to 70:30), and finally detected using a Photo Diode Array (PDA) detector at a wavelenth of 286 nm and 250 nm for carbendazim and linuron, respectively. The limit of quantification was 0.01 mg/kg for both target compounds, whereas the recoveries at two spiking levels of 0.05 and 0.1 mg/kg were in the range from 71 to 100%, and from 63 to 100% for carbendazim and linuron, respectively. A total of 118 samples of fruits, vegetables and cereals collected from the Western region of Poland were analyzed for the presence of residues of the abovementioned pesticides. None of these samples contained residues of carbendazim at a concentration exceeding the maximum residue level (MRL) for this compound, but one sample of parsley contained linuron above the relevant MRL level, which was 0.02 mg/kg.

MULTI-RESIDUE DETERMINATION OF PESTICIDES IN WATER SAMPLES USING GAS CHROMATOGRAPHY/TANDEM MASS SPECTROMETRY (GC/MS/MS) AND ULTRA PERFORMANCE LIQUID CHROMATOGRAPHY/TANDEM MASS SPECTROMETRY (UPLC/MS/MS)

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The use of pesticides has become essential for modern agriculture in order to control various pests and plant diseases and thereby improve the quality on quantity of obtained crops. But, any potential detrimental impact of pesticide residues on the environment has to be investigated, and therefore carrying out monitoring surveys on the presence of these substances in waters is extremely important. In this work, a comprehensive multi-residue method employing gas chromatography/tandem mass spectrometry (GC/MS/MS) and ultra performance liquid chromatography/tandem mass spectrometry (UPLC/MS/MS) for the analysis of 73 pesticides is presented. Water samples were passed through graphitized carbon black (GBC) columns (commercially named Carbograph) to enrich pesticides then analyzed concurrently using both techniques. In this way, both GC-amenable pesticides such as e.g. obsolete organochlorine insecticides as well as new-generation pesticides such as sulfonylurea herbicides and nicotinoid insecticides could be analyzed in any sample extract after a single enrichment step. The use of tandem mass spectrometry at the final determinative step provided adequate specificity to enable unequivocal identification and reliable quantification of detected pesticide residues in any analytical run. The method performance was evaluated through the analysis of spiked water samples, which yielded the recovery rates in the range of 65-98% with associated relative standards deviations below 15% for the majority of pesticides. The maximum permissible limit of 0.1 μg/L set by Directive 2000/60/EC for drinking water was readily met for all the targeted pesticides. The developed method have been used for the practical determinations of pesticides in water samples collected in areas of extensive agricultural practice of the Wielkopolska province. Most frequently determined pesticides were atrazine, simazine, metolachlor, metamitron, metconazole and tebuconazole at concentration levels up to 1.12 μg/L. This highest concentration was determined for the herbicide metolachlor. It has to be pointed out, however, that high concentrations of pesticides occurred in the samples collected from field drainage containers, from which the water had been hardly taken for any household use. No residues of pesticides were determined in analyzed samples of river water, whereas several samples of lake water contained residues of triazine herbicides or diazinon at low levels far below 0.1 μg/L.

SOLID-PHASE EXTRACTION TECHNIQUE AS ENRICHMENT STEP FOR THIRAM ANALYSIS IN WATER SAMPLES BY HPLC-UV: INFLUENCE OF NATURAL ORGANIC MATTER AND COPPER IONS ON THE SPE RECOVERIES

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Thiram is a dithiocarbamate compound applied worldwide, not only in agriculture as fungicide, but also in rubber industry as vulcanization accelerators and anti-oxidants [1-3]. In Portugal, thiram is one of the most used fungicides and its sales have increased significantly, according to the reports available (2002-2004) [4]. In order to evaluate the risks of its intensive use, thiram determination in environmental matrices is necessary. What concerns the application of solid phase extraction (SPE) to the preconcentration /extraction of thiram from natural waters, the results published in the literature are contradictory and some authors have reported recovery values with no analytical significance [5-7].

A C_{18}-SPE procedure combined with HPLC-UV was applied to river water samples spiked with thiram. The results obtained showed that thiram recoveries depended on the equilibration time after spiking; i.e. when the analysis was performed immediately after thiram spiking, the recoveries were always higher than 75%, but when thiram was equilibrated with the river water for 24 h or more, the recoveries decreased significantly, to values lower than 40%. The influence of natural organic matter and Cu(II) on thiram recoveries from standard solutions was studied as possible interferences for such result.

The metal ion chosen for this study was Cu(II), since it is usually applied in agriculture as inorganic fungicides, frequently in conjunction with, or during the same season as thiram is used. Besides, in Portugal, Cu(II) based fungicides are in third place among the most used fungicides while dithiocarbamates are in second [4].

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KINETIC STUDY OF MERCURY REMOVAL FROM CONTAMINATED WATER BY ZEOLITE X

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Water pollution due to heavy metals is a very serious environmental and public problem [1], which becomes even more critical when the heavy metal in account is mercury. Considered as one of the most toxic metals present in the environment, mercury can cause harmful effects both to biota and Human beings, as the well known Minanata and Iraq disasters may confirm. The enormous damage caused by mercury pollution has led to an important effort to develop efficient methods for its removal from water. The use of zeolites as ion exchangers is perhaps one of the most promising technique for such a purpose because these materials have high ion-exchange capacity, selectivity and environmental compatibility, since the exchangeable ions (Na^+, Ca^{2+} and K^+) are relatively harmless [2, 3]. In the present work we used isothermally batch stirred experiments to study the kinetics of mercury (Hg (II)) removal from water using a commercial zeolite X as ion-exchanger. A solution-zeolite suspension containing 50 μg L^{-1} of Hg (II) and 8 mg of zeolite X was magnetically stirred at 1400 rpm. Mercury remaining in solution along time was analysed by cold vapour atomic fluorescence spectroscopy (CVAFS), on a PSA cold vapour generator, model 10.003, associated with a Merlin PSA detector, model 10.023 and using $SnCl_2$ as reducing agent. The data were analysed using pseudo-first order Lagergren and pseudo-second order kinetic equations. The so obtained results reveal that zeolite X has a valuable ability to remove mercury (II) from solution, a high inferred capacity to hold it (10.1 mg g^{-1}) and that the kinetics of mercury removal is reliably described by a pseudo-second order kinetic model ($R^2=0.999$).

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VALIDATION OF THE SPE-ICP-MS TECHNIQUE FOR THE DETERMINATION OF PGES IN ATMOSPHERIC WATER SAMPLES

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The growing use of automobile catalysts leads to the emission of the platinum-group elements (*PGEs*), mainly platinum, but also palladium, rhodium, ruthenium and iridium into the environment. The number of studies have demonstrated the increasing concentrations of *PGE* in different environmental and biological samples (roadside soils, dusts and plants). However there is still a lack of studies concerning determinations of these analytes in water samples (atmospheric precipitation, road runoff, throughfall, surface water). The investigations of the contents of *PGEs* in these types of samples might provide useful information concerning the biologically available fraction of the analytes in the environment.

In rain and runoff waters samples, the ultra-low concentration (ng/L) of *PGEs* together with the high concentration of interfering matrix components often requires a sensitive determination method and a preconcentration/enrichment step combined with a matrix-separation.

The aim of this work was to develop applicable procedure with the ultimate goal to determine *PGE* at ng/L concentration levels in atmospheric waters samples. Due to the very low detection limit and multielement capability of *ICP-MS*, this method is considered as the most appropriate for determination of *PGEs* in atmospheric water samples. However, the determination, made by means of this technique, is restricted owing to interferences caused by environmental sample matrices. A possible way to overcome these spectral interferences is by matrix separation/*PGEs* preconcentration methods. For that purpose the solid-phase extraction (*SPE*) technique based on ion-exchange process has been used. Additionally, the basic validation parameters of the proposed method have been calculated.

TRACE ELEMENTS IN HUMANS BY FAAS AND ICP-OES

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The role of various elements (essential and toxic) in human biochemistry has been the subject of a large number of medical and scientific studies in recent years. Several techniques have been used so far in trace element analysis of human material, such as atomic absorption spectroscopy (AAS), atomic emission spectroscopy (AES), neutron activation analysis (NAA) and X-ray fluorescence (XRF).

In this paper, the concentration of Cd, Cr, Cu, Mn, Pb and Zn in human tissues (brain, n=10; stomach, n=9; intestines, n=5; duodenum, n=1; liver, n=15; kidney, n=9; lung, n=3; spleen n=2) and body fluids (blood, n=20; urine, n=5; bile, n=9) obtained from autopsy cases of non-poisoned people by flame atomic absorption (total n=88 samples) and inductively coupled plasma atomic emission (total n=74 samples) methods, is presented. Data obtained by both methods do not vary considerably for Zn, Mn and Cu. For trace amounts of Cd, Cr and Pb, however, the ICP-OES method was more sensitive than FAAS.

The accuracy of the methods was checked through the use of standard reference material, SRM 1557b, consisting of lyophilised bovine liver.

Establishing of the concentration of trace elements in human body can tell us about the possible health effects resulting from both chronic and acute exposure to potentially toxic elements as well as about the implications of deficiencies and excesses of essential elements in human homeostasis.

MANGANESE CONCENTRATION IN HUMAN AUTOPSY TISSUES AND BODY FLUIDS

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Manganese is ubiquitous in the environment, it occurs in soil, air, water and food. Food is the major source of Mn intake for human, however, this element can be also absorbed by inhalation, and through the olfactory pathway. The absorbed Mn is rapidly eliminated from the blood, and it first concentrates in the liver, and, with the bile, is then excreted into the intestines.

Mn is an essential element for humans and animals, and it is a normal component of biological material. The analysis of biological samples for this element is now performed mainly by use flame atomic absorption spectrometry method (FAAS), but it is also possible to use inductively-coupled plasma atomic emission spectrometry (ICP-OES).

In this paper, the concentration of Mn in human tissues and body fluids obtained from autopsy cases of non-poisoned people (n=177), aged from 14 to 80 years, between 1990-2007, is presented. The following values were found by FAAS method (mean ± SD, median, range, in μg/g or μg/ml): brain 0.18 ± 0.06, 0.17, 0.07-0.33 (n = 53); stomach 0.26 ± 0.18, 0.21, 0.06-0.87 (n=79); intestines 0.62 ± 0.44, 0.51, 0.12-1.88 (n=40); liver 0.76 ± 0.34, 0.72, 0.15-1.97 (n=106); kidney 0.55 ± 0.20, 0.53, 0.24-1.24 (n=93); lung 0.19 ± 0.14, 0.15, 0.06-0.56 (n=20); spleen 0.38 ± 0.26, 0.46, 0.01-0.60 (n=4); heart 0.20 ± 0.05, 0.19, 0.16-0.26 (n=3); bile 1.38 ± 1.56, 0.70, 0.21-5.33 (n=10); blood 0.12 ± 0.14, 0.09, 0.030-0.64 (n=53); urine 0.037 ± 0.040, 0.020, 0.030-0.13 (n=11). The accuracy of the method was checked out through the use of standard reference material: Bovine Liver 1577b (certified values: 10.5 ± 1.70 μg Mn/g, found values: 9.50 ± 0.20 μg Mn/g, n=6). Some samples (n=74) were analyzed for Mn by ICP-OES method. The results obtained by ICP-OES were compared with those found by FAAS. There was no statistical differences (test rang Kruskala-Wallisa).

The data on the Mn concentration in the human body can be used to estimate the amounts occurring in healthy persons and those, found in cases of chronic or acute poisonings with its compounds.

INVESTIGATION OF WATER AND SEDIMENT QUALITY AS POLLUTION INDICATORS BY USING ICPMS TECHNIQUE

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Water and sediment pollutions can be caused by excessive use of herbicides, pesticides, fertilizers in agricultural activities, anthropogenic discharges due to increase in urban population, and industrial effluents. It is well known that industries without having water treatment utility have direct effects on water pollution and indirect effects on soil and plant contaminations.

In this study, Lower Sakarya River basin was chosen as a research area and the samplings were started from February 2007 and last January 2008 for 12 months period. Water and sediment samples were collected along the Sakarya River basin from pre-determined sampling stations and analysed for trace elements (38 elements in sediment and 40 elements in water) by using ICP-MS technique as pollution indicators. Water and sediment samples were also measured for their physico-chemical parameters either at the sampling station or in the lab where necessary.

The results indicated that the Sakarya River water were polluted by the sources of antimony, beryllium and thallium which exceeded the limits set by the several authorities such as WHO, US EPA, EU, TSE. The results also provide useful data for the conservation of Black Sea where Sakarya River ends.

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STUDIES OF VOLATILE COMPOUNDS EMITTED DURING THERMOOXIDATIVE DEGRADATION OF POLY(BUTYLENE TEREPHTHALATE)

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Poly(butylene terephthalate) (PBT) is one of the major thermoplastic polyesters. Because of its very good mechanical, thermal and electrical properties PBT has found application in many fields, including use at elevated temperatures. Under influence of temperature and oxygen in polymeric materials degradation and decomposition processes occurs and emission of degradation products may be observed. The aim of this work was to study the volatile compounds emitted from poly(butylene terephthalate) during thermooxidative degradation in different conditions. The experiments were carried out in a flow tubular furnace at the temperatures of 200, 300, 400, 500, 600 and 700°C in the air atmosphere. The weight losses of PBT at different temperatures were evaluated. The composition and concentrations of emitted volatile compounds were determined using gas chromatography with different detectors (FID, TCD, MSD) and colorimetric method. The studies showed that the main volatile substances evolved from PBT are carbon dioxide, carbon monoxide and 1,3-butadiene. Among the other degradation products, with significantly lower concentrations, tetrahydofurane, benzene, toluene, ethylbenzene, acrolein, acetaldehyde and formaldehyde were determined. The temperature effect on the composition and the amounts of the emitted compounds was considered.

DETERMINATION OF HEAVY METALS IN CEMENT-BASED LEACHATE BY FAAS AFTER EXTRACTION WITH PURPURIN FUNCTIONALIZED RESIN

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Some heavy metal ions such as Cd(II), Cr(III) and Pb(II) in leachate from cement-based stabilized waste were determined by flame atomic absorption spectrometry (FAAS) after extraction using a new chelating resin synthesized by functionalization of a polymer support, Amberlite XAD-2 with purpurin. The optimum conditions for the extraction were investigated by batch method. The optimum pH for all metal ions was at 4.0. Their sorption equilibrium was reached within 1 h. The sorbed Cd(II) and Pb(II) were eluted by 1% HNO_3 within 10 min with the desorption recovery of >90%. The elution of Cr(III) by 3% H_2O_2 in 0.1 M NaOH was achieved within 30 min with the desorption recovery of >80%. The sorption capacity of Cd(II), Cr(III) and Pb(II) onto the resin estimated from the Langmuir model was 54.1, 46.5 and 55.7 µmol g-1 resin, respectively. This newly developed chelating resin was successfully applied for the extraction in batch system with the recovery of 86.5 and 89.9% for Cd(II) and Pb(II) and RSD less than 2.3% (n=14).

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DETERMINATION OF FENTANYL IN BIOLOGICAL AND WATER SAMPLES USING SINGLE-DROP LIQUID-LIQUID-LIQUID MICROEXTRACTION COUPLED WITH HIGH PERFORMANCE LIQUID CHROMATOGRAPHY

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Fentanyl citrate, N-(1-phenyl-4-piperidyl) propionanilide citrate, is a potent synthetic (man-made) narcotic analgesic extensively used for anesthesia and analgesia in the operating room and intensive care unit [1-3]. A single-drop liquid-liquid-liquid microextraction (LLLME) method coupled to high performance liquid chromatography (HPLC) was developed for the determination of fentanyl in biological (plasma and urine) and waste water samples. Fentanyl was extracted from basic sample solution maintained at 0.01 M NaOH (donor solution) into a thin layer of organic phase (100 µL), then back-extracted to 5-µL of the acidic acceptor microdrop (1×10^{-3} M $HClO_4$) immersed in the organic membrane from the tip of a 25-mL HPLC syringe. After the extraction, the receiving drop was withdrawn into the syringe and injected directly into a reversed-phase HPLC system for analysis. Parameters influencing extraction efficiency (organic solvent and its volume, drop volume, composition of donor and acceptor phase, stirring rate, temperature, salt addition, pre- and back-extraction times) were optimized. At optimal conditions, an enrichment factor (EF) of 355 was obtained. The detection limit (LOD) was 0.1 ng mL^{-1} (based on S/N=3) and the method proved to be repeatable as its R.S.D. values were less than 9%. The calibration graph was linear within the ranges of 0.5-1000 ng mL^{-1} with correlation coefficient (R^2) of 0.9998. Finally, the feasibility of the proposed method was evaluated by extraction and determination of fentanyl in plasma, urine and waste water samples.

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Keywords: Single-drop liquid-liquid-liquid microextraction; HPLC-UV; Fentanyl; Plasma; Urine; Water

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DESIGN OF HAZARDOUS COMPOUNDS VAPOURS GENERATOR FOR POLLUTANTS AND EXPLOSIVES VAPOUR DETECTORS CALIBRATION

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A controlled concentration vapours generator of hazardous compounds is a great challenge to evaluate detectors performance, as sensitivity and threshold. The capability to provide high-concentrated vapours allows to generate lean flow diluted in high relative humidity rate air stream. This generating system was used to calibrate quartz-crystal microbalance (QCM) based detectors with various explosives vapours.

Introduction

Due to the law enforcement application for the detection of compounds such as explosives [1], which will be used against the terrorist threat, narcotics or pollutants [2,3], very high sensitive chemical gas sensors are developed worldwide today. In order to evaluate real performances of such devices, new generator of low-concentrated (sub ppbv) and calibrated vapours are needed, particularly in presence of interfering compounds or high relative humidity level.

To this purpose, a continuous-flow trace vapour source of a nitroaromatic compound (NAC) was designed and evaluated in terms of flow and temperature dependence and outlet concentration stability, by means of a quantitative liquid chromatographic method.

Experimental

The vapour generator is composed of a bubbler containing the NAC compound. The gaseous feed was obtained by passing dry air through the bubbler at various flow rates. Outlet NAC level in air was determined by sampling in two consecutive vials containing acetonitrile, subsequently analysed by high performance liquid chromatography.

Results and discussion

By varying temperature of the thermostated system, in the range 15 to 19°C, NAC vapour source of concentrations between 500 and 1150 ppbv (part per billion) was obtained.

It also appeared that air flow strongly affects the concentration delivered by the bubbler: the higher is the flow rate the higher is the outlet concentration (figure 1).

In the investigated concentration range, NAC vapour was generated at 100 ppbv in a large relative humidity rate domain (0 to 87% at 20°C).

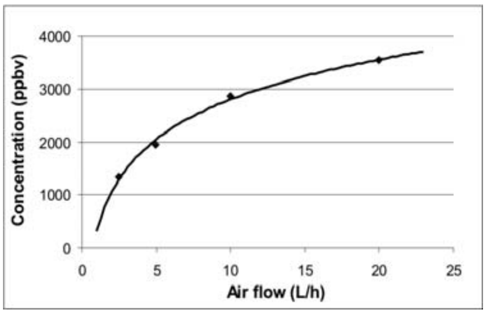

Figure 1. Influence of air flow on the outlet concentration.

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EXPERIMENTAL FACTORS BIASING COMPENDIUM METHODS MONITORING OF VOLATILE ORGANIC COMPOUNDS USING GC/MS/FID WITH CANISTERS

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This study focused on experimental factors biasing the compendium methods canister sampling and gas chromatographic analysis of volatile organics. 6l silico canisters were used to test stability of TO-14A (halo-alkanes, halo-aromatics, aromatics) and TO-15 (esters, ethers, alcohols and ketones) compounds in dry and wet canisters. Stability was tested for storage over 20 days at test intervals of 1, 7, 14 and 20 days. The change in concentration was in both positive and negative directions depending on the functional group volatile organic compound (VOC). The effect of temperature on analyzing conditions was also evaluated. The ideal temperatures for efficient trapping and desorbing of VOC were optimized. The obtained results can eventually be considered to incorporate as amendments to standard methods of VOC analysis.

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CLOUD POINT EXTRACTION FOLLOWED BY FLOW INJECTION ICP-OES FOR PRECONCENTRATION AND DETERMINATION OF ALUMINIUM ION IN AQUEOUS SAMPLES

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Aluminium (Al) is a non-essential, toxic metal to which humans are frequently exposed. It is recognized as an important toxic substance causing considerable morbidity and mortality, particularly in patients with chronic renal failure. Also, elevated levels of Al have been implicated in the aetiology of Alzheimer and Parkinson's diseases. Determination of very low levels of aluminium is very important and therefore extraction and preconcentration steps are necessary [1-2]. In this study a simple and efficient cloud point extraction method followed by flow injection system coupled to ICP-OES was developed for preconcentration and determination of trace amounts of Al^{3+} ions in aqueous samples. In this method, the Al^{3+} ions were formed complexes with morin reagent and extracted in the presence of Triton X-114 as a non-ionic surfactant. After extraction, the micellar media containing Al^{3+} ions was analyzed with ICP-OES using flow injection system. The various parameters affecting the extraction efficiency were studied and optimized with orthogonal array design. At the optimum conditions, enhancement factor of 54.7 and RSD% value below 3.1% was obtained. The calibration curve was linear in the range of 1-500 $\mu g\ l^{-1}$ with $r^2 > 0.9977$. Finally, the accuracy of the proposed method was evaluated by extraction and determination of the metal ions from different matrixes and satisfactory results were obtained.

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ACTIVITY OF RADIONUCLIDES ^{137}Cs AND ^{40}K AND CONCENTRATIONS OF SOME HEAVY METALS IN SOIL SAMPLES TAKEN FROM HIGH TATRA MTS

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The activities of artificial ^{137} Cs and natural ^{40}K radionuclides have been measured in soil samples taken from High Tatra Mts region ((in Mieguszowiecka Valley (Slovakia) and in Sucha Wooda and Rybi Potok Valley (Poland)).The radioactive ^{137}Cs was introduced into the natural ecosystem of the Tatra National Park by nuclear tests conducted in the middle of the 20-th century, and in 1986 - as a result of the failure of the Chernobyl nuclear reactor. The gamma-spectrometric radionuclides measurements were performed in the Laboratory of Chemistry and Radiochemistry at the Institute of Nuclear Physics. All soil samples were taken for gamma spectrometric measurements with low-background gamma spectrometer equipped with Silena HPGe detector (10% efficiency). The obtained results were calculated on surface deposition and were presented as [Bq/m^2] (the total deposition of a given radionuclide in the first 10 cm layer of soil and it was calculated as the sum of the surface deposition in all slices of the initial sample). The maximum concentration of caesium has been observed in the places of the altitude over 1300 m asl and accumulated usually in the organic surface layers (Ofh) or in the illuvial layers (Bhfe). The radioceasium level in the surface accumulation layers is a result of sorption and cation exchange properties of organic matter. Maximum deposition of ^{137}Cs exceeds 5 times the average ceasium concentration in soils in Poland. The changes in caesium activity indicate significant variability. The concentration of ^{137}Cs depends mostly on the volumetric soil density, altitude of sampling site and on depth of soil profile. For instance, the caesium concentration determined in Pathway from Hinczowy Lake (1680 m. asl is 68,67 Bq/kg whereas the ^{137}Cs activity measured in Hinczowy Lake (1777 m asl) is 1540,8 Bq/kg. Although measured ^{137} Cs level was high, it does not affect in a hazardous way neither human nor animals life.

Theother issue of presented abstract is showing the spatial heavy metals (Zn and Cr) distribution in soil samples taken from High Mts area. The measurements were made using two analytical techniques: AAS (atomic absorption spectroscopy) and micro-PIXIE (proton induced X-ray emission).The chosen heavy metals concentrations were determined in soil (surface layer 10 cm depth). Our evaluation indicates that Zn and Cr levels measured for mountains region were comparable to the data presented by other authors. Furthermore, the concentrations of heavy metals is strongly correlated with their natural concentrations in parental rock. We also observed that zinc was prone to accumulate in surface, rich in organic matter, soil levels.

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IDENTIFICATION OF VOLATILES IN RAW SPIRITS BY HEADSPACE SOLID-PHASE MICROEXTRACTION AND GAS CHROMATOGRAPHY-MASS SPECTROMETRY

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Volatile substances in raw spirits can originate at every production stage - they are present in raw materials, they come into being during the technological process and they are also created during storage of distillates. Therefore, the aroma of the raw spirits depends on the type and quality of the raw materials, and the fermentation and storage conditions in the distillery. The composition of volatile byproducts like carbonyl compounds, alcohols, esters, acids, acetals and others is generally diversified and complex, and the bouquet of the distillate is the result of a huge number of chemical compounds with different olfactory properties, in addition occurring in very wide ranges of concentrations.

In accordance with Polish and European Union Legislation, only a few of the volatile compounds are determined in the production of the raw spirits and spirit beverages. Furthermore, analytical methods do not take into consideration various effects of different compounds on the flavor of the product. Some of the volatiles, occurring in the raw spirits, affect them positively and others change their sensory properties negatively even in trace concentrations.

The aim of the study was to develop a method for the determination of volatile compounds in raw spirits of different quality or produced from various raw materials. The determination of volatiles from raw spirits was conducted by means of headspace solid-phase microextraction and gas chromatography coupled to mass spectrometry (HS-SPME/GC-MS). The extraction of volatile compounds from raw spirits was performed in accordance with methods developed earlier, where all the conditions, such as suitable stationary phases of the fiber, temperature and time of extraction, and sample volume were optimized to ensure a high efficiency of volatiles isolation. The compounds were identified by comparing retention times on two columns of different polarity and mass spectra with own and literature data and mass spectral databases.

The procedure developed here should enable a more precise quality assessment of the raw spirits and final products in conjunction with sensory analysis and other recommended analytical methods.

DICHLOROMETHANE EXTRACTED ORGANIC COMPOUNDS FROM LAKE SEDIMENTS: GC/MS ANALYSIS AND TOXICOLOGICAL TESTING

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Lake sediments contain thousands of substances of natural and anthropogenic origin. Taking into account that an unknown number of them are toxic, the presence of some compounds may have a negative influence on an aquatic ecosystem. Therefore, it is very important to obtain reliable information about the toxicity of the lake's sediments.

