ISTITUTO SUPERIORE DI SANITÀ

XI Italian-Hungarian Symposium on Spectrochemistry

New challenges in human health protection: anthropic and remote areas

Venice (Italy), October 19-24, 2003

ABSTRACT BOOK

Edited by
Sergio Caroli and Clarissa Ferreri
Laboratorio di Tossicologia Applicata

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The Italian-Hungarian Symposium on Spectrochemistry is now in its eleventh edition. This biennial conference, since its onset in 1983, aims at providing scientists from both countries with a permanent forum for discussing the results of their studies in the field of human health and environmental protection, exchanging views on priorities to be set for future action and planning further joint projects. The most recent advances of spectrochemistry and other analytical techniques for investigating current aspects of human health and environmental protection will be taken into account, in particular as regards the challenges posed by urban settings and remote areas. As for all the previous editions of this event, a number of prominent scientists from other countries will also participate in the Symposium, thus further expanding the coverage of topics which by definition are of a global nature.

Key words: Human health, Spectrochemistry, Anthropic areas, Remote areas, Environment, Cooperation between Italy and Hungary.

Istituto Superiore di Sanità
XI Simposio Italo-Ungherese di Spettrochimica. Nuove sfide nella protezione della salute umana: aree antropiche e remote. Venezia, 19-24 ottobre 2003. Riassunti.
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Il Simposio Italo-Ungherese di Spettrochimica ha ora raggiunto la sua undicesima edizione. Questa manifestazione biennale mira, sin dal suo esordio nel 1983, a mettere a disposizione dei ricercatori di entrambi i paesi un'occasione permanente per l'esame degli esiti dei loro studi nel campo della salute umana e della protezione ambientale, per lo scambio di idee sulle priorità future e per la pianificazione di ulteriori progetti bilaterali. Saranno presi in esame i più recenti progressi della spettrochimica e di altre tecniche analitiche utili per lo studio dei vari aspetti della protezione della salute umana e dell'ambiente, con particolare riferimento alle sfide poste sia dagli ambienti urbani che dalle aree remote. Come per tutte le precedenti manifestazioni di questa serie, parteciperanno ai lavori del Simposio anche alcuni ricercatori di particolare rilevanza provenienti da altri paesi, contribuendo così a fornire un quadro ancora più completo su argomenti che, per definizione, sono di natura globale.

Parole chiave: Salute umana, Spettrochimica, Aree antropiche, Aree remote, Ambiente, Cooperazione tra Italia ed Ungheria

Si ringraziano l'Università Ca' Foscari di Venezia, l'Università Eötvös Loránd di Budapest e l'UNESCO per aver collaborato all'organizzazione di questo evento.

Chairmen of the Symposium: Sergio Caroli (ISS, E-mail: caroli@iss.it), Gyula Záray (ELTE, MTA-SM).

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PREFACE

The XI Symposium features nine oral sessions and one general poster session to be held throughout the entire duration of the event. Presentations will focus on issues such as pollution from industrial plants and motor vehicles, occupational hygiene, pathologies caused by urban living as well as health aspects of importance under extreme conditions.

The XI Symposium is organized in close cooperation with the University Ca’ Foscari of Venice under the supervision of P. Cescon and C. Barbante and is sponsored and hosted by UNESCO through the management of H. Moore and Ph. Pypaert.

Sergio Caroli

ORAL PRESENTATIONS

Session 1
Opening ceremony and *lectio magistralis*

GALILEO IN VENICE

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Galileo's greatest scientific work, *Discourses and mathematical demonstrations on two new sciences concerning mechanics and local motion*, opens with a tribute to the Venetian arsenal: "A large field of philosophical investigation is offered to speculative minds by frequenting your famous arsenal, Venetian Gentlemen, and particularly in that branch which is called mechanics". A familiarity with the practice of Venetian shipbuilders spurred Galileo's mind to speculate on the breaking point of timbers of different sizes and to formulate a mathematical theory of it. The other new science, *i.e.* the mathematical theory of local motions, was also conceived and elaborated during the period from 1592 to 1610, during which Galileo was appointed by the Venetian Senate to the post of mathematical lecturer at the Padua University. Then he discovered the law of falling bodies and succeeded in giving a mathematical demonstration of this phenomenon.

Galileo's most famous philosophical and literary work, *Dialogue on the two greatest world systems, the Ptolemaic and the Copernican*, is also set in Venice, where the daily occurrence of tides stimulated him to work out an ingenious, though wrong, mechanical explanation by explaining the phenomenon on the basis of the Copernican hypothesis of the rotation of the Earth. It was during his last year in Venice that he perfected the telescope and, by pointing it to the sky, discovered the mountains on the Moon and Jupiter's satellites. After moving to Florence as a Mathematician and Philosopher at the Court of the Grand Duke of Tuscany, Galileo never lose contact with Venice, keeping a frequent correspondence with his old Venetian friends and remembering with nostalgia the Venetian years as "li diciotto anni migliori di tutta la mia età", *i.e.*, the best eighteen years of my life.