Chemical analysis provides only a part of the knowledge necessary to evaluate and assess the toxic potential of compounds for wildlife and humans. This is due to different bioavailability of the forms in which pollutants exist in the environment and their different biological activities. Furthermore, the complex interactions between environmental chemicals are not completely understood. The parallel use of selective biotests and chemical analysis provides more complete information about 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 Mała Panew River. The sources of pollution for Mała Panew River waters are mainly agricultural activity, municipal waste waters and industrial wastes. The industry, concentrated in the upper and central part of Mała Panew River basin includes mining and metallurgy of silver, zinc and lead, manufacture of cellulose, chemical production, ferrous and glass metallurgy. Due to that fact, Mała Panew River supplies Lake Turawskie with polluted water and a large quantity of sediments contaminated by heavy metals.

The toxicity of aqueous extracts of sediments 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. Additionally, chemical analyses were performed. The chromatograms obtained using coupled gas chromatography - mass spectrometry (GC-MS) indicated a very complex composition of the examined dichloromethane extracts. The aim of these analyses was an attempt to identify chemical substances responsible for the observed toxicity effects.

SEQUENCE EXTRACTION OF THE SELECTED ELEMENTS IN SLUDGE SUBJECTED TO THERMAL HYDROLYSIS BY CAMBI SYSTEM IN "KAPUŚCISKA" SEWAGE TREATMENT PLANT IN BYDGOSZCZ

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Thermal hydrolysis is one of the methods of sludge treatment employed prior to fermentation in closed sludge digesters, where methane is obtained in the process of mesophilic fermentation. Raw sludge and excessive sludge dehydrated to 16% of dry mass were supplied to CAMBI system in "Kapuściska" sewage treatment plant. Dehydrated sludge after heating and homogenization is pumped into reactor where it is hydrolyzed under condition of high temperature and high pressure. In the next step, pressure and temperature of sludge in reactor are reduced in the successive digester. After hydrolysis, sludge is directed into separated sludge digesters (SSD).

The subject of our studies was sludge from "Kapuściska" sewage treatment plant in Bydgoszczy sampled from CAMBI thermal hydrolysis system. Three-stage sequence extraction of elements was conducted prior to supplying into CAMBI system: in dehydrated sludge (raw and excessive) - sludge 1, in sludge after heating and homogenization - sludge 2 and in sludge after thermal hydrolysis - sludge 3. Sequence extraction of elements (Cd, Co, Cr, Ni, Cu, Pb, Zn, Fe, Mn) was performed by BCR method (Community Buremu of Reference) [1,2]. The fractions were obtained as follows: fraction I - by extraction of sludge with acetic acid (0.11 mol·L^{-1}), fraction II - by extraction of residue sludge with solution of hydroxylamine hydrochloride (0.1 mol·L^{-1}), fraction III - by successive application of hydrogen peroxide (8.8 mol·L^{-1}) and ammonium acetate (1.0 mol·L^{-1}) as extractants. The sequence solution obtained by extraction were filtrated, replenished with water to the required volume and then, analyzed by emission spectroscopy in inductively coupled plasma (JY 38S apparatus).

As a result of analyses of the elements carried out both in sludge subjected to processing in CAMBI system and raw sludge, it was found that thermal hydrolysis had a significant effect on elution of elements from sludge. It was found that stage of heating and homogenization resulted in elution of larger amount of zinc, iron and manganese in the first stage of extraction in relation to raw and excessive. Moreover, it was observed that in the case of cobalt, nickel, copper and lead, conversion of sludge in the process of thermal hydrolysis resulted in lower bioaccessibility of those elements both in relation to the raw sludge before introduction to CAMBI system and sludge after the stage of preheating and homogenization.

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SOLVENTLESS METHODS FOR THE DETERMINATION OF VOLATILE FATTY ACIDS IN WATER AND SLUDGE SAMPLES

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Volatile fatty acids (VFAs) are low-molecular-mass organic acids with a strong hydrophilic character. They originate from aerobic biodegradation of carbohydrates, proteins and fats. Therefore, they are widely present in activated sludge, waste and landfill leachates and wastewaters. Recently, the determination of VFAs became of increasing interest since it has been found that they are involved in different processes, i.e. the biological removal of phosphorus from waters or nitrification-denitrification in activated sludge [1].

Conventional extraction methods, such as liquid-liquid extraction (LLE), solid phase extraction (SPE), distillation or purge-and-trap techniques are the most commonly used sample pretreatment methods for the isolation and/or enrichment of volatile fatty acids prior to GC analysis.

However, free fatty acids, especially the small-chain ones (C_2-C_5), are strongly hydrophilic compounds, and the conventional methods often have poor efficiency and analytical precision. Liquid-liquid extraction is the most popular method, however, it involves extensive cleanup procedures which are very time consuming. Also, it uses large amounts of organic solvents that are hazardous to the environment and human health and very expensive to dispose of. Therefore, the development of a new method which is simple, fast, and solvent-free is crucial [2].

An alternative preconcentration method for sample preparation, the technique of solid-phase microextraction (SPME) has been applied to the determination of a large variety of volatile and semi-volatile analytes in several types of environmental matrices [3].

In recent years, the attractive technique of single-drop microextraction (SDME) has been developed as an alternative to SPME. SDME avoids some problems of the SPME method, such as sample carry-over and fibre degradation; it is also fast and inexpensive and uses very simple equipment [4].

In our work, the results of studies on development of methods to the determination of volatile fatty acids (C_1-C_6) by employing single-drop microextraction technique (SDME) and solid-phase microextraction (SPME) have been presented. The methods developed were applied to the determination of VFAs in water and sludge samples.

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THE QUALITY OF PLANT SAMPLING IN BIOINDICATION STUDIES

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The quality of analytical measurements depends on assuring the quality of every phase of the measuring process. According to many authors, field sampling results even in larger values of uncertainty than the other steps of the analytical path [e.g. 1]. It is obvious that sampling cannot be overlooked when the quality assurance in chemical analyses gets top priority influencing laboratory reputation. The chemical analyses of environmental materials require appropriate sampling strategies. These impose cooperative action of analytical chemists and environmentalists who have knowledge of factors that influence the chemistry of environmental materials to be sampled.

Bioindication studies are widely performed to assess the quality of the environment and the potential toxicity of some chemical species to living organisms. Many of the organisms, particularly plants, meet the criteria of a good bioindicator [2]. The authors present the most important issues linked to sampling of lichens, mosses, coniferous and deciduous trees based on a long-standing experience gained during the studies of forest ecosystems in Poland and USA.

Lichens and mosses are widely used in air pollution studies because these organisms take up elements and organic compounds mostly from atmosphere [3]. The uncertainty of sampling arises from different sources: (i) sampling of mixed moss species (these should be checked on the day of sampling for the presence of alien species), (ii) sampling of dead and living parts of mosses, and (iii) sampling of lichen species growing on different trees.

Tree bark is a very useful bioindicator of soil and air pollution. Different studies have shown that trees accumulate non-essential elements in their bark. In contrast to mosses and lichens, tree bark is always accessible to sample collection. When collecting bark samples, it is important to keep in mind that the outermost bark layers (cork, dead and non-functional phloem) show the highest element accumulation ability.

Pine needles are used as bioindicators of both air and soil quality. The chemical analyses of tree bark, pine needles and soil are the best way to assess bioavailability of pollutants. It should be stressed that pine needles of different age classes cannot be mixed due to the differences in physiological activity that lead to enrichment of the youngest needles in many trace elements.

There are some general rules to obey when collecting samples of plant bioindicators. There is a possibility of contamination during sampling from sampling tools. Composite samples should be produced from a number of single plants, but similar in their age, exposure to sun etc., to assure the same environmental conditions. Only specific plant parts plants should be collected due to differences in element accumulation abilities.

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INVESTIGATION OF LIGANDS INVOLVED IN PLATINUM(II) AND PLATINUM (IV) BINDING IN *ARABIDOPSIS THALIANA*

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Since many years the influence of metals on plants (accumulation, stress, e.t.c.) has been investigated, also for the noble elements. Understanding the mechanism of metal bioaccumulation, sequestration and assimilation by plants may give an insight into the metabolic pathways of metals and their chemical forms which can be responsible for various toxic effects (metal or oxidation stress).

In present study *Arabidopsis thaliana* was treated with selected platinum compounds ($PtCl_4$, cis-Pt and $Pt(NH_3)_4(NO_3)_2$), and then leaves and roots extracts were examined using RPLC-ESI MS. It has been found, that plant's response was different depending on form of platinum and its oxidation state. More sulfur-containing compounds were found in extracts, when plants were exposed to Pt(II), more biocompatible than Pt(IV). The exposure to Pt(IV) resulted in intense synthesis of glutathione, but not phytochelatins and it could indicate domination of oxidation stress. Exposure of plants to cis-Pt resulted in stimulation growth of plants and synthesis of unknown peptides.

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INVESTIGATION OF PAHS DESORPTION IN AQUATIC ENVIRONMENT - MODEL RESEARCH

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Determining the entire content of organic pollutants in surface waters, such aspolycyclic arenes, is not sufficient to determine the risk caused by their presence in the environment. Such information can be obtained by physical speciation analysis. Through determination of a state in which xenobiotics occurs, the harmfulness to and possible influence on living organisms can be ascertained; thus it has become a basic trend in modern analytics.

The work describes the results of model research of the process of desorption of polycyclic aromatic hydrocarbons (PAHs) from sediment (reference material: Metranal 2, Analityka). The experiment was carried out using model water-sediment systems prepared and kept in glass bottles. After a specified storage time, analytes were isolated from each phase of the samples (water, sediment, sides of bottles) and were subject to final measurement. 3 series of model systems were prepared, containing samples of sediments and water in different proportions (3 grams of sediment and 500, 250 and 150 cm^3 of water) and about 5 mg of $HgCl_2$ (biocide). Each series involved 5 samples and one blank sample (without sediment). The samples were kept in the dark, at a constant temperature for 11 days and were shaken every day. After conditioning, analytes were isolated, both the analytes present in the aqueous phase and in the sediment. Those in the aqueous phase were extracted using sorption tubes with the bed of C_{18} bonded phase, and the analytes in the sediment were extracted by liquid extraction (using dichloromethane). Additionally, the sides of the empty and dry bottle were rinsed with dichloromethane (20 ml), and the extract was put into a phial. The excess solvent was evaporated in a stream of neutral gas (nitrogen). The samples of the obtained extracts were analyzed chromatographically using GC-MS in order to determine the quantities of each analyte.

The obtained results show that regardless of water volume in the systems similar quantities of PAHs desorb from sediment. A comparison of the amount of PAHs desorbed from sediments with their dissolubility in water shows that the dissolubility of these compounds in water is not the desorption-limiting factor. Comparison of obtained partition coefficients of PAHs in sediment/water systems with values of the octanol/water partition coefficient and the boiling temperature of these compounds, shows a correlation between the partition coefficient in a sediment/water system and the physico-chemical properties of the analytes.

PROCEDURE FOR TRACE CONTENT OF HIGH-BOILING POLYCYCLIC AROMATIC HYDROCARBONS (PAHS) DETERMINATION IN TECHNICAL PRODUCTS

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The communication presents a novel method of sample preparation for the determination of trace concentration of polycyclic aromatic hydrocarbons (PAHs) in petroleum fractions (vacuum residue, asphalts, aromatic extracts from vacuum distillates, base oils, plasticizers, etc.) and rubber products. The studies revealed that in order to separate most of interferences from the analytes without a significant loss of PAHs it is necessary to use size exclusion chromatography (SEC) as the first step of sample preparation, followed by adsorption using normal-phase chromatography.

The first stage of sample preparation enables selective isolation of the fraction containing PAHs and the removal of components having higher molar masses than PAHs from matrixes. However, the investigations show that the use only of size exclusion chromatography as a sample preparation step for the determination of trace PAH amounts in technical products was found to be insufficient. The isolated fraction contained large amounts of compounds with molar masses similar to those of PAHs and similar or higher polarity. This precludes final determination by means of reverse phase - high performance liquid chromatography technique (RP-HPLC). It is necessary second stage of sample preparation - adsorption in normal phase conditions. Potentially second stage can be realized using SPE or HPLC techniques. The use of HPLC is a better choice than SPE due to a very complex composition of the fraction isolated by SEC. Although HPLC is more expensive and less amenable to automation, it ensures improved selectivity of separation and considerably better reproducibility of the results.

In order to reduce the limit of quantitation (LOQ) for the entire procedure, preparative liquid chromatography is preferred. The lower the required limit of LOQ of PAHs is, the larger the scale of preparative liquid chromatography in both steps of sample preparation is needed. The final determination of PAHs was carried out using RP-HPLC technique coupled with ultraviolet - diode array detector or/and fluorescence detector and gas chromatography technique with mass spectrometer or phothoionization detector. The analytical procedure, its main validation parameters and dependence of LOQ of PAHs on scale of sample preparation and techniques of final determination will be presented.

DETERMINATION OF BROMATE IN MINERAL AND SPRING WATERS BY tITP-CZE COMBINATION IN AUTOMATED ELECTROPHORETIC ANALYSER

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Bromate, belonging to a group of disinfection by-products (DBP), is not currently present in natural waters and it is formed from bromide, present in some ground and source waters, during an ozonization process [1].

Bromate is known to be an animal carcinogen [2] and it is classified in a group 2B - possibly carcinogenic to humans by the International Agency for Research on Cancer (IARC) [3]. The World Health Organization (WHO) [4] and US Environmental Protection Agency (US EPA) [5] classified bromate as a potential carcinogen, even at very low μg/l. Health effect studies indicate it to be suspected human carcinogen which exhibits a potential 10^{-4} risk of cancer after the lifetime exposure in drinking water at 5 μg/l and potential 10^{-5} risk at 0,5 μg/l [6].

US Environmental Protection Agency (US EPA) established the maximum allowable contaminant level goal (MCLG) of zero and a maximum contaminant level (MCL) for bromate in drinking water to 10 mg/l [7]. Bromate has been regulated in EC by the Drinking Water Directive EC98/83 that fixed a bromate limit to 10 μg/l, defining analytical determination limit of 2,5 μg/l. [8]

At present, various methods as employed to monitor bromate at low level include ion chromatography with conductivity detection, post column reaction detections, mass spectrometry and inductively coupled plasma-mass spectrometry.

On-line combination of capillary isotachophoresis with capillary zone electrophoresis was studied for direct determination bromate in mineral and spring waters. The method developed in this study was validated and it is suitable for direct determination of bromate in mineral and spring waters containing high amounts of minerals without sample pretreatment. The concentration limit of detection (cLOD) of bromate in mineral and spring waters was found to be 0.6 μg/l.

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IDENTIFICATION OF ARSENIC COMPOUNDS IN WHITE MUSTARD (*SINAPIS ALBA*) GROWN UNDER HYDROPONIC CONDITIONS

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Toxicity of arsenic highly depends on its form. Inorganic species such as arsenites, arsenates and especially arsine are usually the most toxic species for organisms. Organic arsenic species such as monomethylarsonic acid (MMA) and dimethylarsinic acid (DMA) are less harmful. Some of the organic species (arsenobetaine, arsenocholine) are considered non toxic.

The aim of the investigation was to define the influence of different arsenic compounds added to nutrient solution on growth of White mustard (*Sinapis alba L*). Transformation of arsenic compounds in plant tissues was also investigated. Plants were grown under controlled conditions in Knopp nutrient medium with addition of four arsenic compounds (arsenites, arsenates, MMA, DMA). Concentration of each arsenic compound in nutrient solution was 1 g/L. After 6 weeks plants were harvested and divided into leaves, stems and roots. Total arsenic concentration was determined by ICP-MS after sample digestion in microwave digestion system. The majority of arsenic (80-90% of total amount) in plants grown with addition of arsenites, arsenates and MMA is located in roots. In White mustard grown with addition of DMA, approximately 50% of total arsenic is located in above-ground organs. Moreover, plants grown with addition of DMA contain the smallest amounts of arsenic (up to 8 mg/kg) in their tissues. It is in contrast with plants grown in nutrient solution with addition of As (V) in which case concentration of arsenic in roots is up to 200 mg/kg.

Arsenic speciation analysis was carried out after arsenic extraction from dried plant material. Water was used as an extractant. Arsenic compounds was separated chromatographically (HPLC) on anion-exchange column and arsenic was determined using inductively coupled plasma mass spectrometry (ICP MS).

In leaves and roots of plants grown with addition of arsenites and arsenates only inorganic arsenic species were identified. However, in stems of these plants also small amounts of MMA were found. In White mustard grown with addition of MMA, mainly this compound is present in plant tissues. However, approximately 50% of arsenic included in leaves occurs as inorganic species. In plants grown with addition of DMA about 40% of arsenic occurs as inorganic species and roots include the highest amounts of inorganic arsenic. DMA is a predominant species in this case, however noticeable amounts of MMA was found in roots.

Investigations showed that arsenic uptake by White mustard is highly dependent on arsenic form added to the nutrient. Moreover, in investigated plants besides arsenic form added to the nutrient medium, different arsenic species was also identified.

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EGGPLANT LEAF WAXES MAY INDICATE AND AFFECT PLANT SUSCEPTIBILITY TO INSECT HERBIVORES

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Pesticides are one of the most common persistent organic pollutants in the environment. As they are often highly toxic for mammals, birds and water organisms, either in native or metabolised form, there is a continues need to reduce their use in agriculture. Growing of more resistant plant cultivars is one of the most promising ways in achieving this task. Among many factors, secondary metabolite profile seems to be important issue helping to understand plant susceptibility to insect herbivores. Chemicals located in the thin layer of surface (or cuticular) waxes are known to be responsible for both resistance and susceptibility to insects [1]. Eggplant (*Solanum melongena*) was chosen as a model plant because of its susceptibility to a number of insect herbivores from various taxonomic groups. Large amounts of pesticides are needed to keep the plant healthy during growth and ripening of the fruits [2]. In this paper we present composition of alcohol and sterol fractions of the surface waxes from leaves of seven eggplant cultivars. Possible impact of cuticular triterpene alcohols on the susceptibility to aphids (*Myzus persicae* and *Macrosiphum euphorbiae*) is discussed. Correlation between amount of triterpenes and degree of aphid infestation is presented. We also suggest usefulness of cuticular sterols profile in estimating the scale of infestation and damage of tissues.

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A NOVEL METHODOLOGY TO DETERMINE THE PRESENCE OF ß -N-METHYLAMINO-L-ALANINE NEUROTOXIN IN NATURAL WATERS

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ß-N-methylamino-L-alanine (BMAA) is a non-protein amino acid. This neurotoxin has been associated with the illness amyotrophic lateral sclerosis/parkinsonism-dementia complex (ALS/PDC) that has an extremely high rate of incidence among the Chamorro people of Guam compared with incidence rates of ALS/PDC elsewhere. BMAA, can be produced by all known groups of cyanobacteria and it accumulates in ascending trophic levels. This hypothesis gained attention when BMAA's presence was discovered in the brain tissues of the Chamorro people who died of ALS/PDC, but has not been found in patients that died of neurodegenerative diseases. Their exposure is thought to come from the consumption of cycad fruit on which, as well in the roots of the plant, cyanobacterias are found. Also BMAA was recently discovered in the brain tissues of nine Canadian Alzheimer's patients, but it was not detected in the brain tissues of 14 other Canadians who died of causes unrelated to neurodegeneration. Because cycads are not part of the Canadian flora, it was suggested that cyanobacteria might be the ultimate source of the BMAA in the Canadian Alzheimer patients. The presence of cyanobacteria in natural waters opens the possibility of exposure to these toxins. A practical analytical methodology for its detection in natural waters is needed. A method based on Solid Phase Extraction/High Performance Liquid Chromatography/ Ultraviolet-Visible (SPE/HPLC/UV-VIS) to determine BMAA in natural waters is being developed. Derivatization with 2, 4, 6, -Trinitrobenzenesulfonic acid (TNBS) is necessary for the neurotoxin's detection. This is a rapid and easy derivatization. Another method of detection that is being tested is Gas Chromatography/Mass Spectrometry (GC/MS) with direct derivatization in water [1]. Different SPE disks and resin like SCX, Anion-SR and SDB-RPS were used to optimize the extraction and isolation. SCX resin gave the best recoveries in the range of 88%. Spikes of BMAA in natural waters at ppb levels can be detected in the universal mode and ppt in the selected ion monitoring.

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ANALYSIS OF FLAVONOIDS FROM KIWI FRUITS BY LIQUID CHROMATOGRAPHY COUPLED WITH DIODE-ARRAY DETECTOR AND ELECTROSPRAY MASS SPECTROMETRY

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The flavonoids are among the most widely occurring groups of plant secondary metabolites and one of the most diverse groups both structurally and functionally.

Flavonoids are polyphenolic compounds with antioxidant properties [1] and several studies have shown that a high intake of flavonoids is correlated to a decrease in heart disease, and other biological effects of this class of compounds have been described in several *in vivo* and *in vitro* studies [2,3].

Mass spectrometry (MS) is among the powerful techniques for the elucidation of flavonoids structure. During the past decade, electrospray ionisation (ESI) MS has emerged as a highly useful methodology for direct coupling with liquid phase separation techniques such as chromatography and electrophoresis [4]. The utility of high performance liquid chromatography (HPLC) separations was greatly enhanced by mass spectrometric detection, which allowed the confidently identification of the substances in plant materials. Liquid chromatography coupled to mass spectrometry (LC/MS) can give information on sugar and acyl moieties in flavonoids witch not revealed by the UV spectrum without the need to isolate and hydrolyse the compounds [5].

A high-performance liquid chromatography (HPLC) method with photo-diode array (DAD) detection and mass spectrometry (MS) was developed to separate and quantify flavonoids in cabagge leaves and kiwi .

This method is based on the separation of flavonoid glycosides present in the methanolic extracts from fruits using high performance liquid chromatography (HPLC) followed by detection with electrospray ionization mass spectrometry (ESI/MS). Chromatographic separation of the analytes of interest was achieved on a LiChroCART C-18 250x4 column with detection in negative ion mode. Calibration graphs were obtained by determining the area between external standard of each major compound. Analyses were performed with a HP1100 LC from Agilent, equipped with an automatic injector. MS was performed using a VL quadrupole mass spectrometer (Agilent) equipped with electrospray ionization (ESI) ion source (nitrogen flow rate 10 L/min). Mobile phases consisted of 0.25% formic acid in water (A) and 0.25% formic acid in methanol (B). Separation was carried out under the following conditions: gradients starting at 5% B to 100% B in 55 min. The column was equilibrated for 10 min prior to each analysis. Flow rate was 1.0 mL/min and injection volume was 50 μL. Drying nitrogen was heated to 300°C. Peaks were identified on the basis of comparison of retention times, UV-Vis, and MS spectra with standards .

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SPECTROPHOTOMETRIC DETERMINATION OF SOME ORGANOPHOSPHORUS PESTICIDES IN FORMULATIONS AND ENVIROMENTAL SAMPLES

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Two rapid, simple, reproducible and sensitive spectrophotometric methods (A and B) for the determination of some organophosphorus pesticides, i.e. malathion and dimethoate is described. The two methods are based on the oxidation of organophosphorus pesticide with slight excess of Cerium (IV) sulfate and the determination of unreacted oxidant by a decrease in the red color of chromotrope 2R (C2R) λ_{max} of 528 nm for method A or a decrease in the orange pink color of Rhodamine 6G (Rh6G) at a suitable λ_{max} of 525 nm for method B. A regression analysis of Beer-Lambert plots showed a good correlation in the concentration range of 80-800 ng mL^{-1}. The apparent molar absorpitivity, sandell sensitivity, detection and quantification limits were calculated. For more accurate analysis, the Ringbom optimum concentration ranges are 100-700 ng mL^{-1}. The developed methods were successfully applied to the determination of organophosphorus pesticide (malathion, and dimethoate) residues in their formulations and environmental samples.

Keywords: Spectrophotometric; Organophosphorus pesticide; Cerium (IV) sulfate; Chromotrope 2R; Rhodamine 6G

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SOLVENT MICROEXTRACTION - FLAME ATOMIC ABSORPTION SPECTROMETRY FOR DETERMINATION OF ULTRATRACE AMOUNTS OF CADMIUM IN MEAT AND FISH SAMPLES

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A simple, low cost and highly sensitive method based on solvent microextraction (SME) for separation/preconcentration and flame atomic absorption spectrometry (FAAS) was proposed for the determination of ultratrace amount of cadmium in meat and fish samples. The analytical procedure involved the formation of hydrophobic complex by mixing the analyte solution with an ammonium pyrrolidinedithiocarbamate (APDC) solution. In the suitable conditions, the complex of cadmium-APDC entered the micro organic phase and thus separation of the analyte from the matrix was achieved.

Under optimal chemical and instrumental conditions, a detection limit (3σ) of 0.8 ng L^{-1} and enrichment factor of 93 were achieved. The relative standard deviation for the method was found to be 2.2% for Cd. The interference effects of some anions and cations were also investigated. The developed method has been applied to the determination of trace Cd in meat and fish samples.

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SOLVENT MICROEXTRACTION (SME) OF COPPER IN NATURAL WATERS BEFORE IT'S DETERMINATION BY FLAME ATOMIC ABSORPTION SPECTROMETRY (FAAS)

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A simple and sensitive method using cupron-octanol single drop microextraction has been developed for separation and preconcentration of trace copper prior to it's determination by flame atomic absorption spectrometry. Parameters, such as solvent type, pH, cupron concentration, extraction time, organic drop volume, stirring rate and extraction temperature were investigated. Under the optimized conditions, a detection limit (3σ) of 0.9 ng L^{-1} and enrichment factor of 96 were achieved. The relative standard deviation for the method was found to be 2.4% for Cu. The interference effects of some anions and cations were also investigated. The developed method has been applied to the determination of trace Cu in natural water samples.

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CHEMOMETRIC EVALUATION OF THE HEAVY METAL DISTRIBUTION IN *SADURIA ENTOMON* FROM THE SOUTHERN BALTIC RELATIVE TO ITS ELEMENTAL COMPOSITION

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The Baltic Sea, especially the Gulf of Gdańsk, is continuously exposed to high anthropogenic stress. The Tri-City, i.e. Gdańsk, Gdynia and Sopot, emits sewage into the Gulf, as does the River Vistula, which drains most of Poland including the major industrial regions and cities. Pollutants such as heavy metals tend to be accumulated in bottom-dwelling marine organisms that are potentially affected because of their living in or on the sediments. *Saduria entomon* is one of the widely distributed crustaceans in the Baltic Sea. It appears that the crustacean exhibits ability to assimilate trace elements from bottom sediment so it seems to be a good biomonitor of content these metals in Baltic waters.

The aim of the study was to examine the distribution and degree of accumulation of Ag, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb and Zn in *S. entomon* from the southern Baltic.

Samples of benthic invertebrates were collected from the Gulf of Gdańsk and open Baltic waters. The sampling was carried out onboard the M/S Hestia and R/V Baltica between March 2001 and July 2002. The individuals of *S. entomon* were sorted out into size classes and sex. Dried and homogenized samples were digested in Microwave Digestion System (MLS 1200 MEGA) using concentrated nitric acid. The levels of metals were determined by atomic absorption spectroscopy (FAAS) method. The accuracy and precision of the method used was checked out in a separate comparative study of metals with standard reference materials, i.e. TORT-2 (lobster hepatopancreas). The obtained results were in good agreement with the certified values.

The Statistica for Windows (Release 7.1 Copyright© StatSoft, Inc.) program was used for the statistical work-up of the results. In order to reduce relatively large number of variables to smaller number of factors, the original data were treated using multivariate statistical technique, factor analysis (FA), allowed for the correct interpretation of the data set. The distribution of the points corresponding to the individual elements shows that factor F1 achieves the highest loadings for Cd, Fe, Ni, Pb and Zn. These loadings are responsible for identification of samples originated from the Gulf of Gdansk, which are clearly distinguished from the group of Co, Cr, Cu and Mn, attributable to open waters of the southern Baltic. Factor 3 is responsible for the discrimination of specimens which inhabit the different type of sediments. Ag, Cd, Co, Cu, Fe, Pb, Ni and Zn are responsible for higher values of F3 while lower values are noted for Cr and Mn. The content of these metals shows tendency to distinguish the organisms inhabited the muddy bottom from those lived in sandy sediments. It seems that the granulometric composition of the sediment have influence on the trace metals bioavailability from labile fraction of sediment. The results presented show that *Saduria entomon* tends to be sensitive and valuable biomonitor of chosen heavy metals contamination of the southern Baltic.

DETERMINATION OF VOLATILE COMPOUNDS IN FLUE GASES

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Limitation of emission of primary air pollutants is related to protection of air purity.

Main contents of air pollution are: carbon dioxide, carbon monoxide, nitrogen oxides, sulfur dioxide, hydrogen chloride, hydrogen fluoride, suspended dust, volatile organic compounds, stable hydrocarbons which contain polycyclic aromatic hydrocarbons, polychlorinated dioxins and furans, polychlorinated biphenyls and heavy metals [1-2].

Volatile organic compounds (VOCs) are known as one of the most destructive pollutant of air directly after NO_x [3].

One of the problems related to the estimation of environmental condition is lack of method which allows to evaluate concentration of volatile organic compounds and other pollutions which are transferred into the air with gases from combustion of fossil fuels and biomass.

The purpose of the present work is doctor's thesis manuscript that refers to identification and estimation of quantitative composition of volatile organic compounds which are emitted from combustion of fossil fuels and biomass.

Realization of this work involves: elaboration of method of collections of samples, method of identification and quantitative estimation of VOCs, validation of elaborated analytic method and application of elaborated method for the estimation of concentration of volatile organic compounds which are emitted from combustion of fossil fuels and biomass.

Result of this work should enable analysis of quantitative and quality composition of chosen VOCs in combustion gases from exemplary fossil fuels.

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DETERMINATION OF ANTIMONY(III,V) BY ANODIC STRIPPING VOLTAMMETRY USING AN *IN-SITU* BISMUTH FILM ELECTRODE

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Antimony exists as antimony(III,V) in environmental, biological and geochemical samples. Antimony and its compounds are listed as pollutants of priority interest by the Environmental Protection Agency of US and the Council of the European Communities. Therefore, the determination of trace antimony is quite meaningful and beneficial. Because of toxicity of mercury, bismuth film electrode as an alternative has been developed for the determination of metal ions in aqueous samples [1,2]. The purpose of this study is to develop a sensitive method for the determination of antimony(III,V) using bismuth film electrode by Osteryoung squre wave anodic stripping voltammetry.

[Experimental] All experiments were carried out with a BAS Model CV-50W Voltammetric Analyzer. An edge-plane pyrolitic graphite disk was used as a working electrode, and was cleaned at 800 mV for 30 s prior to analysis.

[Results and Discussion] The experimental factors such as HCl and Bi(III) concentrations, L-cysteine and KCl concentration, deposition potential and time were investigated for the determination of traces antimony(III,V). Two different concentrations of 0.4 and 2.0 M HCl were chosen as suitable acidic media. The preliminary deposition of antimony was performed at -400 mV *vs.* Ag/AgCl for 180 s. The anodic response for antimony was enhanced at 450 mV by using bismuth film electrode. The anodic peak current was directly proportional to antimony(III, V) over the concentration ranges of 0.01 to 0.10 μg L^{-1} and 0.10 to 1.00 μg L^{-1}. The detection limits for antimony(III) and antimony(V) calculated as 3 sigma from 0.01 μg L^{-1} were 0.4 and 3.4 ng L^{-1}, respectively. The successful recovery tests in model samples and the application to sea water demonstrate the validation of the proposed method.

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SIMULTANEOUS DETERMINATION OF Cr(III) AND Cr(VI) BY ADSORPTIVE STRIPPING VOLTAMMETRY USING EDTA AND DTPA AS COMPLEXING AGENTS, RESPECTIVELY

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Chromium is a major pollutant introduced into environment from a variety of industrial wastewaters including steel production, metal plating, spray painting, leather tanning and wood preserving. Among the species of chromium there are two common oxidation states present in the environment, Cr(III) considered to be a trace element species essential for the proper functioning of living organisms and Cr(VI) potentially highly toxic and carcinogenic agent. Therefore it is necessary to control the level of chromium species in various natural samples. In the present study, the technique of catalytic adsorptive stripping voltammetry to simultaneous determination of Cr(III) and Cr(VI) was adapted. For this purpose the voltammetric measurements were performed in two steps. At the beginning sample solution, acetate buffer, KNO_3 and EDTA were added to the voltammetric cell. At these conditions Cr(III) present in the sample forms Cr(III)-EDTA stable complex and after 5 min deaeration time the voltammetric signal corresponding to Cr(III) as Cr(III)-EDTA complex was recorded. Next in the second step DTPA was added to voltammetric cell and voltammetric signal coming from Cr(VI) adsorbed on surface electrode as Cr(III)-DTPA and Cr(III) as Cr(III)-EDTA was recorded. Cr(VI) signal was calculated from the difference obtained from the current peaks. It should be noted that Cr(III) forms very stable complex with EDTA, that does not convert into Cr(III)-DTPA complex after adding of DTPA and thanks to that the high precision of Cr(VI) determination has been obtained. Calibration curves and limits of detection were calculated both for Cr(III) and Cr(VI). In the case of Cr(III) the detection limit is about 1000 times higher because Cr(III)-EDTA complex does not adsorb on the electrode on contrary to the Cr(III)-DTPA complex, which efficiently adsorbs on HMDE. The effects of potential interferents commonly present in natural water samples are investigated. The accuracy of the proposed procedure was tested by analyzing river water samples spiked with Cr(III) and Cr(VI).

PROTOCOL FOR EXTRACTION AND DETERMINATION OF Cr(VI) WITH A HIGH Cr(III)/Cr(VI) RATIO USING EDDS AS A LEACHING AGENT FOR Cr(VI) AND A MASKING AGENT FOR CR(III)

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To quantify toxic Cr(VI) concentrations in a solid matrix a preliminary extraction of Cr(VI) is necessary. Various extracting solutions to the extraction of Cr(VI) have been used to this time, for example good results were obtained for extraction procedures with the exploitation of complexing agents, EDTA or DTPA, because they provide the quantitative extraction of all Cr(VI) species, both soluble and insoluble forms [1,2]. The presence of a complexing agent in the extraction mixture additionally prevents the oxidation of Cr(III) to Cr(VI), the obtained extract is in the form making the further analysis easy and procedures of extraction are fast and easy to perform. It must be noted that the extraction procedures exploiting complexing agents are not selective for Cr(VI). Cr(III) generally present in the natural samples in large excess comparing to Cr(VI) is also transferred to solution, so before Cr(VI) voltammetric determination Cr(III) must be masked. The main aim of this research is elaborating the extraction procedure of Cr(VI) from solid samples making it possible to obtain extract containing total Cr(VI) in the electrochemically active form and Cr(III) in the electrochemical non active form. Such procedure would make it possible to directly determine Cr(VI) with unselective voltammetric analytical methods with no necessity of further Cr(III) masking. EDDS has proved to be a very good solution in proposed procedure of this kind. In the proposed procedure EDDS is exploited to complexation of metal ions that form an insoluble chromate like Pb(II) and total Cr(VI) as a soluble salt (sodium or potassium chromate) goes into the solution. Simultaneously EDDS plays the role of a masking agent forming strong nonactive electrochemically complexes with Cr(III) ions passing from solid samples to solution. In connection with it in the detection step a direct determination of Cr(VI) in extract by catalytic adsorptive stripping voltammetry in the presence with DTPA and nitrates without additional masking of Cr(III) can be applied. During the optimisation of the proposed protocol different variables were investigated for extraction of Cr(VI) including concentration of EDDS, pH and concentration of ammonia buffer, time and temperature of extraction. The influence of these variables on simultaneous masking Cr(III) by EDDS were also taken into account. The proposed procedure makes the determination of total Cr(VI) in solid samples rapid and possible for performing even in the presence of 1000 - 2000 fold excess of Cr(III) without its noticeable influence.

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MODERN TECHNIQUES OF FOOD QUALITY EVALUATION

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Food composition analysis is an important issue for the food industry and regulatory authorities as well as consumer. Analytical methods are essential for quality assurance and are indispensable in the assessment of consumer intake levels for both beneficial and harmful food components including bioelements and heavy metals. Food is the primary source of essential elements for humans, but chemical composition of different food products varies depending on cultivation and breeding conditions, weather conditions, use of fertilizers and the state of the plants and animals maturity. Certain levels of trace elements as well as toxic metals may pose a serious health hazard, therefore it is necessary to monitor food products quality. Analytical techniques such as flame atomic absorption spectrometry (FAAS), electrothermal atomization-atomic absorption spectrometry (ET-AAS), hydride generation- atomic absorption spectrometry (HG-AAS), cold vapor-atomic absorption spectrometry (CV-AAS), inductively coupled plasma-atomic emission spectrometry (ICP-AES), inductively coupled plasma-mass spectrometry (ICP-MS), ion selective electrode (ISE), anodic stripping voltammetry (ASV), neutron activation analysis (NAA) and colorimetry are commonly used in foods analysis [1]. The more and more popular in foods quality monitoring are chemometric techniques such as principal components analysis (PCA), factor analysis (FA), linear discrimination analysis (LDA), canonical discriminant analysis (CDA), end-member analysis (E-MA), cluster analysis (CA) and artificial neural network (ANN) [2,3]. They provide analysis when there are many independent variables or many dependent variables, all correlated with one another to varying degrees. Due to the application of these techniques it is possible to reduce the number of variables. Multivariate techniques have proved to be an effective statistical tool in analytical evaluation of food quality [3]. Based on the mineral composition data, it was possible to record the influence of the analysed elements on the distribution of particular object samples and classify food products according to their country of origin, type and genetical classification. What's more, these techniques may be useful in detecting fraud which is essential in preserving the brand name of the original product and in protecting the consumer from being deceived. This presentation will discuss current challenges and research directions in the food quality and safety evaluation in view of foods mineral composition. The applicability of chemometric methods to estimate food products quality in view of their mineral composition will be also assessed.

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MICRONUTIRENTS IN FOODS IN VIEW OF THEIR ROLE IN HUMAN ORGANISM

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Minerals are inorganic elements, which constitute natural components of Earth's crust and widely occur in nature. Food is a very good source of bioelements though its groups differ significantly in trace element composition. Diversified diet is the only way to supply organism with proper amount and proportion of trace elements. Dietary minerals are the chemical elements required by living organisms for maintenance of the normal cellular metabolism and tissue function. They constitute from 0.2 to 0.3% of the total intake of all nutrients in the diet [1]. Generally, they are divided into two subcategories: macroelements and microelements, which differ by their relative content in the body. Micronutrients or trace elements are needed in minute quantities for the proper growth, development, and physiology of an organism. The definition of "trace element" in the IUPAC Compendium of Chemical Terminology [2] is as follows: "Any element having an average concentration of less than about 100 parts per million atoms (ppma) or less than 100 μg per g". This group includes: B, Co, Cr, Cu, F, Fe, I, Li, Mo, Mn, Ni, Rb, Se, Si, V and Zn. These metals generally function as cations complexed with organic ligands or chelators, participating in the metabolic functions. Excess or lack of some chemical elements or their compounds in an organism often results in pathological states [1,3,4]. Especially pathogenic are heavy metals such as Pb, Cd and Hg - contaminants of the environment. Bioavailability of the contaminants to humans depends on the speciation of the contaminant in the food, dietary composition and the nutritional status of the individual [5]. The presentation will focus on the data concerning micronutrients' content in food products of plant and animal origin in view of Dietary Reference Intake recommendation. Role of each element in human organism will be also discussed.

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ONE YEAR RECORD OF HYDROGEN CONCENTRATION MEASUREMENTS IN THE AIR OF KRAKÓW BY NEW GC/PDHID METHOD

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The globally averaged hydrogen concentration in 2002 was about 0,5 ppm (parts per million). An average annual increase of 1,2 ± 0,8 ppb hydrogen per year was observed [1]. The application of hydrogen technology may cause higher growth of hydrogen concentration in the atmosphere because hydrogen is an easy-diffusing gas through different materials and it may escape to the atmosphere both from vehicles and from production installations. As a result the additional hydrogen may lead to reduction of hydroxyl radicals (OH), influencing methane concentration in the atmosphere, methane being the third greenhouse gas after water vapor and carbon dioxide. On the other hand, the use of fuel cells in vehicles will restrict the emission of nitrogen oxides, carbon monoxide or carbon dioxide, which will reduce the air pollution [2].

Photochemical reactions, which can follow in the troposphere after the introduction of a hydrogen economy, are not well enough known to unequivocally define the direction of changes. That is the reason for the emergence of continuous hydrogen concentration measurements in the air.

In the Department of Physicochemistry of Ecosystems localized in the Institute of Nuclear Physics Polish Academy of Science in Krakow the gas chromatographic (GC) method of hydrogen concentration measurements in the air (with the use of a Fisons gas chromatograph) was developed. An air sample is analysed in two chromatographic columns filled with a molecular sieve of type 5A working in the "back-flush" mode. For the hydrogen detection a Pulsed Discharge Helium Ionisation Detector (PDHID) was used.

The continuous measurements of hydrogen concentration in the air are made in a one-hour cycle, in the following sequence of injections: standard sample -air sample. During a one-year period we observed higher concentrations of hydrogen in spring and lower in autumn. The same phenomenon is observed at other stations in the world, because hydrogen shows a tendency of seasonal changes [3]. Sometimes episodes are observed. These episodes show a correlation with hydrocarbons such as: $CHCl_3$, F-11 and F-113. This could indicate the same sources of hydrogen and hydrocarbons. This could be connected with anthropological sources of these compounds in Kraków or the inflow of air masses with their higher concentrations from outside the Kraków region.

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STUDY OF BIOACCUMULATION OF AS(III) AND AS(V) SPECIES FROM WATER SOLUTIONS BY TWO STRAINS OF THE GENUS *ASPERGILLUS NIGER* USING HYDRIDE GENERATION ATOMIC ABSORPTION SPECTROMETRY

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In the present work, continuous hydride generation atomic absorption spectrometry was used for simple, rapid, sensitive and accurate determination of total inorganic arsenic and selective determination of As(III) in waste water and in solutions after arsenic bio-accumulation by two species of fungus Aspergillus niger. Strain An1 was isolated from the Eutric Fluvisols FMm (pH H_2O/KCl 7.7/7.4). Strain An2 was isolated from the stream sediment with natural amount of As 363 mg/kg (pH H_2O/KCl 5.27/4.8) from the Pezinok region (Slovakia). Simple solutions with different As(III); As(V) concentrations, mixed solution of As(III)+As(V), waste water and solutions after mycelium removal, were used to study arsenic bio-accumulation. The digests of dry mycelium samples were decomposed and used for total inorganic arsenic determination. The absent of As(III) represents methylated arsenic species formed during the growth of the fungus in arsenic solutions. The accuracy of the method for As(III) determination was evaluated by analysing spiked water samples. Recoveries 96-102% of added spikes were obtained. Limits of detection for total inorganic arsenic determination and As(III) determination were 0.22 μg l^{-1} and 0.28 μg l^{-1}, respectively [1].

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APPLICATION OF SOLID PHASE EXTRACTION FOR SEPARATION AND PRECONCENTRATION OF TOTAL INORGANIC ANTIMONY IN NATURAL WATERS

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The aim of the present work was to propose an optimal procedure for preconcentration of total inorganic antimony in natural waters prior its determination by electrothermal atomic absorption spectrometry (ETAAS). Nanometer-sized TiO_2 (which has a high surface area/body weight ratio, high adsorption capacity, and strong coordination of titanium) has been used as a solid-phase extractant in this study.

Three different modes for preconcentration of antimony were compared: (I) direct TiO_2-slurry sampling after adsorption of antimony onto TiO_2, (II) batch mode after elution of antimony from TiO_2 by a mixture of EDTA and HNO_3, and (III) column system using a minicolumn packed with TiO_2. Advantages and disadvantages of the three procedures were discussed and evaluated. Briefly, all procedures are effective for preconcentration of inorganic antimony in natural waters. Direct TiO_2-slurry sampling offers relatively easy preparation but the high attention has to be pay to the stability of TiO_2-slurry and a serious problem with the damage of a graphite tube leads to the worst reproducibility of all the three procedures. Batch mode is the most laborious (tending to the higher risk of contamination) but in spite of that it offers higher reproducibility than TiO_2-slurry sampling mode. Minicolumn system is flexible, since different initial volumes of a sample can be used (resulting in different enrichment factors and detection limits), reuse of the column is possible after regeneration and high reproducibility is achieved. From the three studied methods, the column system offers the most elegant way for preconcentration of total inorganic antimony.

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GC-MS METHOD TO ANALYZE 4-DESMETHYL AND 4, 4-DIMETHYLSTEROLS DURING LINSEED MATURATION

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Phytosterols (plant sterols) which comprise a major portion of the unsaponifiables in vegetable oils are divided into three main classes: 4-desmethylsterols, 4-monomethylsterols, and 4,4-dimethylsterols (triterpene alcohols) [1]. Methylsterols are generally present in much lower amounts in vegetable oils than 4-desmethylsterols. It is necessaryto enrich these sterols prior to quantification [2]. The main aims of this study were to carry out a qualitative and quantitative characterization of 4-desmethylsterols and 4,4-dimethylsterols during linseed development, obtained with TLC. At maturity the free sterols were mainly composed of 4-desmethylsterol (213-319 mg/100g oil), followed by 4,4-dimethylsterols (150-400/100g oil). The greatest change in these compound occurred in the early development Period .4,4-Dimethylsterols and 4-desmethylsterol followed the same accumulation pattern during seed maturation. ß-sitosterol represented the main component of the phytosterols, at maturity the three varieties H52, O116 and P129 had concentration of 150 mg, 153.35 and 116.35 mg (100g) of oil, respectively. The 4,4- dimethylsterols were mostly cycloartenol and 24-methylene cycloartenol with only small amount of lanosterol. The evolution of these three components during linseed maturation, expressed as a function of total lipid content, showed that the proportion of cycloartenol gradually decreased and reached a constant value of 60 $mg/100g^{-1}$ oil at the second week after the 45th flowering day. The qualitative and quantitative differences observed in 4-desmethylsterols, and 4,4-dimethylsterols (triterpene alcohols) suggested that these two minor fractions may be used as markers for the detection of oil adulteration and may be important as an indication of the potentially economical utility of these seeds as a new source of edible oils.

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CHEMICAL ELEMENTS IN MACOMA BALTHICA AND THE ASSOCIATED BOTTOM SEDIMENTS FROM THE SOUTHERN BALTIC

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Marine bivalve are often used as indicators of metal pollution. The information on metal concentration in the tissues of bivalves is of great importance since it reflects the magnitude of environmental contamination more accurately [1].

The aim of investigations was to evaluate the coassociations of Cd, Ni, Cu, Fe, Mn, Zn and Co in soft tissues of *Macoma balthica* and the adjacent sediments from the southern Baltic Sea. The biological samples were collected during ship cruises of M/S Hestia and R/V Baltica in July - August 2006. Specimens of bivalve were pooled with respect to their size (age) and next homogenized and dried to a constant weight. Three replicate subsamples were prepared from each sample and were digested in Microwave Digestion System (MLS 1200 MEGA) using analytically ultrapure HNO_3. Sediment samples were sieved to obtain <63 μm granulometric fraction and then 1 g of dried sample was extracted with 10 cm^3 1 M HCl. The heavy metals were determined by flame atomic absorption spectroscopy (FAAS). The accuracy and precision of the method used were checked by the analysis of reference material (NCS ZC78005 Mussel) and the obtained results were in good agreement with the certified values. ANOVA Kruskal-Wallis test was used to investigate influence of sampling site and size classes on variations of metal contents ($p<0.01$, $p<0.05$). For instance, specimens from the open Baltic waters were characterized by higher levels of Mn than those from the Gulf of Gdańsk. It is also found that *M. balthica* has a greater affinity to Zn, Cd and Cu and lower to Fe and Ni. Moreover, e.g. concentration of the metals dependent on age of the organism; e.g. the concentration of Zn was higher in older specimens. It seems that *M. balthica* has ability to accumulate some elements (Cu, Zn) in its soft tissue relative to the adjacent sediments [2].

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TRACE METALS CONTENTS IN SURFICIAL SEDIMENT FROM THE SOUTHERN BALTIC SEA

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The distribution of selected elements in bottom sediments has received increasing attention in recent years [1]. Sediment contamination is a major environmental issue because of its potential toxic effects on biological resources and often, indirectly, on human health. People can be exposed to dangerous levels of toxic contaminants when they eat animals occupying high levels of the food chain. There is also the potential danger for exposure to toxic contaminants through direct contact with contaminated sediments [2].

The aim of this study was to recognize the distribution and coassociations of chosen elements in the adjacent sediments from the southern Baltic Sea. The samples were collected at 19 stations from the Gulf of Gdańsk, Pomeranian Bay and open Baltic waters during cruise of the M/S Hestia and R/V Baltica in July - August 2006. Sediment samples were sieved ($<63\ \mu m$) and then 1 g of dried sample was extracted with 10 cm^3 1 M HCl. The levels of Fe, Co, Mn, Cd, Ni, Zn and Cu were determined by flame atomic absorption spectroscopy (FAAS). R-Spearman rank order correlation coefficients were calculated using STATISTICA for Windows (version 7.1, Copyright© Statsoft, Inc. 2005) to see if there is any relationship between concentrations of chemical elements in the bottom sediments. The concentration data were also processed statistically using ANOVA Kruskal-Wallis. The average abundance of the elements studied in sediments decreased in the following sequence: Fe>Mn>Zn>Ni>Cu>Co>Cd. There are many significant coassociations ($p<0.01$, $p<0.05$) between concentrations of chemical elements in bottom sediments. Positive correlations between Co-Cu, Ni-Fe, Cu-Ni, Cu-Zn, Fe-Zn, Ni-Co, Ni-Zn ($p<0.01$) and Co-Zn ($p<0.05$) were observed. ANOVA Kruskal-Wallis test was used to investigate influence of sampling site on variations in metal concentrations in sediments ($p<0.05$). The data obtained show that the surficial sediments from the Gulf of Gdańsk and open Baltic waters contained higher levels of labile Fe as compared to those from the Pomeranian Bay.

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OPTIMIZATION OF A NOVEL SBSE-TD-HRGC-HRMS PROCEDURE FOR DETERMINATION OF VOLATILE HALOORGANIC COMPOUNDS IN WATER AND HUMAN URINE SAMPLES

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Volatile haloorganic compounds (VOX) such as bromodichloromethane ($CHCl_2Br$), dibromochloromethane ($CHClBr_2$), tribromomethane (bromoform, $CHBr_3$) and tetrachloroethene (tetrachloroetylene, perchloroetylene, C_2Cl_4) are belonging to important pollutants of indoor air and workplace environment. People are exposed to these compounds in their homes and workplaces and during varying activities of everyday life. Haloorganic compounds can enter human body via many different routes, for example, by inhalation, dermal contact, or inadvertent ingestion from hand to mouth contact. After intake, chemicals enter the bloodstream and in the body, they may accumulate or are excreted, usually with urine (in non-metabolised form).

Liquid samples usually require special treatment prior to the final analysis, e.g. by gas chromatography. Special attention has recently been paid to the use of the so-called solvent-free analyte isolation and/or enrichment techniques, which can be attributed to the widespread area of green analytical chemistry.

Stir bar sorptive extraction (SBSE) can constitute the technique of choice for this task. This technique has been already applied at the step of preparation of different types of liquid samples prior the final determination of a wide variety of analytes.

The aim of this study was to evaluate the SBSE technique followed by thermal desorption and HRGC-HRMS analysis, for the determination of bromodichloromethane, dibromochloromethane, bromoform and tetrachloroethene in water and human urine samples. Stirring rate and time of extraction were optimized.