Session 2
Novel analytical applications

DETERMINATION OF FULVIC ACID, Ca, Mg AND CARBON DIOXIDE CONCENTRATION IN WATER PERCOLATED THROUGH RENDZINAS AND RED CLAY

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Fulvic acid, Ca, Mg and CO_2 concentrations as well pH and electric conductivity of soil solutions were determined after injecting doubly-distilled water onto glass columns filled with different soils (black rendzina, brown rendzina, red clay rendzina, red clay) characteristic of the Aggtelek karst system (Hungary). Identification and determination of fulvic acid were achieved by Size Exclusion Chromatography (SEC) and Adsorption Chromatography (AC), respectively, with fluorescence spectrometric detection. The Ca and Mg concentration of the samples were determined by Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES). CO_2 concentration was determined by using a selective electrode. According to the SEC analysis, the apparent molecular weights of the fulvic acid of the samples were between 500 and 1600 Da. The fulvic acid concentration values of the percolated water samples decreased as a function of the soils investigated from black rendzina to brown rendzina, red clay rendzina and red clay. This is consistent with the organic matter content of these type of soils. The results obtained for pH, electric conductivity, CO_2, Mg, Ca and fulvic acid concentrations of water samples collected from the column filled with red clay were in good agreement with those of a groundwater sample collected from an observation station built in red clay above the Béke Cave (Aggtelek). Since the artificially prepared red clay column was exposed to same temperature and humidity conditions as in the case of the red clay from the sampling site, this method seems to be suitable for modelling infiltration of fulvic acid and metals from red clay into groundwater under laboratory conditions.

ANALYTICAL CHEMISTRY AT THE INTERFACE BETWEEN METROLOGY AND PROBLEM-SOLVING

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The confluence of the principles and practices of metrology in chemistry and problem-solving procedures in the analytical framework can lead to conflicts and synergies that are well illustrated by a number of real-life examples. All of them allow one to infer the importance of such an essential topic in establishing the aims and objectives of analytical chemistry. Interestingly, no systematic approaches to this interface have been developed despite the crucial role it plays in modern analytical chemistry. The major intrinsic features of metrology in chemistry are also outlined through a systematic comparison of physical and chemical measurement processes. A brief approach to solving analytical problems using a five-step procedure is described.

The most serious conflicts between metrology in chemistry and problem-solving arise from the following complementary generic approaches: *i)* contradictory relationships among analytical properties; *ii)* systematic adoption of client information needs crucial analytical references (in addition to the classical ones, *viz*., measurements and written standards); *iii)* the two facets of the analytical excellence (*viz*., consistency between the information delivered and that required, also called referential information); and *iv)* the two paradigms of routine laboratories, *i.e.*, compliance with norms and client satisfaction. Due account being given to the weakest aspects of metrology in chemistry and in the problem-solving process, some strategic approaches are proposed with a view to converting the conflict into synergy. In this context, the largest black holes of metrology in chemistry are highlighted.

ADVANCES IN QUADRUPOLE INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY

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Inductively Coupled Plasma Quadrupole Mass Spectrometry (ICP-QMS) has now become a well-established instrumental technique for trace element determination in industrial, geoenvironmental, and biological applications. The growing popularity of the combination of quadrupole mass spectrometers with the high-energy argon plasma stems from the unique properties of this ionization source. These merits include versatile sample introduction devices, enhanced particle - plasma interaction in the axial column of the plasma resulting in reduced matrix effects, multielemental capability, extended linear range of calibration, enhanced Limits of Detection (LoDs) and isotopic information. Despite this well-established popularity large strides in instrumental development are still witnessed.

In this presentation, recent innovations in instrumentation and applications are reviewed. The need to improve analytical performance for the determination of very low concentrations of toxic and diagnostic elements and element species in solutions and in solid samples has resulted in the development of innovative, robust and high efficiency plasma - mass spectrometer interfaces. The development of high ion transmission interfaces, chicane ion guides, off-axis quadrupole analysers, Xi cones, and the recent 90° reflecting ion optics and curved fringe quadrupole rod configurations provide very low instrumental background of less than 1 cps and typically more than 1 GHz tunable sensitivity. These devices allow considerable versatility to be achieved for ultratrace element determinations and for extending the dynamic concentration ranges.

Reaction and collision cells using energy discrimination result in a substantial attenuation of polyatomic interferences on isotopes of problematic elements, thus enhancing their LoDs. The coupling of advanced sample introduction devices, such as gas chromatographic generators, allows for metal speciation thus extending the domain of the technique. New UV Nd-YAG lasers extend as well the scope of direct bulk and surface analysis of solid samples. These assets are described using conventional figures of merit and typical geoenvironmental applications. It is concluded that this new arsenal of instrumentation has resulted in the renaissance of trace element surveys and research.