In total, 91 water samples and 5 human urine samples were analyzed. The isotope dilution method was used for calculation the basic metrological parameters such as linearity, limit of detection (LOD) and limit of quantification (LOQ) of 42 water samples and all urine samples. Isotope dilution technique caused some costs for standards, but supports precision of the method. The SBSE-HRGC-HRMS procedure is sensitive and shows a good linearity between 0.5 and 10 mg/l for all compounds tested. This procedure is characterized by very low limits of detection and quantification, lower than 0.0017 μg/l for all four volatile compounds. The examined analytical procedure is easy to handle, solvent-free, fast and was successfully applied for the simultaneous determination of high volatile trace compounds in water and human urine samples.

DETERMINATION OF CHLORITES IN DRINKING WATER AS BY-PRODUCTS OF WATER TREATMENT

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The World Health Organization recommends using chlorine dioxide for water treatment purposes [1]. This agent is effective owing to its strong oxidizing properties, as well as good antiviral and antibacterial activity. Unfortunately, the products, chlorate and chlorite ions, of this water treatment process ($2ClO_2 + H_2O = HClO_2 + HClO_3$) are damaging to health. In accordance with the WHO report the monitoring of chlorite concentration in water is especially important task, because of chlorite ions are recognized as much more harmful than chlorate ions.

The flow-injection indirect determination of chlorite in drinking water has been developed. The proposed method is based on oxidation of Fe^{2+} ions to Fe^{3+} ions using chlorites ions in an acid environment, according to equation
$ClO_2^- + 4Fe^{2+} + 4H^+ = Cl^- + 4Fe^{3+} + 2H_2O$.

A flow system coupled with spectrophotometric detection was used. An analytical signal was measured for coloured complex formed between Fe^{2+} and o-phenathroline ($\lambda = 512$ nm).

On the basis of validation studies carried out the linearity, limit of detection (LOD) and limit of quantification (LOQ) were found to be 2.0, 0.010 and 0.022 mg L-1, respectively. The obtained results were of satisfactory accuracy and good precision (RSD 0.40%, n = 10), while the time for a single measurement was approximately 35 seconds.

The influence of different anions (e.g. NO_3^-, SO_4^-, PO_4^-) and cations (e.g. Cu^{2+}, Mg^{2+}, Ca^{2+}, Al^{3+}, NH_4^+, Zn^{2+}) within the ranges of the concentrations at which they occurred in water classified into four different quality standards [2] on the analytical signal were evaluated. The positive values of the interference effect (E_f), approximately 5%, for cations e.g. Mg^{2+}, Ca^{2+} were observed. A higher effect (E_f 14%) for NO_2^- mainly for quality class IV waters was examined. This phenomenon can be of importance during spring melt, when rivers receive waters from the fields which are rich in the components washed out from the soil.

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EVALUATION OF SOLID PHASE EXTRACTION AND HOLLOW FIBER LIQUID EXTRACTION FOR THE PRECONCENTRATION OF PHARMACEUTICALS FROM WATER SAMPLES

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In recent times the use of pharmaceuticals still increase and presents an environmental problem, therefore the control of pharmaceuticals has become a routine practise in many laboratories. A primary and the biggest challenge in monitoring pharmaceuticals is the sample treatment, because usual drug concentrations in sample water range from ng/l to μg/l levels.

This study is devoted to the development of a method for the determination of pharmaceuticals in water samples (e.g. surface water and wastewater). Therefore that, every method needs preliminary sample treatment for the preconcentration and clean-up of the analytes previously to the detection, two different techniques: solid phase extraction (SPE) and hollow fibre extraction, we were compared for this purpose.

Solid-phase extraction (SPE) is one of the most applied methods because of its simplicity and large number of solid phases available. For this reason different solid phases have been evaluated: Oasis HBL, Strata X, Isolute ENV$^+$, and Bekerbond H_20-philic, in order to find the best of type of SPE cartridge for the extraction of these pharmaceuticals. Also the objective of our studies was to test the suitability of hollow fibre liquid membrane extraction device and to optimize this technique, in order to obtain the highest extraction efficiency. We investigated various process parameters such enrichment time and solvent membrane affect extraction.

All water samples were analyzed by high performance liquid chromatography (HPLC). Chromatographic analysis was performed on a HPLC instrument with diode array detector. Separation was carried out through reverse phase mechanism using a Luna column packed with Si-C18 and protected guard column. The HPLC method was optimized to reduce time needed for separation and re-equilibration, therefore the influence of the mobile phase composition and of the flow rate, was evaluated.

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DETERMINATION OF SULFIDE IN MINING LEACHATES

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Sulfide is often used for the precipitation of copper and other base metals in both metal winning and environmental control. For an effective and economic operation of the SART Process (sulfidization, acidification, recycling, thickening), control of the sulfide concentration is essential. Sulfide ions are used, for example, to precipitate cupric ions from cyanide leachates under weakly acidic conditions ($pH \approx 5$):

$$2\,Cu(CN)_3^{2-} + H_2S + 4\,H^+ \rightarrow Cu_2S + 6\,HCN$$

Normally sulfide is determined by acidifying the sample and collecting the H_2S gas through a membrane into a buffer. The collected gas is then determined spectrophotometrically at 230 nm or - after undergoing the methylene blue reaction - at 600 nm. The method is very time-consuming and prone to interferences by other species present. Another problem is the fact that at a pH value below 10, sulfide forms H_2S gas, which is prone to be lost by evaporation. A direct measurement at the SART process site is therefore preferable to offline measurements in the laboratory. As a further advantage, the online measurement provides faster and more accurate results.

This paper presents the determination of sulfide anions using a gas diffusion cell coupled to an ion chromatograph and subsequent spectrophotometric detection.

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ION-PAIR MEMBRANE EXTRACTION OF QUATERNARY AMINE SURFACTANT

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Consisting of a hydrophobic and a hydrophilic part, surfactants accumulate at surfaces, reduce surface tension and can form micelles. These properties have lead to their widespread use in both household and industrial applications, such as various detergents, personal-care products, textile processing, flotation, paints and more. After use, surfactants may reach sewage treatment plants (STP), where they are generally well degraded [1], but some surfactants, like alkylphenol carboxylates, have low biodegradability and cationic surfactants are toxic to microorganisms [2]. This poses the need for development of analytical methods to determine surfactants in waste water. SPE may be used for clean-up and preconcentration of surfactants. However, membrane extraction may decrease solvent consumption even more and increase enrichment factors. Such extraction has previously been applied to both cationic [2] and anionic surfactants [3].

In this work, a 2-phase hollow fibre (HF) liquid phase micro extraction (LPME) method was developed for the cationic surfactant dicoco dimethyl ammonium chloride. This compound is a quaternary amine and is positively charged in the entire pH-range, unless ion-paired with carrier (e.g. carboxylic acid). In a buffered system (50 mM carbonate at pH 10), the carrier and the analyte formed a hydrophobic ion-pair complex that diffused into the organic liquid in the pores of the HF membrane, stabilised on a metal support. After extraction, analyte was desorbed from the pores of the fibre into 100 ml methanol, which was analysed directly by LC-MS.

The method was optimised with regard to membrane organic liquid, fibre length, desorption mode, choice and concentration of anionic carrier, sample volume, stirring speed and extraction time. The maximum enrichment factor achieved was 737 times in buffer. For a lower and more practical sample volume of 250 ml, the enrichment was around 400 times. Due to matrix effects, the enrichment factors achieved when industrial process water was used were considerably lower (around 1/3) but linearity was still good. A similar extraction method has been developed for linear alkylbenzene sulfonate (LAS) and may also be developed for other surfactants.

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ANALYSIS OF VOLATILE SUBSTANCES EVOLVED FROM HERBICIDAL FORMULATIONS

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Herbicidal formulations are widely used in present agricultural practices, causing the contaminations of the environment and foodstuffs. Volatilisation may be an important factor for the dissipation of herbicides in the environment. Some references on herbicides volatilization from soil and plants can be found in literature [1]. For some compounds, such as trifluraline, 90% of the application dose may be lost within a few days through volatilization [2,3]. Unfortunately, except biological active substances, herbicidal formulations contained often other more volatile substances as solvents. The aim of this work was to analyse the volatile substances evolved from herbicidal formulations. Three different formulations of trifluraline were the objects of these studies. The composition and concentrations of volatile substances evolved from water emulsions of Treflan 480 EC, Triflurex 480 EC and Triflurotox 480 EC were determined using gas chromatography with FID and MSD detectors. The studies were performed by using a static headspace technique at different temperatures. Experimental data indicated that from Triflurex 480 EC and Triflurotox 480 EC p-xylene was emitted in the biggest amount. The main volatiles evolved from Treflan 480 EC were 1,2,3-trimethylbenzene and 1,3,4-trimethylbenzene.

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VOLATILE ORGANIC COMPOUNDS EMITTED INTO THE ATMOSPHERE FROM LEAF LITTER AND LITTER-DESTROYING FUNGI

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Litter decomposition has long been recognized as an important process in forest ecosystems, both for nutrient recycling and humus formation. In comparison, there are only a small number of studies to describe VOC emission from leaves litter into the atmosphere. For land ecosystems, the litter biomass is estimated to be $(5\text{-}80)\times10^{15}$ g. Even for this reason alone it should be regarded as a potentially important VOC source in the atmosphere.

In this communication we report the results of qualitative and quantitative GC-MS investigations of VOC emitted into the gas phase from leaves litter of ten species of deciduous and coniferous trees. The list of identified substances contains more than 100 organic compounds of different classes: saturated and unsaturated aliphatic hydrocarbons, terpenes, aldehydes and ketones, alcohols and esters, sulfur- and chlorine-containing compounds. It was established that the qualitative composition of VOC emitted by leaves litter is species specific. Highly volatile oxygenated VOC (acetaldehyde, acetone, methanol, ethanol) are probably secondary products of the activity of litter-destroying fungi. It was established, that a leaves litter contains great amounts of low volatile and non-volatile (but easy biodegradable) compounds: unsaturated aliphatic acids, polyols and carbohydrates. Hence, it is reasonable to include into the methodology of studying litter as a source of atmospheric VOC the determination of a store of these substances that can be precursors of OVOC formed during microbiological decomposition of "dead" plant material.

A combination of solid-phase microextraction (SPME) and GC-MS was used for determining of VOC emission rates from leaves litter and litter-destroying fungi. According to our estimations, emission rate of terpene hydrocarbons from Scots pine, common spruce, and European larch litter is on average 1.2 ± 0.3 μg/(g × h) at 22 °C.

The previous results of a long-term field experiment of studying chemical changes in decomposition of Scots pine, common spruce are also reported.

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SPME-GC/MS IDENTIFICATION OF VOLATILE ORGANIC COMPOUNDS EMITTED FROM MUNICIPAL SEWAGE SLUDGE

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The identification of organic compounds, emitted to air by sewage sludge formed in the process of treatment of municipal wastewater in the sewage treatment plant in Białystok was carried. Samples taken directly after finishing of the technological process of sludge processing as well as sludge stored on the land of the sewage treatment plant were tested. Compounds were being extracted with the solid phase microextraction technique from the headspace above the sample and determined with gas chromatography technique coupled with mass spectrometry. Over 170 compounds of different structure were identified. The biggest part of gaseous emission from the sludge constituted linear, branched and cyclic aliphatic hydrocarbons and aromatic hydrocarbons i.e. benzene and naphthalene and their derivatives. Examined sewage sludge emits to air also numerous alcohols, esters, carbonyl compounds as well as compounds of sulphur, nitrogen and chlorine. Particularly large content of sulphur compounds, part of which is the product of metabolism of microorganisms forming the active sludge, has been recorded in the air above sludge stored on the heap. The considerable part of gaseous emission from the sewage sludge make natural compounds, easily undergoing biodegradation and originating from plant tissues and being products of metabolism of different organisms. In the sludge identified was also a considerable group of xenobiotics - alkylbenzenes, chlorine compounds, remains of personal care products, plasticisers, butylated hydroxytoluene etc., which hardly undergo biodegradation, thus can accumulate in sludge and in natural environment.

DETERMINATION OF SOME TOXIC ELEMENTS BY HELIUM AND ARGON+HELIUM MICROWAVE INDUCED PLASMA OPTICAL EMISSION SPECTROMETRY

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Both helium and Ar-He mixed gas microwave induced plasmas (MIP) have been investigated for use as an excitation source for optical emission spectrometry (OES) with solution nebulization. A prototype instrument, based on the TEM resonator, with an annular-shaped helium MIP coupled to a sequential optical spectrometer was used. The plasma was operated at 350 W with 2.2 l min^{-1} plasma gas, 0.5 l min-1 nebulizer gas and 0.1 ml min^{-1} sample flow rate [1]. A filament-type argon+helium MIP at atmospheric pressure was generated by using TE101 integrated microwave resonator. Aqueous solutions are introduced into a robust atmospheric pressure helium MIP for the detection of metals and metaloids by ultrasonic nebulization with a NOVA-1 nebulizer without desolvation. To demonstrate the plasma robustness both the tolerance for water loading and the excitation capability for some elements were investigated. To minimize problems caused by sample introduction into a helium MIP a hydride generation technique was applied.

This study has resulted in a significant improvement in the analytical performance of the He MIP as an excitation source for the optical spectrometric determination of metals and metaloids in aqueous solution. Relatively low detection limits (ng/ml) for certain elements were obtained by using a prototype MIPOES instrument. The annular He-MIP is capable of ionizing elements with ionization potential in the range 6-10 eV efficiently. Determination of selenium is possible down to the low ppb level. Analytical characteristics include detection limits in the range from 1 to 70 ng ml^{-1}, linearity of three orders of magnitude and signal stability of between 0.8 and 2%. As and Se by hydride generation showed linearity of more than 3 orders of magnitude.

The addition of He to Ar produces a plasma capable of ionizing metals with ionisation potential in the range of 6-10 eV more efficiently than the pure Ar plasma. The best excitation conditions for metallic elements were obtained with the Ar+20% He plasma. The detection limits for ionic lines of some metals for the Ar-He mixed gas MIP-OES are 2-7 times superior to the results obtained in Ar MIPOES [2]. The analysis of difficult-to-atomize elements and hard to ionize elements (As,Se) in the He MIPOES requires the application of a forward power lower than 400W.

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REVALIDATION OF A NOVEL PROCEDURE FOR DETERMINATION OF VOLATILE CHLOROORGANIC COMPOUNDS IN WATER AND HUMAN URINE SAMPLES BASED ON APPLICATION OF PERVAPORATION COUPLED WITH DAI-GC-ECD METHOD

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The determination of volatile organic compounds in liquid biological samples, especially the most common organohalogens considered to be potentially carcinogenic for humans, constitute a challenge for analytical chemists by the complex and often variable matrix composition of the samples. Typical biological samples usually require special pre-treatment prior to analysis by chromatography or related techniques. Special attention has recently been paid to the use of the so-called solvent-free analyte isolation and/or enrichment techniques, which can be attributed to the widespread area of green analytical chemistry.

One of the most useful techniques in separation of the trace substances from samples characterized by the complex and often variable matrix composition is pervaporation. Pervaporation is a technique in which the liquid sample is in contact with one side of a membrane whereas the permeate, in a vapour state, is continuously removed from the other side into the vacuum. Pervaporation appears to be promising especially when the preferentially permeable component is present in the sample at low concentration. Therefore, the selective isolation and pre-concentration of low contents of volatile organohalogen compounds (VOX's) from aqueous solutions through polydimethylsiloxane (PDMS) membranes and analysis by direct permeate injection into a thick film, non-polar gas chromatographic column coupled with electron capture detector, presents a large opportunity for the analytical application of pervaporation.

The aim of this study was to revalidate a PV-DAI-GC-ECD procedure of determination of five volatile organohalogen compounds in water and human urine. The new version of procedure (miniaturization of the feed vessel) has been validated and the full uncertainty budget has been calculated.

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THE USE OF DIFFERENT EXTRACTION TECHNIQUES FOR DETERMINATION OF POLAR PESTICIDES IN A SOIL/PLANT SYSTEM

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The study of a fate of environmental pollutants requires efficient methods for quantitative extraction of analysed compounds from environmental matrices and from other commodities come into contact. Different extraction methods had been used for extraction of polar pesticides from plant and soil samples analysed for assessing the environmental fate of pesticides [1]. The result of the use of different methods is big differences in analysed content of investigated pesticides in environmental samples. The same problem is often found in the case of extraction of pesticides from plant samples in contact with soil samples and/or other solid environmental matrices. Low extraction recovery is often connected with poor reproducibility of analysis. Application of different extraction methods often used as a part of preparation of food samples for pesticide analysis was tested for analysis of soil and plant samples in this study. QuEChERS developed especially for pesticide extraction [2] from food samples is the best choice for extraction of polar pesticides from individual parts of plant including root systems even for samples of soil used for plants growing. As a simple and highly reproducible method QuEChERS can be used in the study of transport of currently used pesticides in the environment. Changes of the content of pesticides Clomazone, Fluazinam and Metribuzine in the individual parts of plant/soil systems are described during growing of selected plant.

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ION-PAIR EXTRACTION OF ANIONIC SURFACTANTS FROM ENVIRONMENTAL WATER SAMPLES USING HOLLOW FIBER SUPPORTED LIQUID MEMBRANE FOR THEIR ANALYSIS USING HPLC

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Excluding soap linear alkylbenzene sulfonates (LAS) is one of the largest single surfactant used in detergents. LAS is used in most powder and liquid laundry detergents, dishwashing liquids and all-purpose cleaners. In 2001 the global production volume of LAS was more than 3^*10^6 t. High use of LAS caused that large part of the literature is focused on the environmental problems arising from LAS. In this work hollow fiber supported liquid membrane (HF-SLM) with ion-pair was used to extract LAS from different environmental sample. Extraction conditions such as time, pH, ion strength, speed, concentration of ion-pair reagent were investigated. Extracts were analysed by HPLC- FLD with C18 columns witch enable separations of homologues and isomers. The proposed methods were applied to estimate the concentration of LAS in the environment. Three different water samples: water before sewage treatment plant (STP), STP effluent and water after STP were extracted with the established method. Estimation of concentration of LAS in environmental samples was carried out by using Standard Addition Methodology.

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APPLICATION OF CHEMOMETRICS FOR DESCRIPTION OF URANIUM ^{238}U INFLOW FROM THE VISTULA RIVER CATCHMENT AREA

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On the basis of determination of ^{238}U in samples from Vistula river and their tributaries catchments area we are used following chemometric techniques for statistical description of uranium inflow from this area:

- Cluster analysis (CA) - is an exploratory data analysis tool for solving classification problems. Its objective is to sort cases into groups, or clusters, so that the degree of association is strong between members of the same cluster and weak between members of different cluster. Each cluster thus describes, in terms of the data collected the class to which its members belong; and this description may be abstracted through use from the particular to general class or types.
- Correlation and regression analysis - is description of dependence between different chemical and statistical parameters.
- Basic statistical and parametric or non parametric tests (Kołmogorow-Smirnow, Kruskal-Wallis's and U Mann-Whitney's tests).

The received description permits to quality of derivation sources of uranium in Vistula river and also their tributaries.

This study was financial supported by Ministry of Science and Higher Education under grants: DS-8210-4-0086-8 and BW/8000-5-0137-8.

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APPLICATION OF CHEMOMETRICS FOR DESCRIPTION OF PLUTONIUM $^{239+240}$PU INFLOW FROM THE VISTULA RIVER CATCHMENT AREA

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Many statistical multivariate techniques are used for the control of environmental pollution. The traditional chemometric approaches like cluster analysis (CA), principal component analysis (PCA), correlation and regression analysis have been tried in gain specific information on the monitoring data structure from the region of interest. On the basis of plutonium determination in Vistula river water samples and their tributaries we are applied these chemometric technique to interpretation of inflow of anthropogenic and strong radiotoxic $^{239+240}$Pu radionuclides from this area:

- Cluster analysis (CA) - is an exploratory data analysis tool for solving classification problems. Its objective is to sort cases into groups, or clusters, so that the degree of association is strong between members of the same cluster and weak between members of different cluster. Each cluster thus describes, in terms of the data collected the class to which its members belong; and this description may be abstracted through use from the particular to general class or types.
- Correlation and regression analysis - is description of dependence between different chemical and statistical parameters.
- Basic statistical and parametric or non parametric tests (Kołmogorow-Smirnow, Kruskal-Wallis's and U Mann-Whitney's tests).

The received description permits to quality of derivation sources of plutonium in Vistula river and also their tributaries.

This study was financial supported by Ministry of Science and Higher Education under grants: DS-8210-4-0086-8 and BW/8000-5-0137-8.

RESEARCH ON COMPOUNDS OF INDUSTRIAL EFFLUENTS AFTER OXIDATION OF ASPHALT RESPONSIBLE FOR ODORS AND BIO-TOXICITY

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Odor is a volatilized compounds, generally at a very low concentration, which humans perceive by the sense of olfaction. However, there is an almost endless variety of toxic odors affecting our environment, most of them are a by-product of our modern industrial society, like chemical, petroleum, papermaking, tannery, food industrial, battery farms and sewage farms. In the last time problem of odors elimination become more important causing s.c. "Odor Directive" of EU. Many of compounds of such sewastes are also toxic for biological part of sewage treatment plant (appear bio-toxicity).

The research on odors are advanced but there exist many questions yet. Nobody formulated unequivocal definition of odor enabled to instrumental verification. Not exists objective instrumental analytical procedures to determination of bad-smell. The analytical difficulties in odor measurements are related to the high number of volatile components (belonging to several chemical classes) when the concentration of many individual compounds is lower than the detection limit of the technique used for the measurement. The bio-toxicity of many compounds of industrial sewages is today also unknown.

This work presents objective analytical instrumental techniques and methods for determination of individual compounds and groups of compounds to influence on intensity of odors and on bio-toxicity of industrial sewages. It need employ very sensitive and very selective detection methods like gas chromatography with mass spectrometry (GC-MS) or liquid chromatography - mass spectrometry (LC-MS or LC-MS-MS). The alternative separation and detection techniques and procedures is group type separation of the industrial sewages or absorbents to liquid of odorous compounds using high performance liquid chromatography.

The research have been supported the thesis of possibility of group - type separation and determination of odorous individual compounds and groups of compounds after pre-concentration in liquid using reverse phase high performance liquid chromatography (RP-HPLC) or Hydrophilic Interaction Chromatographic (HILIC) technique and isocratic or gradient elution with spectrophotometric (UV-DAD) and electrochemical (ELD - in voltamperometric mode) and fluorimetric (FLD) or LC-MS or refractometric detection (RID - in isocratic conditions only). In research were used such adsorbents, like CN, DIOL, NH_2, Phenyl, C8, C18 and such eluent components, like methanol, acetonitryle, dioxane, water with acidic or basic additives to mobile phase.

The presented procedures can be successful used for the instrumental monitoring of odors after oxidation of asphalt and during asphalt expedition or asphalt using for road building, as well in the petroleum refinery or by bitumen's end-user's and also by environmental policy.

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APPLICATION OF ION CHROMATOGRAPHY FOR THE ANALYSIS OF ATMOSPHERIC PRECIPITATIONS FROM POLAR AREAS

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Ion chromatography is an innovative analytical technique that has significantly improved analysis of anions and cations. The most important advantages of ion chromatography are: broad range of applications, well-developed hardware, many detection options, reliability (good accuracy and precision), high selectivity, high speed, high separation efficiency, good tolerance to sample matrices and low cost of consumables. With this included ion chromatography is widely accepted as standard, reference methodology in water and waste water analysis.

Environmental analysis is one of the most important fields of application in ion chromatography and can be divided into water, soil and air analysis. Ion chromatography has become an essential tool for the analytical chemist, especially in the area of trace analysis. In many cases, this method has been used to replace conventional wet chemical methods, which are labor-intensive, time-consuming, and occasionally susceptible to interferences.

Sample preparation has been a growing and developing area in ion chromatography over the past years. The variety of sample preparation methods for trace analysis is great and it is not always easy to find a suitable method for the specific problem to be solved. For one and the same problem there are often several versions so that the user has to make a decision based on different criteria.

In the work the possibilities of application of ion chromatography for the analysis of atmospheric precipitations from polar areas are described. The specific of analysis of inorganic anions (F^-, Cl^-, NO_2^-, NO_3^-, PO_4^{3-}, SO_4^{2-}) and cations (Li^+, Na^+, NH_4^+, K^+, Ca^{2+}, Mg^{2+}) as well as organic ions (carboxylic acids) in samples such as snow, rain, firn and ice from Arctic and Antarctica are taken into consideration. Moreover, the sampling, sample transport, storage and preparation has been described.

The development of ion chromatography includes the development of new stationary phases offering different separation selectivities and detection modes to those available currently, the increased usage of ion chromatography in hyphenated techniques and first of all further advances in research of trace and ultra trace analysis of inorganic and organic ions.

The work has been done within the confines of international grant POLARCAT "*International Polar Year - Polar study using aircraft, remote sensing, surface measurements and models, of climate, chemistry, aerosols and transport*" (Polish sub-grant: "*The influence of gaseous and dust pollutions in troposphere on the chemical composition of atmospheric precipitation and climate changes in Arctic and Antarctic*"). Grant of Ministry of Science and Higher Education, no 1173/IPY/2007/01 from June 12th, 2007.

VOLTAMMETRIC DETERMINATION OF A DIAGNOSTIC METABOLITE: SUCCINYLACETONE

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Succinylacetone (SA, 4,6 diketoheptanoic acid) is primary diagnostic metabolite for inherited disorder hepatorenal tyrosinemia type I (HT1) [1]. Hereditary tyrosinemia type I is an autosomal recessive disorder caused by deficiency in fumarylacetoacetate hydrolase (FAH) in the tyrosine degradation. The deficiency of FAH leads to an accumulation of the metabolites fumarylacetoacetate and maleylacetoacetate, which together form succinylacetone. Since succinylacetone is not found in normal body fluids, the presence of succinylacetone in urine, blood or amniotic fluid is pathognomonic of tyrosinemia [2].

This work describes the voltammetric determination of SA which examined by means of adsorptive stripping square wave and cyclic voltammetry. All voltammetric measurements were carried out with a Metrohm electrochemical analyzer (757 VA Computrace). A hanging mercury drop electrode (HMDE) was used as working electrode, a platinum wire served as a counter electrode and the reference electrode was an Ag/AgCl (3M KCl). Aliquots from succinylacetone standard solution were added to the voltammetric cell for electrochemical analysis. Potassium chloride (0.1mol L^{-1}) was selected as supporting electrolyte. Pure nitrogen was bubbled through the sample solutions for five minutes before voltammetric measurements. The adsorptive stripping square wave voltammetric operating conditions were as follows: equilibration period: 5s, voltage step: 0.01V, pulse amplitude: 0,05V, frequency: 50Hz. Succinylacetone was deposited on HMDE applying -1.3V deposition potential for 10s. Under these operating conditions, succinylacetone gave a reduction peak at -1.46V versus Ag/AgCl reference electrode. Linearity range was between $2.16\text{x}10^{-7}$ - $2.15\text{x}10^{-6}$mol L^{-1}. Limit of detection (LOD) and limit of quantification (LOQ) were calculated as $9.92\text{x}10^{-8}$ mol L^{-1} and $3.30\text{x}10^{-7}$ mol L^{-1} respectively. The electrochemical reduction of SA was calculated to proceed with one electron transfer.

The developed method seems promising due to its simplicity and reliability. The voltammetric method is much cheaper than the methods used for succinylacetone analysis such as GC/MS, CE, HPLC.

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BIOMAGNIFICATION OF MERCURY IN THE VISTULA LAGOON ECOSYSTEM

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In a natural environment, mercury comes from both anthropogenic activities and natural sources. The anthropogenic sources of Hg include industrial emission from plants that use or manufacture mercurial compounds. Most of Hg pollution resides in the aquatic environment, rapidly incorporates into a food chain and bioaccumulates in organisms. As elements are transported along the successive levels of the food chain, their concentration rises at each higher trophic level. This effect is known as biomagnification [1, 2]. The birds and the fish were collected at the Vistula Lagoon. Carefully separated tissues of the organisms were immediately deeply frozen, lyophilized and homogenized. 55 specimens of cormorants (Phalacrocorax carbo) and 7 fish species (15 individuals of each species), constituting of cormorant's diet, i.e. herring (*Clupea harengus*), tench (*Tinca tinca*), roach (*Rutilus rutilus*), european smelt (*Osmerus eperlanus*), rufie (*Gymnocephalus cernuus*), crucian carp (*Carassius carassiu*s), prussian carp (*Carassius gibelio*) were collected. The samples were processed using the Mercury/MA-2000 system (NIC - Japan). Mercury was extracted from the samples by thermal decomposition at 800°C. Its total content was determined by cold-vapor AAS technique at 253.65 nm. Three independent determinations were run for each sample. The biomagnification factor (BMF) was computed as the ratio of the concentration of an element in a predator (consumer) to its concentration in its prey (food):

BMF = C(predator)/C(prey) [2]

The values of BMF for tropic relation such as cormorant's and their preys are as follows: herring - 62.4, rufie - 37.48, european smelt - 17.44, tench - 13.17, crucian carp- 10.51, prussian carp - 5.51 and roach - 5.18.

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VALIDATION OF METHOD FOR DETERMINATION OF TOTAL MERCURY CONTENT IN GREAT CORMORANT'S TISSUES AND CHOSEN FISH SPECIES USING COLD-VAPOR AAS TECHNIQUE

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Mercury is a dangerous pollution, particularly its vapors and some of its water-soluble salts. One of Hg properties is bioaccumulation in internal organs of living things. One of the most frequently used methods of determination of Hg concentration in biological samples is cold-vapor AAS technique. The method in widely used in biomonitoring of environmental pollution. As the result, the method gives the total amount of mercury in a subjected sample. The soft tissues of 55 individuals of Great Cormorant (*Phalacrocorax carbo*) and chosen fish species, constituting cormorant's diet, were analyzed. All the samples were originated from the Vistula Lagoon area. Mercury was determined in Cormorant's internal organs such as liver, kidney, muscles, esophagus, stomach, intestines, trachea, lungs and heart. The fish species were as follows: herring (*Clupea harengus*), tench (*Tinca tinca*), roach (*Rutilus rutilus*), european smelt (*Osmerus eperlanus*), rufie (*Gymnocephalus cernuus*), crucian carp (*Carassius carassius*), prussian carp (*Carassius gibelio*). The samples were deeply frozen, freeze-dried (lyophilized) and homogenized, then total content of mercury was determined using the mercury analyzer MA-2000 (NIC-Japan). Weights of the samples were between 10 - 50 mg. Validation of any method is an important process in order to assess the accuracy and precision of the analytical measurements [1, 2]. During validation, the following parameters were assessed: linearity, repeatability, limit of detection (LOD), limit of quantification (LOQ) [3], trueness and uncertainty. In order to estimate trueness of the measurement the certified reference materials were used: DORM-2 (National Research Council, Canada), BCR-463 and ERM-CE278 (IRMM, Belgium). The calculated validation parameters did confirm the usability of the method employed for the total Hg determination in samples. The method is linear in the range 0.3 - 100 ng of Hg in a subjected sample. For range 100-1000 ng of Hg, the polynomial calibration curve may be used (that comes directly from the Lambert-Beer law). The calculated LOD value of Hg makes possible detection of trace amounts of Hg. The calculated LOQ amounted to 0.3 ng of Hg, allowing quantification 3 ppb (ng/g) of Hg in 100 mg sample. The estimated value of extended uncertainty for real samples does not exceed 15%, what fully is compliant with the requirements for this type of measurements. Trueness of the method, calculated by processing of three different reference materials, ensures that the results are highly reliable [1].

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TOTAL MERCURY IN MUSCLE, LIVER AND KIDNEY IN THE GREAT CORMORANT IN THE VISTULA LAGOON

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One of the properties of mercury is bioaccumulation in soil, plants, animals and humans. The harmfulness of Hg depends of exposition time and its speciation - especially Hg vapors coming to organisms trough their respiratory systems. Other Hg forms may be also taken with food. Absorbed Hg circulates with blood and accumulates in some tissues. Higher concentration of Hg was observed in the critical organs (kidney, liver) and muscle. Fish eating birds, like Great Cormorant, are mostly exposed to biomagnifications of this metal because of their location at the end of the food chain [1, 2]. The aim of this work is to compare the Hg concentration in Great Cormorants' liver, kidney and muscle relative to their sex. 55 specimens of cormorants were collected at the Vistula Lagoon. Their critical organs (kidney and liver) as well as muscle were carefully separated and deeply frozen, lyophilized and homogenized. Mercury was released from the samples by thermal decomposition at 800°C. Its total content was determined by cold-vapor AAS technique at 253.65 nm using Mercury Analyzer MA-2000 (NIC - Japan).
It is shown that:

- The concentration of Hg is between 0.49-5.56 μg/g (DW) in muscle; 1.4-80.72 μg/g (DW) in liver and 1.25-296.76 μg/g (DW) in kidney;
- The levels of Hg in muscle and kidney was higher in males than in females (ANOVA $p<0.05$).

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APPLICATION AN IN SITU PLATED LEAD FILM ELECTRODE TO THE ANALYSIS OF BIOLOGICAL ACTVE SUBSTANCES BY ADSORPTIVE STRIPPING VOLTAMMETRY

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Voltammetric techniques have found widespread use in drug and organic substances analysis, since the voltammetric procedure usually involve a simple dilution step and most of the excipients used do not interfere in the subsequent determination. In this presentation it was shown that determination of testosterone and folic acid by adsorptive stripping voltammetry was possible using an in situ plated lead film electrode. Testosterone propionate (17β-hydroxy-4-androstene-3-one) is a steroid, the most patent naturally secreted androgen. An accurate measurement of testosterone is needed in many clinical applications for correct diagnosis and appropriate treatment. Folates are an important class of water-soluble B-vitamins that are essential for normal cell division and cell growth. Lack of folic acid gives rise to gigantocytic anaemia, associated with leucopoenia, devolution of mentality and psychosis etc. Folate deficiency remains one of the common vitamin deficiencies world-wide so methods for determination of folic acid in pharmaceutical, clinical and food samples are often required. The lead film plating process and accumulation of testosterone or folic acid were performed simultaneously from an acetate buffer solution at potential -1.1 V and -0,88 V respectively. The relative standard deviation for 1 x 10^{-7} mol L^{-1} of testosterone was 3.8 % and the detection limit was 9 x 10^{-9} mol L^{-1} for an accumulation time of 120 s. The relative standard deviation for 2 x 10^{-8} mol L^{-1} of folic acid was 3.9% and the detection limit was 7 x 10^{-10} mol L^{-1} for an accumulation time of 300 s. Various methods have been reported for the determination of testosterone or folic acid in biological samples and pharmaceutical formulations. However, the most of them required sample pretreatment and time consuming extraction steps prior analysis. In this presentation the proposed voltammetric procedures for determination of testosterone or folic acid were successfully applied to the determination these organic substances in pharmaceutical preparation and human urine samples without the necessity of pretreatment and extraction steps.

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DETERMINATION OF CADMIUM BY STRIPPING VOLTAMMETRY AT LEAD FILM ELECTRODE

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Cadmium is regarded as extremely toxic element. Prolonged intake of cadmium, even of very small amounts, leads to severe dysfunction of the kidneys. At high doses it is known to produce health effects on the respiratory system and has been associated with bone disease. For this reason the measurements of Cd(II) are important in industrial, clinical and toxicological laboratories. Several methods have been already described for the determination of cadmium. Most commonly used are spectrometric techniques. Electroanalytical techniques, anodic stripping voltammetry and adsorptive stripping voltammetry were also commonly used for cadmium determination. In the present communication a simple procedure for determination nanomolar concentrations of Cd(II) by stripping voltammetry at lead film electrode was proposed. Lead film and cadmium were accumulated simultaneously at the glassy carbon electrode, then cadmium was stripped at -0.6 V for 1 s and analytical signal of Cd(II) reduction was recorded by square wave voltammetry. Acetate buffer with added KNO_3 was used as supporting electrolyte. To enhance analytical signal of cadmium we exploited known from literature fact that in the presence of KI in electrolyte improve sensitivity of Cd(II) determination [1]. Parameters influencing sensitivity of cadmium determination such as time and potential of cadmium deposition, potential of cadmium dissolution were investigated. At optimised conditions calibration graph for cadmium is linear from 5×10^{-9} to 1×10^{-7} mol L^{-1}. The relative standard deviation for Cd(II) determination at concentration 5×10^{-8} mol L^{-1} was 4.2 % (n=5). The detection limit for Cd(II) following the accumulation time of 300 s calculated as a 3 σ for a lowest determined concentration of Cd(II) was 1×10^{-9} mol L^{-1}. The method was applied to Cd(II) determination in certified reference material.

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DETERMINATION OF POLYNUCLEAR AROMATIC HYDROCARBONS IN MARINE ENVIRONMENT USING GC/MS

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Polynuclear aromatic hydrocarbons (PAHs) are a group of pollutants of great concern due to their mutagenic and carcinogenic activities. PAHs are recognized as harmful substances in many environmental conventions, including marine environment (e.g. Helsinki Convention). Majority of polynuclear aromatic hydrocarbons in the marine environment is associated with the solid matter. Different extraction, clean-up and detection techniques are used for determination of PAHs in marine samples. This work presents analytical procedure of both unsubstituted and substituted PAH determination in marine sediments and particulate matter (plankton) using gas chromatography. The methodology was developed in Marine Pollution Laboratory IO-PAS. Samples were sonication-extracted, cleaned-up by thin layer chromatography and copper and analysed by gas chromatography equipped with ion trap mass spectrometer detector (GC-MS/IT). The method has been validated on reference material - sediment collected in the river Clyde's estuary in Scotland (IAEA-159). Application of this analytical procedure to PAH determination in samples from the Gulf of Gdańsk is presented.

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MICRONUTRIENTS IN FOOD PRODUCTS OF PLANT ORIGIN - SPECTROSCOPIC ANALYSIS OF BREAKFAST CEREALS

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Micronutrients (vitamins and minerals) are substances, that human body needs in small but steady amounts for growth, normal physiological functioning, and maintaining life. The micronutrients must be supplied by food or, in some cases, from dietary supplements, since the body cannot synthesise them. According to World Health Organization more than 2 billion people in the world suffer today from micronutrient deficiencies caused largely by a dietary deficiency of vitamins and minerals. The best way of preventing micronutrient malnutrition is to ensure consumption of a balanced diet that is adequate in every nutrient [1]. The majority of foods consumed by animals and humans is of plant origin. Breakfast cereals, made of corn, wheat, rice, oats and barley play an important role in the diets of children and adolescents, not only at breakfast but also as snack foods eaten at other times of day. In many countries, breakfast cereals are fortified with micronutrients. It simultaneously denotes necessity of monitoring of minerals levels considering toxicity of elements.

The mineral composition and nutritional properties of twenty four breakfast cereals available on local market in the Wroclaw agglomeration were studied. The products of popular brands widely distributed on international market were selected for investigation. The contents of Al, B, Ba, Ca, Cd, Cr, Cu, Fe, Mg, Mn, Ni, P, Pb, Ti, V and Zn and their bioavailable forms were determined by the use of the ICP-AES method. The total concentrations were measured in samples mineralised with concentrated nitric acid and hydrogen peroxide in a microwave system. The assessed content of the essential minerals and nominal mass of the examined elements declared by the producers were compared to the men nutritional requirements and daily permissible dose. The one-step extraction was applied using as extractants buffered solutions containing α-amylase, pepsin and trypsin. The extraction efficiencies were analysed taking into account bioavailability of elements under conditions simulating digestion processes in the men alimentary system. The results were discussed in point of view of the utility of the breakfast cereals as a source of minerals indispensable for proper functioning of human organism. Analysis of Standard Reference Material was performed for validation of the applied analytical procedures.

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ESTIMATION OF MEASUREMENT UNCERTAINTY OF A GAS-CHROMATOGRAPHY MASS SPECTROMETRY ANALYTICAL METHOD FOR THE DETERMINATION OF BTEX IN WATER

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Benzene, Toluene, Ethylbenzene, and Xylenes (BTEX) are volatile monoaromatic hydrocarbons which are considered to be one of the most often environmental pollutant.

The analysis of BTEX and other substituted benzenes in water samples using extraction with nonpolar solvent, and quantification by gas chromatography with mass spectrometry (GCMS) was developed according to HRN EN ISO 11423-2.

The most influence on estimation of the uncertainty of analytical method have next parameters: recovery, precision, purity of certified reference material (CRM), CRM preparation repeatability.

Analyzing uncertainty sources arising from the procedure of analyses standard uncertainty, combined uncertainty and expanded uncertainty were calculated.

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P-36 C

SINGLE HOLLOW FIBER SUPPORTED LIQUID MEMBRANE EXTRACTION OF FLUOROQUINOLONES IN WATER SAMPLES

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Fluoroquinolones are antibacterial agents related to nalidixic acid, and represent the second generation of quinolones family of antibiotics. They are applied as both in human and veterinary medicine. They primary target is the bacterial enzyme DNA gyrase or topoisomerase II, which renders the DNA molecule compact and biologically active. They are used commonly in livestock farm industries as active disease treatment agents for prophylactics and in case of pulmonary, urinary and digestive infections as feed additives. Fluoroquinolones may cause allergic and phototoxic reactions in human. These medicines have been shown to cause bone development problems in young animals and children. Due to the extensive use of fluoroquinolones in human medicine and farm industries, and the fact that they are largely excreted unchanged, significant quantities of these antibiotics can be found in municipal wastewaters [1].

Therefore, there is a need for development of simple and sensitive methods for determination of fluoroquinolones in water samples.

The aim of this study was to investigate the potential of using hollow fiber membrane based SLM for the extraction of fluoroquinolones antibiotics from water samples. It is a three-phase system, aqueous-organic-aqueous, where the organic membrane is held into the fiber pores, being in contact with the two other phases. This extraction method provides a high selectivity, short extraction time and very low cost for real samples. Parameters such as organic phase composition, extraction time and pH of the acceptor and donor phases were studied and optimized.

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HOLLOW FIBER LIQUID-PHASE MICROEXTRACTION AND HIGH-PERFORMANCE LIQUID CHROMATOGRAPHY FOR DETERMINATION OF TRIAZINE HERBICIDES IN WATER

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Triazine herbicides are one of the most extensively used compounds for crop protection in the world nowadays. This widespread application produces problems with the contamination of the surface and ground waters, and it is considered to be carcinogenic and toxic for human. Furthermore, atrazine and simazine have been proven to be environmental endocrine disruptors. According to the WHO and European Union directive the limited level of pesticides in drinking water is set at 0.5 μg/l. For other matrices, including food, the triazine tolerance level ranges between 100 and 250 μg/kg in the EPA Tolerance Index [1, 2]. Hence, rapid and sensitive methods are needed for monitoring of triazine herbicides and their fate in the environment.

As most environmental samples are very complex and the analyte concentration is usually quite low, an extraction and preconcentration step is necessary prior to chromatographic analysis. The mostly currently used sample pretreatment techniques for triazine herbicides enrichment are liquid-liquid extraction, solid-phase extraction, liquid-phase microextraction as well as solid-phase microextraction and membrane extraction.

In this study the possibility of hollow fiber liquid-phase microextraction for determination of some triazine herbicides at microgram level in water samples was investigated. The hollow fiber extraction procedure has the advantages of low organic solvent consumption and low cost. In LPME, analytes were extracted into organic membrane phase immobilized in the micropores of a polypropylene porous hollow fiber membrane, and back extracted into the acceptor acidic phase filled in the lumen of the hollow fiber. The effect of extraction factors such as sample pH, extraction solvents, acceptor pH, salinity, extraction time, stirring rate and humic acid were study. The optimized method allowed determination of the analytes at the ng/l level in analyzed samples.

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P-38 C

DETERMINATION OF ECOTOXICITY OF SURFACE SEDIMENTS WITH BATTERY OF BIOTESTS

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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.

Although chemical analysis allow to identify and quantify the organic pollutants, they do not provide sufficient information for ecological risk assessment. Furthermore, it is not possible to investigate all substances and their interactions in sediments. Therefore, the chemical analysis should be supported by toxicity measurements.

The toxicity of sediments was assessed applying the battery of ecotoxicity test including:

- bacteria (*Vibrio fischeri*) - destruents (reducents);
- crustaceans (*Daphnia magna*) - consumers;
- crustaceans (*Heterocypris incongruens*) - consumers;
- plants - *Sorghum sacharatum, Lepidium sativum, Sinapis alba* - producers.

SURFACE AND COMPOSITION STUDIES OF CHOSEN ENVIRONMENTAL SAMPLES

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Nowadays, we are witnessing increasing awareness and concern about the adverse effects caused by elevated levels of toxic compounds, not only in abiotic media such as air, water or soil, but especially in biological and human tissues. In the past 30-40 years, due to huge development of powerful analytical techniques, the application of plants as a complementary tool to instrumental methods of atmospheric pollution assessment has become more and more widespread. Studies of plants possess numerous advantages when compared with the traditional analysis of abiotic matrices [1-3]. The aim of our study was to obtain comprehensive information about the composition and surface characteristics of various biological samples (mosses, lichens, needles) collected from Lodz region. The other objective of this study was to compare the usefulness of used methods as a tool for the assessment of air pollution. Unwashed samples were carefully hand-cleaned to remove adhering soil particles and other contaminants, dried at room temperature, homogenized with an agate mortar and mineralised (approximately 200 mg of material) with concentrated nitric acid using microwave system Milestone MLS-1200 MEGA. The analysis of toxic metals (e.g. Pb, Cd, Mn, Cr) was performed with inductively coupled plasma mass spectrometry, X-Series, Thermo Electron Corporation. However, using this 'wet chemical' method, which requires sample homogenization and dissolution, we cannot assign the studied element to a specific particle type and its sources. Moreover, some elements may be preferentially accumulated in comparison with others, as a result of leaching, particle surface reactions, differences in particle size or capture efficiencies. Thus, the combination of "wet" analysis with the surface characterization showing particulates present on the surface, offers a powerful complementary technique to the whole-sample analysis [3]. The content of mercury was determined by Mercury Analyser MERCURY SP-3D, Nippon Instrument Corporation. In order to gain information about the damage of the structure of collected samples connected with the exposure to contaminants and elemental and/or molecular distribution within the analyzed surfaces the studied material was characterized by scanning electron microscopy with field emission S-4700 Hitachi equipped with energy dispersive spectrometer Thermo-Noran (SEM-EDS), and time-of-flight secondary ion mass spectrometry ToF-SIMS IV, ION-TOF. This study found that the applied techniques can be successfully used in the environmental analysis of various biological samples. The surfaces of studied materials containing the highest amount of analyzed elements were, in many cases, covered by exogenous particles of a possible anthropogenic origin.

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STUDIES OF TOTAL MERCURY CONTENT IN HAIR SAMPLES COLLECTED FROM PEOPLE LIVING IN GDANSK REGION

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In general, mercury was not considered as a pollutant of primary importance up to 1950s when many deaths caused by poisoning by mercury took place. Lately, many cases of the so-called adverse effects appearing at relatively low exposure levels have been described in the literature, suggesting the necessity of further analysis of risk for exposed populations connected with mercury accumulation along the food chain [1]. The potential health risk related to mercury exposure has been till now evaluated by the determination of mercury content mainly in breast milk, blood, hair, nail, or adipose tissues. However, among them the best indicator seems to be human hair since the total mercury content in hair is well correlated with the concentration of this toxic metal in organs such as brain, liver and kidney, base accumulation organs for metals in our body. Moreover, human hair samples are quite easy to collect and generally do not require any specific transport or storage conveniences. What is more, it was proven that mercury in hair was found to be stable over a long time, reflects levels of mercury in blood and contains measurable amounts [1, 2]. Fish consumption is identified as a major source of mercury exposure. Many cases of statistical differences between populations characterized by high and low fish intake have been described in the literature [2]. An other well known origin of mercury introduced into human organism are dental amalgamates which contain about 50 % of metallic mercury. The state of environment can also influence the concentration of mercury in hair material. The aim of our work was to study total mercury concentration in hair samples collected from people living in Gdansk region (e.g. Wiślinka, Przegalino, Sobieszewo, Świbno). We attempt to find a connection of the influence of a monthly fish intake, the presence of dental fillings and residence exposure on the level of total mercury in hair. The obtained results were compared with literature data. Approximately 200-300 mg of hair samples including only first 3-4 cm closest to the scalp were collected from the nape of the neck using stainless steel scissors. Mercury concentration in human scalp hair were determined in over 220 hair samples from male and female individuals living in different distances from phosphate waste disposal place. Subjects were asked to answer a questionnaire including information about factors which may affect the mercury content as: e.g. monthly fish consumption, a total number of dental amalgamates and others: sex, hair color, smoking habits. The content of total mercury in human hair was measured with Mercury Analyser MERCURY SP-3D, Nippon Instrument Corporation. Scanning electron microscopy Hitachi S-4700 was used to analyze the morphology of chosen samples containing the lowest and the highest amount of mercury. In general, the obtained results showed that most studied population is not exposed on mercury because in most cases the level of total mercury in hair samples did not exceed 500μg/kg.

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UTILIZATION OF SOLID PHASE EXTRACTION AND CLOUD POINT EXTRACTION FOR SPECIATION OF CHROMIUM IN WATER SAMPLES BY ELECTROTHERMAL ATOMIC ABSORPTION SPECTROMETRY

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The environmental studies of chromium is inevitably connected with the problem of speciation, because in its two main oxidation states, Cr(III) and Cr(VI), are significantly differences in biological, geochemical and toxicological properties. Cr(III) is considered essential for the metabolism of glucose, lipids and proteins in living organisms. Cr(VI) as a strong oxidized is highly toxic, can affect lungs, liver and kidneys, and is also mutagenic, carcinogenic and teratogenic [1]. In the present work a comparative study for determination of hexavalent chromium in water samples was performed using two different extraction methods, namely solid phase extraction and cloud point extraction. The electrothermal atomic absorption spectrometry (ETAAS) was used for the determination of chromium. Using solid phase extraction (SPE) the quantitative and selective extraction was achieved with a Chromabond® NH_2 ion-exchange columns after complexation of Cr(VI) with Alizarin Red S. The effect of different parameters, such as pH, concentration and volume of chelating agent and eluent, were evaluated. By cloud point extraction (CPE), Cr(VI) was extracted from water samples as the hydrophobic complex with the same chelating agent, Alizarin Red S, and subsequently isolated in the micelles of a non-ionic surfactant. The optimum experimental conditions that ensure the efficiency of the procedure, such as effect of the pH, concentration of chelating agent, surfactant, equilibration temperature and time on, have been investigated and are presented in details. Recent advances in extraction methods, results achieved, and comparisons of alternative methods for determination of chromium are discussed.

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ANALYTICAL METHOD FOR PAHS CHEMICAL SPECIATION IN SEDIMENTS

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The aim of this work is to optimize a method to examine the PAHs chemical speciation during the aging of sediments that is important in order to known the toxicological risk of a polluted area. In particular, we have conducted this research in order to determine if the organic contaminants fate is dependent to sediment characteristics and to study the potential role of humin and alkaline-extractable humic substances in the sequestration of PAHs in sediment.

The Polycyclic Aromatic Hydrocarbons (PAHs) include molecules containing fused aromatic rings and are of special concern because of their widespread distribution throughout the environment and their often toxic and carcinogenic properties [1]. The PAHs are hydrophobic compounds and as consequence in aquatic environments, they bind tenaciously to sediment organic matter. Certain members of the PAH family even though have photolysis half-lives that are usually measured in days they are found to be preserved over geological time-scales in ancient sediments indicating that sorption onto a sediment can greatly prolong their lifetime in the environment [2].

From sediments, humic substances were fractionated into humic acids (HA) and humin-mineral fraction (HM) and after extracted, according to the method described by Nam [3]. Qualitative and quantitative determinations were carried out using a gas chromatograph coupled with a mass spectrometer.

The results show the important role of humic substances in the PAHs sequestration and that the sediments characteristics influence the PAHs distribution between the labile fraction and the unavailable fraction.

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STUDY OF BIOACCUMULATION OF CADMIUM FROM AQUEOUS SOLUTIONS BY TWO STRAINS OF THE GENUS ASPERGILLUS NIGER BY FLAME ATOMIC ABSORPTION SPECTROMETRY

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In environmental sciences there is a need to develop technologies that can help by removal of toxic heavy metals found in natural waters and waste waters. Biological substrates such as bacteria, algae and fungus are materials able to accumulate metals from aqueous solutions through the biosorption process. The utilization of microbial cells with combination of sensitive and selective atomic spectrometry techniques used for metal determination is very important from the environmental analytical chemistry point of view for metal preconcentration purposes.

In the present work the removal of cadmium from aqueous solutions under laboratory conditions by fungal biomass of two strains of Aspergillus niger was investigated. Strain An1 was isolated from the Eutric Fluvisols FMm (pH H_2O/KCl 7.7/7.4). Strain An3 was isolated from the stream sediment (pH H_2O/KCl 5.27/4.8) from Pezinok region (Slovakia). Various parameters such as pH of the solutions, different initial cadmium concentrations, time of accumulation have been studied. In order to establish the effect of pH on the biosorption of cadmium ions, the batch equilibrium studies at different pH values were repeated in the range of 2.0-7.0. The optimal pH of cadmium accumulation by fungal mycelia of strains An1 and An3 was observed at pH 7.0 and 3.0 respectively. The relationship between the initial ion concentrations in the solution and cadmium ions accumulated in the biomass was studied. Some experiments were performed for comparison of batch and dynamic equilibrium studies for accumulation of cadmium from waters.

The digests of dry mycelium samples after microwave decomposition were used for determination of cadmium preconcentrated in biomass. The flame atomic absorption technique was used for the determination of cadmium concentration to study cadmium bio-accumulation.

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DEVELOPMENT OF CHROMATOGRAPHIC METHOD FOR SIMULTANEOUS DETERMINATION OF TRACE IONIC LIQUIDS IN AQUEOUS MATRICES USING ION CHROMATOGRAPHY WITH TANDEM ION-EXCHANGE COLUMNS

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Simultaneous trace determination of cations and anions in one chromatographic run from different matrices is a very useful and promising separation technique. This renders to use the single chromatographic procedure and conventional equipment to analysis the mixture of ions. Recently, there are several reports describing simultaneous determination of anions and cations in various environmental media (in most cases inorganic ones) using suppressed or nonsuppressed ion chromatography [1,2]. In this work we demonstrate new, simple and selective method for simultaneous determination of cations and anions as used in ionic liquids in aqueous samples. Ionic liquids under investigation constituted of homologue alkylimidazolium cations, i.e. 1-decyl-, 1-nonyl-, 1-octyl-, 1-hexyl- and 1-butyl-3-methylimidazolium, and following anions: chloride, bromide, tetrafluoroborate, bis(trifluoromethanosulfonyl)imide and hexafluorophosphate. The tandem of columns comprised of silica-based strong anion-exchange and strong cation-exchange packings. The critical part of the research undertaken was the selection of a mobile phase composition in order to obtain satisfactory separation for analytes with opposite charges but also very much different in lipophilicity and lyotropy. The best results were obtained using potassium hydrogen phthalate / phthalic acid in varying ranges. Further, impact of organic modifier content in the mobile phase onto peak shape and selectivity was also investigated. The developed method was further checked for its applicability in the analysis of these ions in environmental waters. The method revealed very good analytical performance parameters.

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APPLICATION OF GRAPHITE FURNACE ATOMIC ABSORPTION SPECTROMETRY TO THE EVALUATION OF THE *IN VIVO* NEPHROTOXICITY OF CHROMIUM TRIOXIDE IN MICE

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Chromium compounds are broadly used in welding industry, chrome plating, tanning and wood preserving [1]. It is known that some occupational environments providing an exposure to toxic chromium compounds, such as chromated copper arsenate (a water-borne preservative timber broadly applied until 2002 due to its reasonable price) treated wood, might be related to their migration into water, soil and food crops setting a risk not only for humans, but also for other life forms [2].

In the present work, to study the nephrotoxicity of chromium trioxide, mice groups were subcutaneously exposed to 20 mg/kg of chromium, during 24h and 96h. After these periods, kidneys were removed and processed for histological and quantitative analyses. In order to determine if selective accumulation of chromium occurred in renal tissue, an accurate and precise methodology based on closed vessel microwave-assisted digestion coupled with graphite furnace atomic absorption spectrometry (GFAAS) with Zeeman effect background correction was developed. To suppress the interferences associated with a complex sample matrix as kidney, the influence of sample weight, the oxidizing agents, as well as, the temperature programs of the wet digestion and the graphite furnace were optimised. Also, several quantification methods were tested and compared. The standard reference material NCSZC 71001 supplied by the China National Analysis Center for Iron and Steel (Beijing, China) was used for validation of the developed analytical method.

The GFAAS results showed accumulation of chromium in the kidney of animals treated during 24h than 96h, being significantly greater than controls. The histological results showed normal kidney structures for control animals and group exposed to CrO_3 (during 24h). However, kidney sections of the animals treated with CrO_3 (during 96h) revealed epithelium cells desquamation, development of hyaline and granular casts in renal tubules lumen.

Ongoing studies are being in progress for the understanding of pathophysiology mechanisms and the chemistry of chromium that leads to kidney damage.

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SPATIAL AND TEMPORAL VARIATION OF OUTDOOR AND INDOOR EXPOSURE OF VOLATILE ORGANIC COMPOUNDS IN GREATER CAIRO

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Megacities with several million inhabitants and an ever-growing urbanization are typical for serious air pollution resulting from high traffic volume, combustion processes and industrial areas nearby. Besides SO_2, NO_x and particulate matter volatile organic compounds (VOC) are an important class of pollutants due to their strong association with adverse health effects. Especially the BTEX aromatics (benzene, toluene, ethylbenzene, and xylene) are known as toxic and carcinogen.

Monthly measurements of volatile organic compounds were carried out in a field study in Greater Cairo in the period of 2005 till 2007. Ten apartments were chosen as sampling sites in different parts of Greater Cairo taking into consideration the traffic volume profile across the city and the suburbs. The concentrations of 29 VOC, which belong to the groups of alkanes, cycloalkanes, aromatic hydrocarbons, halogenated hydrocarbons and terpenes were measured indoor and outdoor at the same time. A strong correlation was found between sites with high traffic volume and the concentration of aromatic compounds. The total VOC burden in the outdoor environment of the whole city is dominated by compounds related to vehicle emission, e.g. the BTEX compounds (benzene, toluene, ethyl benzene and xylene). The spatial variation of the indoor BTEX exposure is similar to the outdoor exposure. This implies a strong infiltration of outdoor ambient air pollution into the indoor environment. The highest monthly indoor BTEX concentration was measured in Attaba (172 $\mu g/m^3$), which is located in the city centre.

The total indoor VOC exposure was additionally influenced by compounds related to special personal activities, e.g. terpenes originating from detergents and room fresheners or high-molecular alkanes originating from redecoration. This direct dependence of the indoor VOC exposure on indoor related activities in apartments in Cairo is in good agreement with investigations in Western Europe and North America.

Significant seasonal cycles with high values in winter and lower values in summer months could be modelled for outdoor concentrations of aromatic hydrocarbons. According to this behaviour in the outdoor environment, seasonal dependencies were also found for the indoor concentrations of aromatic compounds as well as for terpenes. Interestingly, this is in accordance with findings in Middle Europe (Germany) with completely different climate and building constructions [1, 2].

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USING ON - LINE SOLID PHASE EXTRACTION - LIQUID CHROMATOGRAPHY - MASS SPECTROMETRY METHOD FOR RAPID DETERMINATION OF PHARMACEUTICAL IN SEWAGE AND RIVER SAMPLES

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In recent years, an increasing number of pharmaceuticals and personal care products (PPCPs) have been detected at low concentrations in sewage treatment plant effluents, river waters and in some cases drinking water. Several publications report measured river and sewage effluent concentrations of pharmaceuticals in the low $\mu g\ L^{-1}$ or $ng\ L^{-1}$ range. In many of these reports LC/MS and LC/MS/MS techniques have been used to determinate pharmaceuticals in the environment. The application of these techniques to environmental analysis has provided results characterised by high selectivity and sensitivity in combination with good precision and accuracy. However, in many cases it is the sample preparation process that has become the bottleneck in method development prior to analysis.

The key objective of this work was to develop a highly sensitive and completely automated on-line SPE/LC/ESI/MS/MS procedure for the determination of 13 pharmaceuticals (representing different classes) in influent, effluent and river water samples. On-line SPE was performed using a Symbiosis Pharma System (Spark Holland, Emmen, Netherlands) SPE/LC system. Sample (5 mL) preconcentration was performed using Oasis HLB Prospekt - 2 cartridges (10 x 1 mm, 2.5 mg, Waters, Milford, MA, USA). For quantitative analysis a triple quadrupole mass spectrometer (TSQ Quantum Ultra, ThermoFisher) was used with an electrospray source in positive ionization mode ((+)ESI). For increased selectivity, selected reaction monitoring (SRM) was used with the ion transitions monitored. Xcalibur^{TM} (V2.0 SR2, ThermoFisher) software was used for data acquisition and processing.

A simple and universal method was developed, which can be applied to determine selected pharmaceuticals at $ng\ L^{-1}$ levels in different types of water and sewage samples.

AVAILABILITY OF PETROLEUM COMPOUNDS IN RIVERS AND DRINKING WATER WELLS IN VILLAGES AROUND RASHT CITY, IRAN

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Polycyclic Aromatic Hydrocarbons (PAHs) found in the environment; air, water and soil, are potential concern as they are associated with mutations, cancer and cause acute and chronic hazards to human health. These compounds can find their way into aquatic ecosystems by different pathways and are pyrogenic primarily from industrial and domestic sewage as well as petrogenic.

In the present study, 16 PAHs classified by US Environmental Protection Agency (EPA) as indicators were determined in the water samples collected from surface water wells used by rural inhabitants of Rasht as well as in water samples collected from the main rivers of this city including Zarjoub, Goharrud and Pirbazar.

About 40 samples were collected randomly and analyzed. Extraction of compounds from water was done by single drop microextraction (SDME). The extracted samples were analyzed by GC equipped with FID detector. Biphenyl was used as internal standard. The Detection Limit of the method was 0.1 μg L^{-1}.

Only six compounds including Naphthalene, Flourene, Phenanthrene, Anthracene, Pyrene and Benzo(ghi)perylene were detected in a few samples of well water and in some samples of river water.

Naphthalene content varied from 0.74 to 3.90 μg L^{-1} and maximum concentrations belonged to the Kamakol region of Zarjoub River. Flourene (0.76 μg L^{-1}) was detected only in the Siyahestalkh region of the Goharrud River.

The minimum and maximum content of Phenanthrene was 0.55 and 0.88 μg L^{-1}, respectively. Anthracene content varied from 0.63-0.88 μg L^{-1} and maximum levels belonged to well water located in the Nokhodchar village.

Pyrene content varied from 0.69 to 12.7 μg L^{-1} with maximum concentrations found in the Siyahestalkh region of the Goharrud River. Benzo(ghi)perylene (0.87 μg L^{-1}) was found only in the Kamakol region of the Zarjoub river.

No correlation and relationship was found among the various PAHs compounds found in the well samples. It is evident from results that in highly populated regions that sewage and wastewater from human activities enter rivers, these compounds can be found.

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APPLICATION OF NANOSTRUCTURED POLYANILINE AS A SORBENT IN SOLID-PHASE MICROEXTRACTION FOR THE ANALYSIS OF POLYCHLORINATED BIPHENYLS IN MARINE SEDIMENTS

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The synthesized nanostructured polyaniline (PAni) was employed as an extraction phase of solid-phase microextraction (SPME) for the determination of polychlorinated biphenyls (PCBs) in a sediment samples by gas chromatography-electron capture detector (GC-ECD). Considering the amount extracted per unit volume, PAni coating with nanostructure showed higher extraction efficiency compared to that with microstructure. An adsorption mechanism is often observed with a solid coating [1]. The amount of analyte adsorbed is proportional to the total surface area available. On the other hand, the nanostructures increase the surface area and active interfacial sites for adsorption of analytes, thereby leading to more sensitive chemical measurements [2]. The detection limits of the method were lower than 0.01 ng g-1 for PCB congeners and the correlation coefficients were higher than 0.995. The one fiber and fiber to fiber repeatability were lower than 6.9 and 12.1 %, respectively. The method was validated using the certified reference material IAEA-417, sediment sample containing certified values of organochlorine compounds.

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APPLICATION OF ACTIVATED COMPOSITE MEMBRANES FOR REMOVAL OF CR (VI) VERSUS MN (II) FROM INDUSTRIAL WATER EFFLUENTS

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The problem of removal of chromium, especially Cr (VI), from aqueous solutions is important for environmental concerns, knowing their high toxicity at low concentrations [1].

The study on transport, selectivity and stability in ACMs operations, using Aliquat 336 as carrier, is presented. The removal of Cr (VI) versus Mn (II) from industrial water effluents was tested.

Transport tests were performed between 7 and 25 hours at 0.5M Aliquat 336 concentration in the membrane, real matrix of industrial wastewater solution in feed, 2M $NaNO_3$ in permeate solution and at pH higher than 3.00. In feed solutions the concentration of metals ranged from 25 to 120 mg L^{-1} [2, 3].

The fluxes (*J*) were calculated by fitting the experimental data of Cr (VI) and Mn (II) concentration in the feed by linear regression techniques. They were used to calculate the transport selectivity of Cr (VI) ACM separation over Mn (II), given by ratio J_0 (Cr) / J_0 (Mn).

Transport and stability tests at 0.5M Aliquat 335 concentration in membrane were carrier out to compare them in terms of fluxes and lifetime. Experimental data evidenced a lover manganese flux (1.24 mmol h^{-1} m^{-2}) versus (47.67 mmol h^{-1} m^{-2}) from chromium. In real matrix of industrial wastewater, the presence of Mn (II) decrease the removal efficiency but the selectivity rest the same, for chromium ions.

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DETERMINATION OF URANIUM BY ICP-AES USING PRECONCENTRATION ON MACROPOROUS SORBENTS MODIFIED WITH SURFACTANT AND ORGANIC

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The echelle based ICP spectrometer at 27.12 MHz, with power output 1.35 kW, Meinhard concentric nebuliser and CID detector is used for the determination of U. Linear calibration plots for 0.1-50 ppm U(IV) are in solutions containing 1-3% HNO_3 for 385.958 and 409,014 nm. The detection limits are $X_D^{\alpha}=1,26$, $X_D^{\beta}=3,69$ (Graham), $X_D^{m}=1,13$ (Miller) or 0,30 ppm (IUPAC). No interferences at 1-3 ppm U were observed for 100:1 NO_3^- Cl^-, SO_4^{2-}, SiO_3^{2-} , NH_4^+, Na, K, Ca, Mg, Al 10:1 multicomponent containing Br^-, Cl, Br^-, SO_4^{2-}, $PO_4^{3-v}$and Cd, Co, Cr, Cu, Mn, Pb, V, Zn in the absence or presence of internal standard Y (1ppm) except of Fe^{3+} for which the interfering signal 10:1 excess decreases only by 50% in the presence of Y. The macroporous Amberlite XAD 4 conditioned with the cationic surfactant in the presence of 4-(2-pyridylazo)resorcinol, pyrollidincarbodithionate, 8-Hydroxyquinoline-5-sulphonic acid has proved for the preconcentration of U at pH 4-9. The subsequent elution is with mixtures of aceton, and 1M HNO_3 (1:1). The solvent is removed by evaporation prior to the ICP determination.

SOLID PHASE EXTRACTION OF ARSENIC, ANTIMONY, SELENIUM AND TELLURIUM ON SILICA-BASED ANIONIC EXCHANGER FOR THEIR DETERMINATION BY INDUCTIVELY COUPLED PLASMA EMISSION SPECTROMETRY

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Arsenic, antimony, selenium and tellurium were separated and preconcentrated on silica-based strongly basic anion exchanger Separon™ SGX AX prior to their determination by ICP-AES. The sorption of 0,25-5 $mg.l^{-1}$ from 50-1000 ml sample volume in the presence of various organic reagents such as ammonium citrate, sodium malonate, sodium tartrate and 4-(2-Pyridylazo)resorcinol and Pyrollidincarbodithionate was tested. The 100 times efficiency was reached by this preconcentration. The sorption flow rate and pH were optimized. 5M HCl was a suitable eluent in this case.

The influence of Na^+, K^+, Ca^{2+}, Mg^{2+}, Fe^{3+}, Al^{3+} or NO_3^-, Cl^-, Br^-, SO_4^{2-} and PO_4^{3-} as well as the mixture of heavy metal ions on the sorption was studied. Organic solvents and the excess of acids were removed by evaporation prior to the determination by ICP-AES. Optimalized procedures were carried out for the determination of arsenic, antimony, selenium and tellurium in natural waters.

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INVESTIGATION OF ENVIRONMENTAL DEGRADATION OF UNSYMMETRICAL DIMETHYLHYDRAZINE BY MODERN HYPHENATED TECHNIQUES

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Intensive space development led to a contamination of huge areas of landscapes and waters by a rocket fuel and the products of its degradation and burning.

The most dangerous and toxic fuel for a rocket launching is unsymmetrical dimethylhydrazine (UDMH). This compound is able to transform rapidly in environmental samples producing a variety of the degradation products. Their identification in UDMH water solution and water soil suspension were carried out by modern hyphenated techniques -liquid chromatography-mass-spectrometry, gas chromatography mass-spectrometry and preparative HPLC separation followed by NMR investigation.

Previously known as UDMH's oxidation products - dimethylamine, methylhydrazine, 1-methyl-1,2,4-triazole, 1,5,5-trimethylformazane, dimethylhydrazones of formaldehyde, acetaldehyde and glyoxal were confirmed and 1-formyl-2,2-dimethylhydrazine and N,N-dymethylguanidine were established as decomposition products. It was founded that only 1-formyl-2,2-dimethylhydrazine, N,N-dymethylguanidine, dimethylamine and 1-methyl-1,2,4-triazole are enough stable and may to serve for long time in environmental objects.

APPLICATION OF PASSIVE SAMPLING IN MONITORING OF BTEX IN URBAN AIR

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Urban air background concentrations of benzene, toluene, ethylobenzene and xylenens were assessed during 12 passive sampling campaigns in the Tricity area (Gdansk, Gdynia, Sopot) and Tczew applying two type of passive samplers: permeation - type Home-Made passive samplers; diffusive - type passive samplers : Orsa 5 (*National Dräger*) and Radiello (*FS Maugeri*). A difference between the time-weighted annual average concentration of *BTEX* compounds was found in each of the sampling site and type of passive samplers. The obtained results indicate that the *BTEX* concentrations measured in urban air in the Tricity area and Tczew, showed a week seasonal variation with slightly higher concentration during the winter and spring, and lower ones during the summer. The obtained time-weighted annual average level of benzene for the selected passive samplers only slightly exceed the permissible value for the benzene threshold given in the European Directive 2000/69EC of the European Parliament which stipulates a limit value of 5 μg m^{-3}. The values are within the range of the annual tolerance margin, 10 μg m^{-3}, for average weighted benzene concentration.

The lack of correlation between the determined concentrations of benzene and toluene, and the weak correlations between the remaining monitored compounds, confirms the significant influence of industrial plants located in the metropolitan area of Tricity and Tczew on *BTEX* compound levels in the atmospheric air.

The study brought useful data regarding the air concentrations of *BTEX* in the investigated region. Moreover, very good capability of passive samplers for reflecting temporal and spatial fluctuation in concentrations of *BTEX* in atmospheric air was confirmed, which makes them applicable for monitoring on the local scale. The obtained data also suggest that car traffic is not the only source of *BTEX* compounds in the metropolitan area of Tricity and around Tczew.

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MAPPING THE CONCENTRATION OF BTEX IN ATMOSPHERIC AIR IN TRICITY AREA AND TCZEW BY USING THE PASSIVE SAMPLING

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Knowledge of *BTEX* concentration in atmospheric air allows assessment of present and future environment state and can help explain man-made changes in the environment.

In recent years it was proposed that measurement results could be used to present spatial distribution of pollutants in atmospheric air, preparing maps of pollutants concentration, and, what is more important, to assess the concentration of pollutants in areas within measuring network. The maps obtained in this way permit in a simple way to assess exposure of living organisms to detrimental effects of harmful substances present in the environment. Moreover, graphical presentation of the results of atmospheric air quality helps classify the zones where allowable levels of *BTEX* were exceeded.

Visualization of geographical distribution of air pollutants concentration in the form of maps permits to perform complex thematical analyses, helpful in coming to appropriate decision related to environmental protection. In addition, the costs of studies on assessment of environment quality can be reduced.

In order to prepare the maps of *BTEX* levels in the area of Tricity Agglomeration and Tczew, the results obtained with the use of passive dossimetry at the step of sampling were interpolated for the areas between sampling points covering mapping areas.

In the case, on the basis of interpolation techniques it was possible to assess time-weighted average (*TWA*) concentration of the studied compounds at the points where measurements were not made.

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OPTIMIZATION OF METHODOLOGY FOR DETERMINATION OF FOUR FLUOROQUINOLONE ANTIBIOTICS IN WASTEWATERS BY UPLC-MS/MS

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Pharmaceuticals are a class of emerging environmental contaminants that are extensively and increasingly being used in human and veterinary medicine. Antibiotics form large group of pharmaceuticals which are used for treatment of infection diseases. In recent year there is growing concern worldwide about their occurrence in the environment because of their adverse effects mainly on human health. They have been detected in many environmental waters, such as wastewaters, surface waters and ground waters. The main problem of occurrence of antibiotics in the aquatic environment is the development of antibiotic resistance of microorganisms.

Group of fluoroquinolone antibiotics (FQs) belongs to the mostly used antimicrobials for humans. FQs are prescribed as a dose between 300-600 mg per day to the patient for therapeutic treatment. After administration, they are excreted almost as unchanged compounds in urine and thus are consequently discharged into hospital sewage or municipal wastewater and are also effluent from the wastewater treatment plants. Unfortunately nowadays, WWTPs are not able to completely remove these compounds and thus important quantities are released to the aquatic environment.

The aim of this work was to develop sensitive analytical method for determination of four fluoroquinolone antibiotics (ofloxacin, norfloxacin, ciprofloxacin and enrofloxacin) in wastewaters. This method uses Ultra Performance Liquid Chromatography (UPLC) in tandem Mass Spectrometry (MS) resulting in new methodology with high sensitivity. For separation of the standard mixture containing four antibiotics, the Acquity UPLC BEH C18 (100 mm x 2.1 mm) column with 1.7 μm particle size was utilized. The chromatographic separation was performed with mobile phase composed of 0.01% formic acid and methanol (81:19) in isocratic mode at a flow rate of 0.3 mL/min, at 30°C. Mass spectrometry detection was performed using positive electrospray ionization (ESI) and triple quadruple as analyzer in SIM and MRM modes. The optimized and validated method was applied to the analysis of wastewater samples.

In comparison with HPLC-FD method, the novel UPLC-MS/MS method has higher sensitivity, selectivity and possibility of separation in a short time.

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PRECONCENTRATION OF AN ORGANOPHOSPHATE PESTICIDE ON CARBON FIBER ELECTRODE AND CAPILLARY ELECTROPHORETIC ANALYSIS

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Methyl parathion is a selective insecticide, very stable to light, acid and is listed in the toxicity Class I. Trace contamination of pesticides in natural systems creates pollution problems due to their toxicity and bioaccumulation property. Techniques, such as TLC, HPLC, GC/MS, UV, capillary electrophoresis and colorimetry have been used for the determination of pesticides [1]. Capillary electrophoresis(CE) is becoming an advantageous tool for determining pesticide residues in environmental matrices because of its simplicity and high separation efficiency [2].

In general, environmental samples cannot be analyzed without some preliminary sample preparation; this step is frequently the major source of error. Thus, samples are still widely processed by liquid-liquid extraction (LLE) or solid phase extraction (SPE).

In an electrochemical experiment, adsorption of organic molecules onto working electrode is the main problem especially when using carbon electrodes. We tried to use this property for the preconcentration of an organophosphate pesticide, methyl parathion, prior capillary electrophoretic analysis.

Methyl parathion was accumulated by adsorption onto carbon fiber electrode (3mm x 5cm x 0.5cm) by applying a constant potential (-0.4V vs. Ag/AgCl) using a Gambry 600 potentiostat. Accumulation period was 450s. Then the pesticide was extracted for 5 minutes with water/ methanol mixture (15%v/v). Then capillary electrophoretic analysis was performed. Capillary electrophoretic conditions were: +25kV applied potential, 25°C temperature selected while using uncoated fused silica (50cm length, 50μm inner radius column). Borate buffer (20mM, pH 9.0) including 50mM sodium dodecyl sulfate (SDS) and 20 %(v/v) acetonitrile was used as carrier electrolyte for micellar electrokinetic chromatography. A 95% recovery was obtained with ten times enrichment.

The developed preconcentration method is economic and seems promising. Although electrochemistry is frequently and successfully applied as a detector in chromatography and in other separation methods, to our knowledge, it has very rarely used for enrichment.

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ANALYSIS OF BIOLOGICAL SAMPLES WITH ON-LINE COUPLED PYROLYTIC INJECTOR CAPILLARY GAS CHROMATOGRAPHY (CGC-FID)

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Pyrolysis in combination with capillary gas chromatography (CGC) is very powerful tool for the analysis of the solid samples. In pyrolysis, the sample is thermally decomposed at high temperatures (800-900°C) in a non-oxidative atmosphere. The degradation products are transferred to the capillary column for chromatographic separation. The chromatographic position and relative abundance of the peaks in the resulting pyrogram give **fingerprint** of the analyte which useable for identification purposes.

Pyr-CGC-FID coupled system has been applied for analysis of cyclohexyl methacrylate (CHMA) monomer in Algae (Chlorella kessleri) tissue after long term exposition. Algae solution was exposed in a static renewal system for 3 weeks into 0.2 ppm (mg/l) of CHMA aqueous solution. After filtration and impurities removing, the solid sample has been applied directly to pyrolytic injector. The system was set up using an on/line pyrolytic injector linked to a polar stationary phase chromatographic capillary column **Sol-Gel Wax**.

The main attentions have been paid on solid sample preparation, pre-treatment procedures and characterize bioaccumulation of CHMA in algae. The ratio between CHMA concentration of dominate peaks (fingerprint) is constant that confirms presence of CHMA from algae body. The toxicity of CHMA on algae (chlorella kessleri) was investigated after one week from incubation when we found out that (1μl CHMA in 10ml algae solution) is acute toxic, since the color of the algae solution (green) is declared compared to the lowest amount (0.2μl CHMA in 10ml algae solution) which was without significant changes. Therefore, it was found out high bioaccumulation of CHMA in algae.

USE OF TWO DIFFERENT SOLID-PHASE SORBENTS FOR SAMPLING TAR IN GAS OBTAINED FROM PEAT GASIFICATION IN LATVIA

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Gasification of biomass for producing synthesis gas is regarded one of the most promising options for its utilization. The producer gas contains several undesirable constituents, including dust (ash and char) and tar. A high-temperature biomass tar mainly consists of such highly stable aromatic compounds as benzene (60-70%), naphthalene (10-20%), and other polyaromatic hydrocarbons (10-20%).

In the present work, a solid-phase adsorption (SPA) method for determining concentration of tar compounds has been chosen as a basis for further research. The SPA method was developed by The Royal Institute of Technology in Sweden to measure tar compounds ranging from benzene to coronene. Traditional methods are based on cold solvent-trapping (CST). They proved very impractical for light compounds and require lengthy sampling times (15-60 minutes per sample). By contrast, the SPA method is easy to handle, and one sample is typically taken in only 1 minute. According to this method, tars are sampled by collecting on a column with a small amount of amino-phase sorbent. But this method does not allow for determining such volatile organic compounds as benzene, toluene, and xylenes. In the previous paper [1], an improved system of sampling by adding one more adsorbent cartridge loaded with another sorbent was suggested and described. The best results were obtained while using activated coconut charcoal as the second sorbent. A modified sampling device consisting of 500 mg of amino-phase sorbent and 100 mg of activated coconut charcoal was chosen as optimal for sampling tar (including its volatile organic compounds) in synthesis gas produced in biomass gasification.

For research in real life context, the Circulating Fluidised Bed (CFB) gasifier situated in eastern Latvia (Rezekne region) was chosen. Peat extracted several kilometres from the gasifier was employed as biomass. Tar was sampled at the temperature of producer gases reaching 250°C. Effectiveness of adsorption, which depends on the amount of gas drawn through the adsorbent cartridges, was explored. Amounts of producer gases such as 50, 100, 150, 200, and 300 ml were drawn through the sampling device. In all cases, benzene and toluene did not get completely adsorbed, besides, in case of drawing 300 ml of producer gases, xylenes, styrene, benzofuran, and indene did not get adsorbed either. What is more, the bigger are the amounts of the drawn gas, the lower is the rate of adsorption of benzene and toluene on the amino-phase sorbent and, correspondingly, the higher the rate of their adsorption on the activated coconut charcoal. The total amount of tar on two adsorbents was practically similar in all cases, about 1.8 g m-3 which fully corresponds to the specialist literature data for this type of gasifier [2]. The resulting composition of tar appeared as follows benzene (60%), toluene (10%), naphthalene (7%), fluorene (4%), phenathrene (10%), and more than 50 other compounds that were detected and identified.

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P-ANION EXCHANGE EXTRACTION AND ANALYSIS OF CHEMICAL WEAPONS CONVENTION RELATED PHOSPHONIC ACIDS AND BENZILIC ACID FROM WATER

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In the context of the verification of the Chemical Weapons Convention (CWC), fast versatile methods for the analysis of alkyl alkylphosphonic acids (AAPAs), alkylphosphonic acids (APAs), sulfonic acids or benzilic acid from water samples are required [1]. AAPAs and APAs are degradation products of very toxic chemical warfare agent, i.e., nerve agents (such as sarin, soman and VX) [2] and hence, they are good markers. The AAPA's and APA's were included in CWC as schedule 2.B.04 [1]. Benzilic acid which is precursor and degradation product of psychotoxic 3-quinuclidinyl benzilate (BZ), and is classified in CWC as schedule 2.B.08 [1].

In the literature, many sample preparation protocols can be found for the analysis of AAPAs and APAs in water and water extracts of soil. Since all these CWC related acids can not be directly analysed by gas chromatography and mass spectrometry (GC-MS), they need to be derivatized. The most popular derivative for these acids is the silyl derivative. The presence of cations hinders the process of silylation [3]. The removal of cations from water samples is generally performed using strong cation exchange (SCX) [4]. Although with SCX AAPAs and APAs were detected at quite low level (at ppb level), it is not selective for acids (many non-polar interfering substances are eluted together with the acids) and further in case of water sample containing excess of cations, breakthrough results in the hindering of silylation. Strong anion-exchangers are highly selective for extracting CWC related acids including AAPAs and APAs.

A simple and highly selective extraction procedure for AAPAs, APAs and benzilic acid from water samples, based on the use of strong anion exchange has been optimized for the on-site analysis. The extraction efficiencies of SAX and SCX were compared, revealing higher recoveries of the target acids with SAX than with SCX. The performance of the optimized SAX procedure has been evaluated and compared with the SCX in various types of water samples like tap water, 10% sodium chloride aqueous solution, water containing polyethylene glycol, formic acid and acetic acid, as well as water extracts of soil sample. The SAX extraction procedure showed to be highly selective even when a high concentration of background was used.

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THE CHEMICAL SPECIATION OF PLUTONIUM IN SEDIMENTS FROM GDANSK BAY

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The plutonium isotopes are amongst the more radiotoxic nuclides. Large quantities of plutonium have been released into the environment over the last half-century as a result of the military and civil applications of nuclear power. In marine environment the highest concentrations of plutonium are found in the sediments. The chemical form of plutonium in the marine environment is very complicated because plutonium shows four oxidation states (III, IV, V, VI). Plutonium adsorbed onto marine sediment is present as Pu(IV).

The chemical speciation of plutonium is still a significant topic to marine radioecology. The determination of the speciation is of prime importance to explain and evaluate the mobility and the toxicity of Pu in marine ecosystem. This work is focused more specifically on the physico-chemical speciation of plutonium. In the paper there are presented and discussed the results of ^{238}Pu and $^{239+240}$Pu concentrations in sediment samples from Gdansk Bay. The following plutonium fractions are isolated: exchangeables, bound to carbonates, bound to organic matter, bound to hydrous oxides of Fe and Mn, acid soluble and residual fraction.

The highest concentration of ^{238}Pu and $^{239+240}$Pu was found in carbonates fraction and the lowest values were accumulated in exchangeables fraction. The total $^{239+240}$Pu amount in analyzed sediments increase with core depth and at 5-6cm sediment layer is estimated at 0,56 Bq·kg^{-1} d.w.

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ASSESSMENT OF EXPOSURE OF ORGANISMS TO PERSISTENT ORGANIC POLLUTANTS IN MARINE COASTAL ECOSYSTEMS

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Coastal ecosystems are areas that are particularly severely affected by human activities. A considerable proportion of pollutants reaches the sea, thereby contributing to the rising contamination of the marine environment. Particular group of xenobiotics are persistent organic pollutants (POPs), due to their chemical stability and the potential for accumulation to toxic concentrations in the tissues of marine organisms. To produce reliable forecasts of the effects of POPs on the marine environment, use of appropriate methods of risk assessment is required. To fulfill this demand, the knowledge of the concentrations of these substances and understanding of the mechanisms of their transfer in marine environment are necessary. Despite the substantial research effort and the large number of publications, knowledge in this field is still incomplete. The objective of the present work was to evaluate selected methods for assessing the risk to organisms resulting from their exposure to POPs in marine coastal ecosystems. In particular, since the bioaccumulation is often utilised in ecological and ecotoxicological risk assessment studies, qualitative and quantitative aspects of POPs accumulation in organisms from different trophic levels are discussed. The Gulf of Gdańsk (southern Baltic) was chosen as model coastal ecosystem. The usefulness of passive sampling technique - semipermeable membrane devices (SPMDs) in quantifying bioavailable fraction of selected organochlorine contaminants and polycyclic aromatic hydrocarbons present in sea water was also evaluated.

ESTIMATION OF MEASUREMENT UNCERTAINTY OF A HPLC METHOD COUPLED WITH FLUORESCENCE DETECTION FOR THE DETERMINATION OF OCHRATOXIN A IN CEREALS

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A routine immunoaffinity column clean-up method for the quantification of ochratoxin A (OTA) in cereal and cereal products was developed. OTA was extracted from cereal products with acetonitrile-water, extract was diluted with a buffer and cleaned-up on an immunoaffinity column before HPLC/FLD analysis. Recoveries of OTA from the studied samples spiked at 0,5-6,0 ng/g level ranged from 76% to 85% with a standard deviation of 5,72%. The limits of detection and quantification of this method were 0,5 and 1,0 ng/g, respectively. Based on the validation criteria (selectivity, linearity, limit of detection and quantification, precision, recovery, trueness and robustness) uncertainty of the analytical result was estimated. A cause and effect diagram was constructed to identify and assay uncertainty sources arising from the procedure. All the standard uncertainties were then combined according to the appropriate rules to give a combined standard uncertainty and an expanded standard uncertainty. An expanded uncertainty of 16% was evaluated and confirmed by proficiency tests.

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TRACE METALS IN UNDERGROUND WATER AT MORADABAD, INDIA : ESTIMATION THROUGH INDUCTIVELY COUPLED PLASMA EMISSION TECHNIQUE

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Ground water is the principal source of drinking water in our country and indispensable source of our life. The problem of ground water quality is acute. Ground water pollution is much more difficult to abate than surface pollution because ground water can move great distances through unseen aquifers. Water pollution is the serious problem in the global context. It has been suggested that it is the leading world-wide cause of death and diseases [1,2]. Trace metals and their toxicity is the concern of present due to their natural abundance by virtue of their universal usage. Several adverse reports on metal exposure and toxicity have made human beings more conscious all over the world [3,4]. Nine different trace metals in underground drinking water at seven different sites at Moradabad, India were estimated for pre monsoon period as well as after onset of monsoon. Trace metals namely lead, cadmium, chromium, cobalt, manganese, nickel, copper, iron and magnesium were estimated by ICP-AES technique and the data was compared with the water quality standard prescribed by W.H.O. The underground water is found to be excessively contaminated with iron, moderately contaminated with chromium, manganese at all the sites and contaminated with lead metal at a few sites during monsoon. The underground contamination is increased after the onset of monsoon. The ground water is deficient of magnesium and it is uncontaminated with reference to other metals estimated. The present study suggests that people exposed to water of contaminated sites are prone to health hazards of metal toxicity and water quality management is needed in the study area.

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POTENTIALS OF ANALYTICAL METHODS OF THE ANALYSIS FOR THE CONTROL OF POLLUTION OVER OBJECTS OF A SURROUNDING ENVIRONMENT

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Rapid development of the industry and increase in number of motor transport in cities inevitably lead to air pollution, waters, soil and, as consequence, to deterioration of conditions of residing of the population [1]. In this connection the importance of laboratories with a representative complex of analytical methods of the analysis which main activity is the control and regulation of quantity of acting polluting substances over objects of a surrounding environment annually increases.

In the report opportunities of a lot of modern analytical methods of the chemical analysis applied at the control of a wide spectrum of pollution in objects of an environment are considered, and also results of numerous researches of a condition of air, water and soil which recently test influence of industrial and motor transportation emissions more and more are presented.

In work it is especially emphasized, that laboratory analytical methods of the analysis are irreplaceable at the control of polluting substances over emissions of the industrial enterprises, especially what related with high-temperature processes: factories on processing industrial and household waste, the enterprises of power system and metallurgy.

The big attention is given to methods and means of the control "the cores" polluting substances in air to which the weighed substances, hydrocarbons concern oxide and dioxide nitrogen, monoxide carbon, dioxide the sulfurs, dust, carbohydrates, phenol, formaldehyde.

It is marked also, that now has ripened necessity of updating of the list of the substances which are a subject the obligatory control over objects of the surrounding environment in large cities and the industrial centers since the substances concerning to proof organic pollutants began to deserve special attention, to hotbed gases (dioxide carbon, methane) and so forth in particular, for an estimation of a condition of atmospheric air the list should include the substances recommended by the World organization of public health services: ozone, aerosol particles in the size less than 10 microns, connections of heavy metals, polycentric aromatic carbohydrates [2].

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POLYCHLORINATED BIPHENYLS FRACTIONING ASSESSMENT IN AQUEOUS BIOREMEDIATION ASSAY WITH *PHANEROCHAETE CHRYSOSPORIUM*

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Polychlorinated biphenyls (PCBs) are known to be world wide spread persistent organic pollutants (POP) [1]. The white rot fungus Phanerochaete chrysosporium is able to degrade PCBs in water, and soil [2, 3]. As POP, PCBs can also be adsorbed onto organic matter, such as Phanerochaete chrysosporium mycelium. This study aims at estimating the fractioning of truly degraded PCBs, adsorbed PCBs and residual PCBs in water in an aqueous bioremediation assay. 500 mL of a mineral solution are stained with PCBs up to a concentration of 10 μg.L^{-1} and inoculated with Phanerochaete chrysosporium grown on Malt extract broth. A 100 mL sample is initially taken for a liquid-liquid extraction with 3x5 minutes sequences of 50 mL of hexane under manual stirring. After 7 days of incubation (ambient temperature) 400 mL are filtrated to 11 μm. The filtrate undergoes a liquid-liquid extraction (3x5 minutes sequences of 150 mL of hexane under manual stirring) and the solid residual is rinsed 3 times with 50 mL of hexane during 5 minutes. All extractions are reconcentrated to a volume of 1 mL under nitrogen steam. Seven PCBs (IUPACC numbers 28, 52, 101, 118, 138, 153 and 180) are analysed with HRGC-LRMS.

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A SIMPLE AND SENSITIVE ANALYTICAL METHOD FOR THE DETERMINATION OF PHARMACEUTICAL COMPOUNDS IN WATER SAMPLES BY COUPLING SPME-MD AND HPLC-DAD

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Recent monitoring of many pharmaceutical compounds in the aquatic environment has gained much interest because they can frequently be found in sewage treatment plant effluents (STPs), river and surface waters.

Environmental matrices are complex and most of these compounds are often present at very low concentrations. For that, a sample pre-treatment is required with the objective to provide a preconcentration with the target analytes and as free as possible from other components. Solid-phase microextraction (SPME) is an alternative sample preparation for extraction of organic compounds from water samples prior to their determination by HPLC [1]. Recently, SPME combined with micellar solutions like desorbent (SPME-MD) agent have been developed to extract and preconcentrate phenolic derivatives in environmental liquid samples [2,3].

In this study, we want to present a simple and sensitive analytical method for simultaneous determination of some pharmaceuticals compounds in environmental water samples combining SPME-MD with HPLC-DAD. Selected pharmaceutical compounds were different analgesics like ibuprofen, ketoprofen, naproxen and phenazone, lipid regulators like bezafibrate and clofibric acid and an antiepileptic like carbamazepine.

Parameters such as absorption time and temperature, using a 65 μm PDMS-DVB fiber, were optimized. Different surfactants for the desorption of the analytes from the fiber were investigated. Variables affecting the desorption process, such as surfactant volume and concentration and desorption time were also studied and compared. Advantages like the combination of time and efficiency, safety and environment friendly process for samples extraction prior to instrumental determination, demonstrate that solid-phase microextraction with micellar desorption (SPME-MD) could be used as an alternative to the conventional methods for the extraction of these types of compounds in natural waters from different origin.

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EFFECTS OF ULTRAFINE PARTICLES ON THE RELEASE OF CATECHOLAMINES IN THE ISOLATED LANGENDORFF-HEART MODEL

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Catecholamines are produced in the cortex, the adrenergic nervous system and the brain of vertebrates as a response to big effort, hypoxie and stress. These stress hormones adrenaline, noradrenaline and dopamine are aromatic amines formed from tyrosine [1]. Environmental parameters as pollution of air and water (chemicals, heavy metals and particulate matter) can cause stress reactions in vertebrates. Measurements of catecholamines and their metabolites in biological fluids are often used as methods in clinical chemistry for diagnosis of various diseases [2]. Ultrafine particles deriving from air pollution were described as a significant factor in respiratory and cardiovascular diseases [3, 4, 5]. Purpose of the present study was the development and validation of analytical methods for the measurement of catecholamines in the heart after exposition with ultrafine particles. The isolated langendorff heart model is a well established system for studies of effects of chemical compounds on the heart [6, 7].

Catecholamine concentrations were determined in the perfusates of langendorff guinea-pig hearts before and after exposition to ultrafine particles using high-performance liquid chromatography (HPLC)-electrochemical detection (ECD). A commercial HPLC kit "Clin Rep® Catecholamines in Plasma" was used for sample preparation and measurements of perfusates and biological control materials [8]. Validation data of biological control materials (blood plasma) and results from perfusate samples showed that the analytical parameters precision, accuracy, and limits of determination were absolutely in the usual range described for this method [8]. The most interesting finding of this study was that catecholamine concentrations in the perfusates of the langendorff hearts were significantly enhanced within several orders of magnitude after exposition with ultrafine particles. The HPLC method described in this study presents a valuable tool for the determination of stress responses in the heart resulting from ultrafine particles.

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COMPARISON OF METHODS FOR DETERMINATION OF METALLOTHIONEINS IN AQUATIC LIFE

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One aspect of environmental degradation in coastal areas is pollution from heavy metals, which are persistent and are bioaccumulated by marine organisms, with serious public health implications.

A conventional monitoring system of environmental metal pollution includes measuring the level of selected metals in the whole organism, or in respective organs. However, measuring only the metal content in particular organs does not give information about its effect at the subcellular level. Therefore, the evaluation of biochemical biomarker metallothionein may be useful in assessing metal exposure and the prediction of potential detrimental effects induced by metal contamination.

There are some methods for determination of metallothioneins including spectrophotometric method, differential pulse polarographic method, electrophoretic-flourimetric assay following with SDS polyacrile amide gel electrophoresis and RT-PCR.

In this paper, different methods are discussed briefly and the comparison between them will be presented.

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THE INFLOW OF POLONIUM ^{210}Po FROM ODRA RIVER CATCHMENTS AREA

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In this study the activity of polonium ^{210}Po in Odra river water samples, collected from October 2003 to July 2004, was measured using the alfa spectrometry. In autumn the highest concentration of ^{210}Po stated in Odra river water from Gozdowice (1.64±0.08 Bq.m^{-3}) and from Nysa Łużycka river (5.21±0.19 Bq.m^{-3}), however the lowest in water from Barycz and Bystrzyca (1.09±0.07 and 1.09±0.06 Bq.m^{-3}). During winter season, in turn, the highest concentration of ^{210}Po was observed in Odra river water collected in Chałupki (3.64±0.03 Bq.m^{-3}) and Słubice (3.62±0.03 Bq.m^{-3}) and the lowest in water from Noteć river (1.00±0.06 Bq.dm^{-3}). In spring the highest concentration was in Słubice (3.32±0.04 Bq.m^{-3}) and Nysa Kłodzka (4.04±0.03 Bq.m^{-3}), however the lowest in Barycz river (1.10±0.05 Bq.m^{-3}) and Odra river water from Głogów (1.04±0.06 Bq.m^{-3}). In summer the highest ^{210}Po concentration was in Nysa Kłodzka water (2.00±0.05 Bq.m^{-3}), the lowest in Odra water from Gozdowice (1.10±0.05 Bq.m^{-3}), and Barycz river (0.60±0.09 Bq.m^{-3}).

The highest quantity of polonium ^{210}Po was transported to Baltic Sea in spring, however the lowest in winter. Annually southern Baltic Sea especially Pomeranian Bay with Szczecin Lagoon waters receive 13.11 GBq ^{210}Po. Among the Odra river tributaries the highest surface run-off was observed in autumn (to 88 kBq.km^{-2}.quarter^{-1} for Nysa Łużycka drainage area), the lowest, on the other hand, in summer (1 kBq.km^{-2}.quarter^{-1} for Barycz drainage area).

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RECENT DEVELOPMENTS IN ANALYTICAL METHODS FOR ISOLATION, PRECONCENTRATION AND ANALYSIS OF IONIC LIQUID TRACES IN ENVIRONMENTAL MATRICES

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Ionic liquids are considered to be highly promising, neoteric solvents. The variability in possible combinations of anions and cations, and thus, the fine-tuning of their chemical properties, has given the chemical industry new target-oriented reaction media for synthesis, extraction and catalysis. Moreover, ionic liquids are associated with the term "green", but this is only because of their very low vapor pressure.

The wide applicability of these compounds also demands reliable, relatively simple and reproducible analytical techniques. These methods must be applicable to very low concentrations that are likely to be present in biological and environmental systems. This presentation therefore outlines methods for separating and analysing ionic liquids in different matrices using selective extraction of solid samples, solid phase extraction of liquid samples, reversed-phase high-performance liquid chromatography, ion chromatography and capillary electrophoresis, where various buffered mobile phases are used. Possibilities for the analysis of anions commonly used in ionic liquids are also discussed.

MINIATURISED POTENTIOMETRIC SENSORS FOR ENVIRONMENTAL ANALYSIS

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Potentiometric sensors are well-known devices suitable for quick and direct analysis of different substances without the need of sample pretreatment. The most popular potentiometric sensors are membrane ion-selective electrodes. Broad dynamic range, short analysis time and low apparatus costs are the main advantages of the ion-selective electrodes. Thanks to this, the measurements with such devices are competitive to other analytical techniques. Constantly growing demand on the environmental analyses makes that field of outstanding importance. On the other hand the miniaturisation, allowing the reduction of the amount of chemicals consumed during the analysis attracts much attention. Miniaturisation provides also cheap, mass production of the sensors, what reduces the costs of the analysis. Moreover, miniaturized sensors can be easily integrated in analytical systems for multiparameter analysis e.g. portable analysers for field measurements. Such devices are especially useful when continuous monitoring of some parameters is required, e.g. in monitoring of heavy metal ions concentration in water reservoirs, or when rapid analysis in the ground is needed.

Various architectures of miniaturised ion-selective electrodes are presented. Different transducers i.e. miniaturised Au and Ag electrodes on the epoxy-glass laminate substrate, $AgI\text{-}Ag_2O\text{-}V_2O_5$ composite, 16 Au or Ag/AgCl microelectrodes integrated on common epoxy-glass laminate substrate were used for the construction of the microelectrodes. The microsensors were obtained by the deposition of PVC-based membranes selective to K^+ ions onto the surface of the developed transducers. Moreover, electrodes with K^+-selective membrane with conducting polymer additive were investigated. A miniaturized reference electrode, compatible with the investigated planar ion-sensitive microelectrodes was also designed. In the proposed construction ionic liquid additive was introduced to the PVC-based membrane, what ensured a stable potential of such an electrode. Finally, complete miniaturised cell was obtained by integrating miniaturised ion-selective electrodes with miniaturised reference electrode on the same support. Described sensors are dedicated to the measurements of the activity of ionic species in aqueous media. Constructed microsensors were applied in the analysis of different mineral water samples and the results obtained were convergent to the expected.

P-73 C

PRECONCENTRATION OF Co(II) AND Ni(II) ON DITHIOCARBAMATE-FUNCTIONALIZED SILICA FOR FURTHER DETERMINATION OF THESE ANALYTES FROM DILUTE SOLUTIONS

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Dithiocarbamate functionalized silica are known for a long time to enable sequestration of heavy metal ions [1, 2]. Such sorbents were however prepared according to two step procedure involving the reaction of CS_2 on aminopropyl grafted silica samples which resulted in incomplete transformation of amine group into dithiocarbamate moieties.

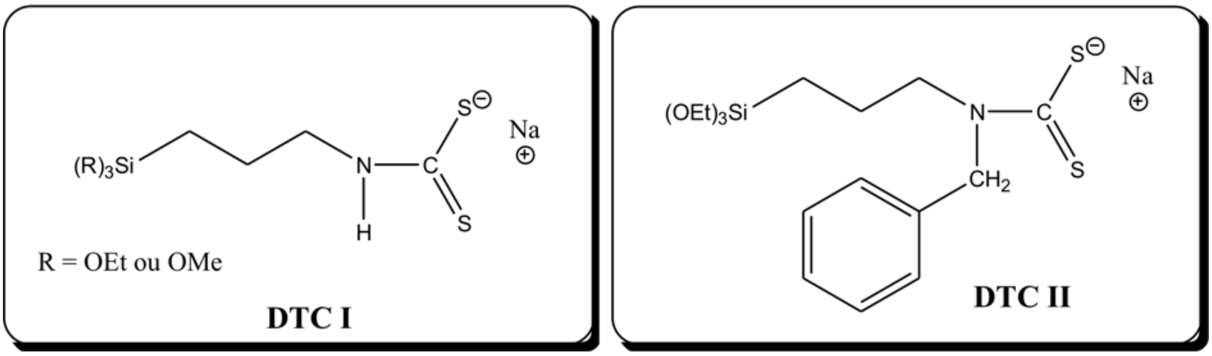

Figure 1. Scheme of siloxydithiocarbamates precursors DTC I (left) and DTC II (right)

In this work, a direct grafting approach is proposed using newly synthesized siloxy-dithiocarbamate precursors (see figure 1) to get amine-free absorbents.

These materials have been applied to the uptake of Co(II) and Ni(II) species from dilute solution in order to preconcentrate these analytes prior to their determination. Both batch and column sorption experiments have been performed. Various parameters effecting the preconcentration effectiveness have been studied, including pH, equilibration time, concentration of the analyte… Special attention was given to ensure fast adsorption in order to enable the use of cartridge containers filled with the material and to ensure quantitative uptake by simple flowing of the analyte sample though the column. Various desorption media were then evaluated and the best results were obtained with a mixture of H_2O_2 (2 M) and HNO_3 (1 M).

The method has been evaluated for the detection of Co(II) and Ni(II) in urine samples with possible application in the field of monitoring of occupational diseases.

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IONIC LIQUIDS AS NEW LIPOPHILIC ADDITIVES TO THE MEMBRANE OF LEAD ION-SELECTIVE ELECTRODES

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Ionic liquids (ILs) form a new class of solvents. They are not volatile or inflammable and conduct the electric current. They have attracted much interest as suitable alternatives to volatile organic solvents in synthesis, catalysis, extraction, separation and over related "green chemistry technologies [1,2]. In the literature the application of ILs to the extraction of many ionic and non-ionic species was described successfully. The mechanism of potential formation of ion-selective electrodes (ISEs) with liquid or pseudoliquid (polymeric) membrane depends strongly on extraction and ion-exchange processes between aqueous and organic phases [3]. Therefore we have decided to use the RTILs as component of polymeric membrane of ISE selective to lead ions, having an entertainment to obtain the electrode characterizing good analytical parameters. The ILs used in this work were: 1-ethyl-3-methylimidazolium chloride, 1-butyl-3-methylimidazolium chloride, 1-hexyl-3-methylimidazolium chloride. These ionic liquid are known to be immiscible in water but soluble in majority plasticizers. It seems that ILs can replace commonly used lipophilic ionic additives (phenyl borates) in the membrane phase, which are introduced to the membrane to reduce the anion interference and to lower the membrane resistance. Additionally ILs keep constant concentration of chloride ions in the membrane phase what guarantee potential stability of internal Ag/AgCl electrode. Three plasticizers, tributyl phosphate (TBP), 2-nitrophenyl ether (NPOE) and bis(1-butylpenthyl) adipate (BBPA)+NPOE (1:1 wt/wt), were used for membrane preparation, the *tetr*-butylcalix[4]arene-tetracis(N,N-dimethylthioacetamide was used as ionophore. In order to evaluate the effect of the addition of ILs to the electrode membrane phase, basic analytical parameters of electrodes containing them in the membrane phase were determined and compared with the parameters of electrodes without ILs in the membrane phase. As the result of conducted research have been found that the properties if studied electrodes, (specially selectivity) are strongly depend on plasticizer used for membrane preparation. The best results have been obtained for electrodes containing in the membrane mixed plasticizer (NPOE+BBPA 1:1 wt/wt). The research has found that ILs can be used instead of lipophilic ionic additives in the membrane phase because they lower membrane resistance and reduce anion interference, altogether improving the selectivity of the electrode.

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LEAD ION-SELECTIVE ELECTRODE WITH SOLID CONTACT

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The need for the determination of lead and other heavy metals increased during the last years because growing environmental problems. Potentiometric ion selective electrodes (ISEs) are known to offer an excellent low cost tool for the selective, sensitive and rapid determination of a vast variety of analytes in different fields of application. In presented paper a new lead ion selective electrode with solid contact is studied. This type of electrode construction, having a membrane phase and no internal solution, possesses all the advantages of the "coated wire " electrode but its lifetime is longer owing to the large volume of the potential creating phase, which acts as a reservoir of the active substance. Furthermore such electrode has allowed for low detection limit, which has been attributed to the absence of transmembrane ion fluxes [1]. It is easier to miniaturize than the classical ISEs with internal filing solution as well as it is also more convenient it use because it have not to work in vertical position. The membrane phase of proposed electrode consists of two layers placed in Teflon holder: the inner layer containing plasticized PVC in which the Ag/AgCl electrode is placed and outer layer contacting with the tested solution and containing the ionophore apart from the inner layer components. Both layers of membrane phase contain additionally ionic liquid- 1-butyl-3-methylimidazolium chloride. This compound improves the analytical parameters of electrode, reducing membrane resistance and enhancing the sensitivity and selectivity. The basic analytical parameters of electrodes, such as the slope characteristic, the detection limit, response time, life time, selectivity coefficients against cadmium, nickel, cobalt, zinc, copper, magnesium, strontium, calcium, potassium and sodium ions as well as the dependence of the electrode potential on pH were determined. The proposed electrode with solid contact is characterized by the good analytical parameters: theoretical characteristic slope, low detection limit, short response time and very long lifetime. The electrode shows very good discriminating ability towards Pb(II) ions in comparison with some alkali, alkaline earth, transition and heavy metal ions. The proposed Pb(II) membrane sensor have been used as end point indicator electrode for the potentiometric titration of lead with Na_2CrO_4. The electrode was also successfully applied to the direct determination of lead in water samples.

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P-76 C

DETERMINATION OF NINE HIGH INTENSITY SWEETENERS IN FOODSTUFF BY LC-MS

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Attention has been focused on simultaneous determination of multiple sweeteners by liquid chromatography and mass spectrometric detection (LC-MS). The sweeteners taken into study were: acesulfame-K (ACS-K), alitame (ALI), aspartame (ASP), cyclamic acid (CYC), dulcin (DUL), neotame (NEO), neohesperidine dihydrochalcone (NHDC), saccharin (SAC) and sucralose (SCL). A method for the determination of those substances in foodstuffs has been developed previously by Wasik et al [1], though, using ELSD detection. The main goal of this work was to adopt the method for MS detection.

Optimisation of LC conditions for separation, MS detection parameters and calibration were studied. Finally, drinks, yoghourt and vegetable samples were analysed in order to verify usability of the method.

LC conditions were optimised to achieve short separation time while keeping resolution at the acceptable level. Characteristics of the column, separation temperature, mobile phase pH, composition, gradient and flow rate were studied.

MS detection parameters (fragmentor and capillary voltage) were optimised by flow injection analysis (FIA) for proper MS detection.

Once the separation and detection conditions were established a working range has been determined in order to achieve linear calibration functions.

Finally, samples were analysed using solid-phase extraction (SPE) technique.

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AIR SAMPLING OF ORGANOPHOSPHORUS PESTICIDES BY SEMIPERMEABLE MEMBRANE DEVICES

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It has been evaluated the use of semipermeable membrane devices (SPMDs) as passive samplers of organophosphorus pesticides from air, in order to determine the contamination of working environments. Additionally, the possibility of using SPMDs as personal samplers has been also considered. The analytical methodology for the determination of organophosphorus compounds in SPMDs exposed to contaminated air was based on microwave-assisted extraction, gel permeation chromatography clean-up and gas chromatography with tandem mass spectrometry determinations (MS-MS), allowing the determination of Diazinon, Chlorpyrifos-methyl, Pirimiphos-methyl, Chlorpyrifos and Fenthion with limit of detection values from 2 to 4 ng/SPMD. A chromatogram is shown in Figure 1 where it can be seen the appropriate separation of the 5 studied compounds from differences in retention time and MS-MS spectra. The evaluation of the air quality of a pesticide laboratory with an intensive use of Diazinon and Chlorpyrifos has been made in order to check the operation safety conditions.

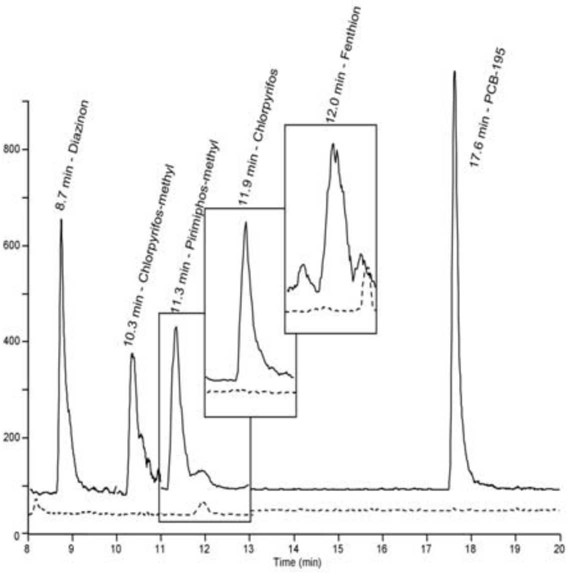

Figure 1. GC-MS chromatograms of a SPMD blank (- - -) and a SPMD spiked with 10 ng of each studied compound (--).

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EVALUATION OF AIR QUALITY IN TANGIER (MOROCCO) BY USING SEMIPERMEABLE MEMBRANE DEVICES

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Semipermeable membrane devices (SPMDs) have been used for the evaluation of the contamination of air in both, the urban and the industrial area in Tangier (Morocco), see a map of the area in Figure 1. Benzene, toluene, ethylbenzene, and xylenes (BTEX), twelve polycyclic hydrocarbons (PAHs) and seven polychlorinated biphenyls (PCBs) were monitored with SPMDs, deployed in six different sites. PAHs and PCBs were determined in SPMD by using a microwave-assisted extraction with gel permeation chromatography clean-up; and BTEX were directly measured by a head-space injector. Gas chromatography with mass spectrometry detection was employed for the identification and quantification of BTEX and PAH, while tandem-mass spectrometry detection was employed for PCB determination. From obtained results, it can be seen that the urban waste deposit and the industrial area of Moghogha present the highest concentrations of BTEX and PAHs, but do not significantly contribute to the contamination of air in Tangier urban area. PCBs were not found in any of the sampled sites. This study shows the versatility and simplicity of the use of SPMDs for the passive sampling of organic pollutants in contaminated air.

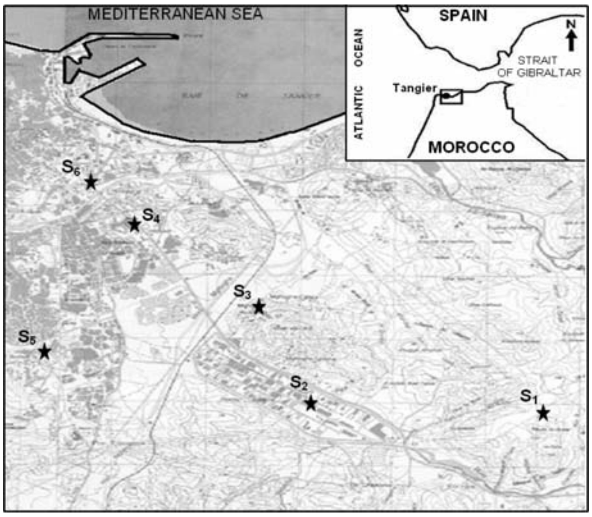

Figure 1. Localization of sampling sites in Tangier area. (S1, urban waste deposit; S2, industrial zone of Moghogha; S3, Moghogha area; S4, urban area; S5, Aouama urban area; and S6, Central bus station).

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INFLUENCE OF AIR TEMPERATURE IN THE PASSIVE SAMPLING OF BTEX BY SEMIPERMEABLE MEMBRANE DEVICES

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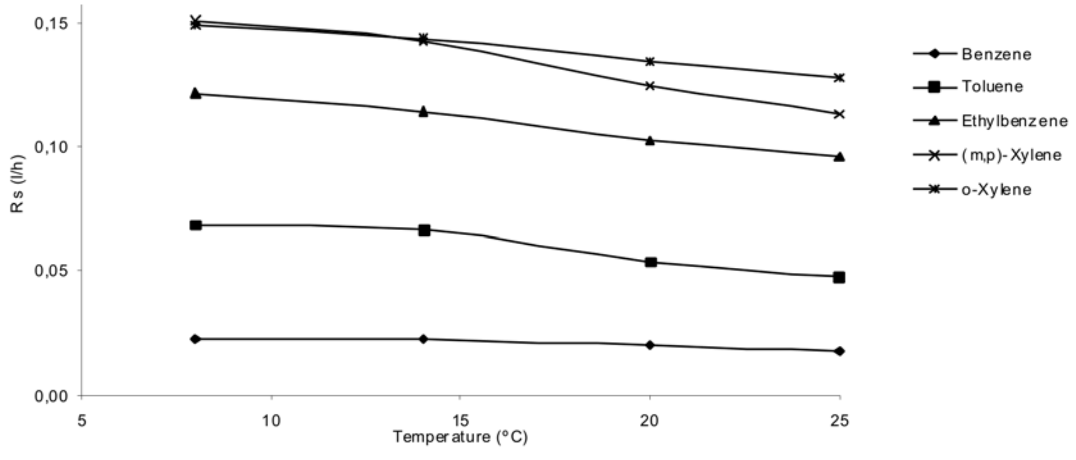
The uptake of pollutants into passive samplers is initially linear over time, then moves into a curvilinear stage, and finally can approach equilibrium [1]. Correlation between the pollutant amount found in semipermeable membrane devices (SPMDs) and the time-weighted average concentration of pollutant in air can be calculated by the estimation of experimental sampling rate (Rs) and the sampler-air distribution factor (Ksa). Rs and Ksa values were calculated for each BTEX compound at several temperatures (8, 14, 20 and 25°C). In both, equilibrium and lineal sampling studies, the uptake of BTEX decreased with the temperature. This behavior is consistent with theory and with other studies that shows the variation in the uptake of naphthalene, o-chlorophenol and p-dichlorobenzene at different air temperatures, from -16 to 40°C [2]. The variation with temperature of Ksa can be explained by using a linear fitting, with correlation R^2 values higher than 0.99 in all cases, but Rs variation can not be fitted to a simple model, so an interpolation was performed in order to obtain the corresponding Rs values for a specific temperature, see Figure. Air contamination of different car parks and boiler diesel tank rooms were evaluated by using SPMDs and Radiello diffusive samplers. Air temperature was monitored in the sampling sites and it range from 4 to 24°C. After a deployment time of 24 hours, each sampler was measured by their respective recommended procedures and results provided were comparables.



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P-80 C

PRELIMINARY RESULTS IN THE USE OF SEMIPERMEABLE MEMBRANE DEVICES FOR THE AIR SAMPLING OF VOLATILE ORGANIC COMPOUNDS

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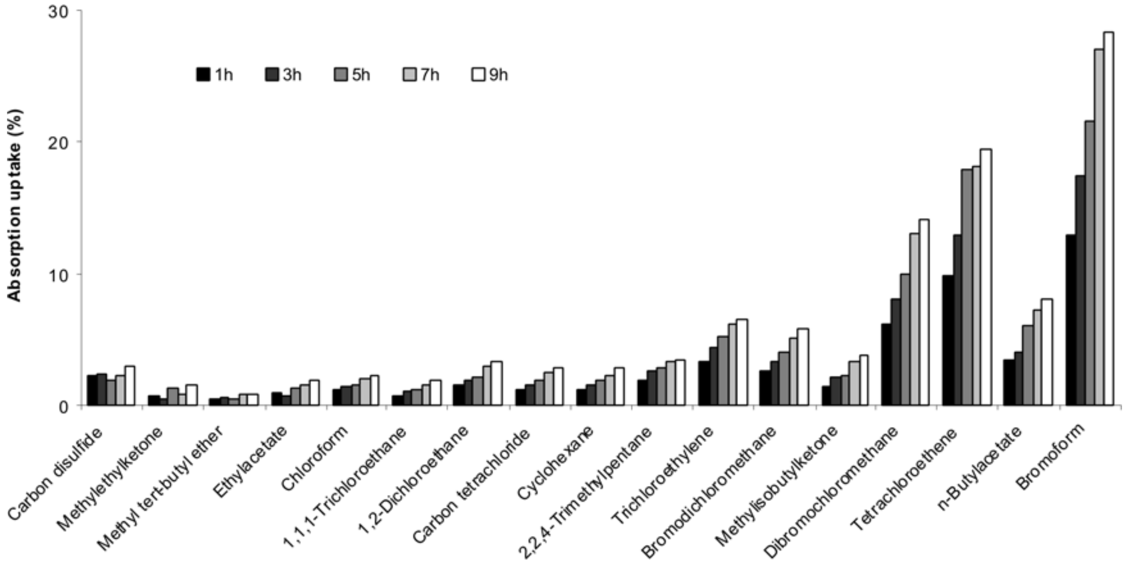
Semipermeable membrane devices (SPMDs) were evaluated as passive samplers for the determination of 32 volatile organic compounds (VOCs) in contaminated air environments. A direct methodology based on the use of head space - gas chromatography - mass spectrometry detection (HS-GC-MS) was developed for VOCs determinations, without any sample pre-treatment and avoiding the use of solvents. An evaporation temperature of 150ºC for 10 minutes was enough for VOCs determination and it provided a limit of detection of less than 5 ng/SPMD for all studied compounds. The absorption uptake for each VOC was established by using 2.85 L glass bottles with air spiked with 1 μg each compound. Then SPMDs were introduced inside each bottle and after different deployed times, from 1 to 24 hours, the total amount of VOCs retained by the samplers was measured by HS-GC-MS. As it was expected, high volatile compounds were slightly absorbed and moderate volatile compounds were absorbed by SPMDs, see figure. In spite of the reduced absorption of some compounds by SPMDs, it was possible the establishment of absorption isotherms using a lineal model. This study is the first precedent of the use of SPMDs for the sampling of many VOCs, being a simple and low cost alternative to ordinary sampling devices such as Radiello diffusive samplers or badge-type solid phase supports.



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EVALUATION OF THE CONTAMINATION BY PHARMACEUTICALS COMPOUNDS IN WASTE WATER TREATMENT PLANTS (WWTP) AND SURFACE WATERS

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The occurrence of pharmaceuticals in the environment is a growing concern. Pharmaceutical ingredients, including their metabolites and conjugates, are mainly excreted in urine or faeces. Hence, they enter municipal sewage treatment systems where they can be degraded, adsorbed to sewage sludge, or eventually diluted into surface water. Compounds that adsorb to sludge can reach the terrestrial environment when sludge is used as an agricultural fertilizer. Agricultural land can also be exposed when manure from medicated in house reared animals is spread. Pharmaceuticals used in animals raised on pastures are excreted directly to the grassland. Pharmaceuticals entering the terrestrial environment can reach surface water and groundwater.

In addition, pharmaceuticals used in aquaculture are released directly into surface water. Hence, many active pharmaceutical ingredients (APIs) for human and animal use are found in samples from surface waters, ground waters, and drinking water reservoirs.

The negative impact on the natural environment that results from the emissions of many substances harmful to human health has been proved. It is recognized that the pollution influences living organisms, humans included, both directly (by affecting their health) and indirectly (via contamination of food and abiotic compartments).

The purpose of this work was to develop a reliable, sensitive method based on off-line SPE and Liquid chromatography -mass spectrometry for the determination of estrogens (Estrone - E1; β-Estradiol - E2; Estriol - E3; Diethylstilbestrol - DES; 17-α-Ethynilestradiol-EE2 and degradation products (17-α-Ethynilestradiol-3-methyl ether - MeEE2; β-Estradiol-17-β-D-glucoronide sodium; β–Estradiol-3,17-diacetate at ng/l levels in water. Almost complete separation of all estrogens was achieved on a C18 column with methanol/water as the mobile phase. Quantification was achieved in the negative ionization mode using multiple reaction monitoring (MRM). The procedure includes solid-phase extraction of 0,3 L of water. Various solid phase extraction (SPE) cartridges were tested for the ability to remove estrogens from clean (milli-Q) water, using different pH and sample volumes. Trace analyte enrichment is always a challenge which led us to test the most recent hydrophilic adsorbents, not restricted to usual Oasis HLB, such as: Abselut Nexus, Strata X, Cromabond HRX, among others.

Recoveries from spiked water were better than 87% at a fortification level of 100 ng L^{-1} with emphasis on the Strata X and Oasis HLB which didn't show significant differences. The aim of this work is to evaluate the efficiency of a municipal WWTP in the removal of estrogens.

Keywords: estrogens, water monitoring, LC-MS-MS, hydrophilic adsorbents

P-82 C

ANALYSIS OF SOAP IN SEWAGE SLUDGE SAMPLES: COMPARISON BETWEEN THREE DIFFERENT EXTRACTION TECHNIQUES

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Soap is by far the most used surfactant worldwide with an estimated consumption of nine million tons [1]. It is widely used in household cleaning products, cosmetics, ubricants and coatings. Uses in household cleaning products include fabric washing products, fabric conditioners, laundry additives, and surface and toilet cleaners. These uses cover chain lengths of C_{10}-C_{22} predominantly with counter ions of sodium and potassium [2].

The fate of fatty acid salts in aqueous systems is strongly influenced by the poor water solubility of their calcium and magnesium salts. As a matter of fact, a number of water soluble and insoluble groups and combinations of these are present in environmental matrices. In practice, while the use of Na salts are by far the most common use of soap in finished products, the predominance of calcium and magnesium ions in waste water leads to rapid formation and predominance of relatively insoluble Ca and Mg salts [3]. As a consequence, moderate or high concentration of insoluble calcium soap in sewage sludge has been found [4].

This research work is focused on two parts: First, the determination of calcium soap in sewage sludge samples ranging from C_8-Ca to C_{20}-Ca and second, a comparison between three different extraction procedures (Soxhlet, ultrasound and microwave). Those methodologies comprise several steps: a) removal of fatty materials (lipids) other than soap through extraction with ether petroleum. b) Reaction with ethylenediaminetetraacetic tripotassium salt and carbonate potassium to transform calcium-soap in potassium-soap. c) Extraction of potassium soap with methanol. d) Derivatization of soap with 18-crown ether and bromomethyl-methoxy-couramin to obtain a suitable fluorescence response. e) Separation and determination of soap using liquid chromatography with fluorescence detection.

Fifteen different sewage sludge samples were analyzed for each procedure to carry out the comparison study. Finally, the obtained results were statically compared.

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DEVELOPMENT OF A NOVEL COLORIMETRIC DOSIMETER FOR THE MONITORING OF HYDROGEN SULFIDE IN INDOOR AND OUTDOOR ATMOSPHERES

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Hydrogen sulfide (H_2S) is a very important trace gas in both indoor and outdoor atmospheres. It is emitted both naturally (e.g. from volcanoes and anaerobic fermentation processes) and from technical processes, and it is of high relevance due to its high toxicity to humans and the strong corrosiveness of this acidic gas to particularly metallic substrates. Notably the latter aspect has created a greater awareness of H_2S concentrations in indoor atmospheres of museums, collections and archives [1]. Hydrogen sulfide which very often is produced internally from the use of materials unsuitable for display case construction, may thus attack vulnerable metallic objects in museums and collections, which ironically are believed to be better protected there than in their natural environment.

There arises thus the necessity to monitor hydrogen sulfide concentrations in indoor air (and, for reasons of comparison also for the outdoor atmosphere). Present state-of-the-art techniques to do so include ion mobility spectroscopy, gas chromatography, UV and IR absorption spectrometry and chemiluminescence techniques [2]. Although most of the above methods, such as gas chromatography or ion mobility spectrometry, are very sensitive for hydrogen sulfide detection with low ppb sensitivities, these are essentially laboratory methods which are difficult to use in the field.

There is thus a considerable demand for the development of alternative monitoring technologies which are field usable, simple, sufficiently sensitive and ideally also of low cost. These criteria are ideally fulfilled by passive samplers for atmospheric trace gases, and partially also by dosimeters [3].

We present here a novel device for the colorimetric detection of hydrogen sulfide in indoor air atmospheres at the low ppb level. It is based on the well-known reaction of silver nitrate with sulfide ions to form black, insoluble Ag_2S. Already when exposed for some days to atmospheres containing medium ppb concentrations of H_2S, this device produces a detectable color change which can be evaluated on a calibrated scale. More sensitive and more precise is the instrumental colorimetric evaluation which allows going down to ppb- and potentially also sub-ppb concentrations of H_2S. The particularly novel aspect of this device is the use of a porous polymeric membrane as diffusion barrier which allows to shield the sulfide-sensitive membrane from direct advection (thereby avoiding overexposure as common with other types of passive samplers) while at the same time it allows the construction of very shallow (essentially flat) passive samplers which respond to the particular requirements that sometimes exist in air monitoring tasks in museums where the dimensions of the passive sampler may decide on its applicability.

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LAST MINUTE SUBMISSION

EMERGING CONTAMINANTS AND THEIR ANALYSIS IN WATER QUALITY RELATED RESEARCH

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Urban and industrial sewage effluents contain important quantities of emerging and priority pollutants (including pharmaceuticals, personal care products and phenolics). However, whilst many of these substances have broad usage, our lack of knowledge concerning quantities emitted into the environment, their environmental behaviour and long-term ecotoxicological impacts need to be addressed if we are to understand the environmental, economic and human health implications. In the environment, once these chemicals are discharged into receiving waters (rivers, estuaries and coastal waters), there are substantial analytical difficulties to detect and accurately quantify the compounds. These difficuties increase with dilution and matrix complexity.

This presentation describes research undertaken at the Plymouth Marine Laboratory to investigate the input and environmental behaviour of pharmaceuticals, personal care products and endocrine disrupters in effluent, riverine, estuarine and coastal waters (including Ibuprofen, Naproxen, Ketoprofen, Diclofenac, Triclosan, synthetic musks, 2-Phenylphenol, 4-tert-Octylphenol and Bisphenol A). The presentation will also describe novel protocols to investigate bioavailable fractions of contaminants through the analysis of invertebrate biological fluids [1] and combined chemical and biological effects assessments of pollution [2]. Finally, recent experiences relating to shipping incidents will be summarised [3].

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PROBLEMS OF CHEMICAL ANALYSIS OF POLYCYCLIC AROMATIC HYDROCARBONS IN OIL SHALE PROCESSING WASTES

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Polycyclic aromatic hydrocarbons (PAHs) are ubiquitous environmental contaminants derived from the incomplete combustion of organic materials, e.g., any kind of fossil fuels, including oil shale. Due to carcinogenic and mutagenic activity of many representatives of this group of compounds, PAHs pollution has become a serious environmental problem [1, 2]. More than 60% of total mistakes of environmental analysis of PAHs occur during pretreatment and cleanup procedures of samples [3]. Soxhlet extraction is a technique that is very efficient in separation of nonpolar PAHs from environmental matrices. New developments of extraction have been applied to the analysis of PAHs in soils and sediments, such as accelerated solvent extraction, supercritical fluid extraction, focused microwave-assisted Soxhlet or ultrasound extraction [4]. The separation methods, including classical and modern ones were characterized and examples of their use for oil shale wastes were demonstrated. Final determination of PAHs commonly involves gas chromatography coupled to mass spectrometry (GC-MS). Deuterated PAHs are widely used as internal standards in GC-MS. However, recently synthesized monofluorinated PAHs (F-PAHs®) are considered to be more promising alternative [5]. From the reagents tested only one internal standard, 9-fluorobenzo[k]fluoranthene, could be used for quantification of PAHs content in oil shale solid wastes. Advantages and disadvantages provided by use of F-PAHs in GC-MS as internal standard for PAH analyses are discussed.

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