STATE-OF-THE-ART IN SAMPLE PREPARATION AND TRENDS OF DEVELOPMENT IN ANALYTICAL ATOMIC SPECTROMETRY FOR ENVIRONMENTAL MEASUREMENTS

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Global ecological problems have resulted in a growing awareness and interest in the analysis of environmental samples. The impact of the effects of trace elements in the environment on man's health has fostered the development of analytical techniques and instrumentation capable of addressing these issues. Sample preparation has long been the bottleneck of environmental analysis for both total and species-specific determinations. Thus, the expanding capabilities of modern trace element analysis techniques have challenged the sample preparation competence of most laboratories. Exceptional analytical detection power, remarkable analysis speed, automated sample presentation and intelligent sample sequencing of modern spectroscopic instrumentation have led to demanding requirements for appropriate sample preparation steps as necessary for trace and ultratrace concentrations and chemical speciation measurements. Contamination control, reliable digestion techniques, preservation of chemical forms, sample matrix management and intelligent sample processing as approached today are often inadequate for the most demanding measurements. Developing new sample preparation chemistry is especially arduous and time-consuming; yet, progress is being made in characterising decomposition and dissolution procedures, especially Microwave (MW) assisted processes.

Current targets for modern preparation approaches for trace element determinations of environmental materials are surveyed. Since the preparation of samples is often dictated by the form in which they can be presented to the instrument, development of new methodologies and improvement of existing techniques for regulatory elemental determinations in environmental matrices constitute a major challenge to the analytical chemist. A variety of instrumental strategies have been proposed to solve environmental analysis problems. Currently available sources for use in atomic spectrometric techniques include flames, arcs, sparks, arc jet plasmas, inductively coupled plasmas, MW plasmas and laser generated plasmas. Forecasts suggesting an enhanced role for laser and spark ablation, direct sample insertion, electrothermal vaporization, direct powder sampling and slurry sample introduction techniques in atomic and mass spectrometry instrumentation have been made for many years. In light of these forecasts, the future of atomic spectrometry for environmental analysis encompasses advances in related technical areas in addition to those of the instrumentation itself. Methodological blanks and validity of data produced are finally discussed.

THE FLOWING CHARACTERISTICS OF THE AIR-ACETYLENE FLAME AND ITS ANALYTICAL CONSEQUENCES

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A study was carried out on the effect of flow characteristics on the atom distribution when introducing Hg vapour samples in flameless jets and air acetylene flames. In the flameless case a free jet flow forms after leaving the burner head. When determining the Hg vapour concentration on the central plane of the free jet two sections can be distinguished, namely, the primary and the mixing section. In the primary section of the jet only the diffusion has an effect on the atom vertical distribution and the absorbance or concentration of the analyte vs. the observation height varies according to Eqn. 1.

$$A_h = \frac{A_0}{\sqrt{1 + kA_0^2 h}} \qquad \text{(Eqn. 1)}$$

where A_h and A_0 are the absorbances at observation height h and 0 (the observation height when the jet emerges from the burner), respectively, and k is a constant. If $kA\sigma_0 >> 1$, Eqn. 1 assumes the form given by L'vov. In the mixing section the atom concentration decreases more than predicted by the diffusion equation.

The width of the flowing jet increases significantly if the flame is on due to the thermal expansion of the jet and the length of the primary section of the jet becomes also much longer than in the flameless case. Since the primary section of flow expands over the analytical zone of the flame, only diffusion will influence the atom concentration above the expansion zone. When introducing aerosols instead of an atomic vapour the above statement is valid only if atomisation is complete and recombination is negligible up to the h_0 observation height. The lateral distribution of atoms will be influenced by both diffusion and mixing. This produces a complex relation between the vertical and horizontal atom distribution according to Eqn. 2.

$$\frac{A_h}{A_0} \approx \frac{\left(T_{A(x)}\right)_h \sigma_0}{\left(T_{A(x)}\right)_0 \sigma_h} \qquad \text{(Eqn. 2)}$$

where A_0 and A_h are the absorbances measured on the central plane of the flame at the reference and h observation height, respectively, $TA(x)_0$ and $TA(x)_h$ are the integrals of the horizontal absorbance distribution function and σ_0 and σ_h are the half widths of the lateral absorbance distribution curve at the reference and h observation heights, respectively.

DIRECT ANALYSIS OF POWDERED SAMPLES BY AN ICP-AES METHOD

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The direct analysis of solid samples has several advantages. No time-consuming sample preparation procedures are needed and loss or contamination phenomena are minimised. Different kind of solid sample introductions to the plasma (*e.g.*, laser ablation, spark sputtering, electrothermal evaporation, slurry technique) have been studied by several authors. The major problem is finding adequate materials and methods for calibration. The most simple method is the slurry technique. In this case the powdered sample of suitable small particle size held in an aqueous suspension of a certain percentage can be directly aspirated into the plasma and analysed. The possibility of using acidic aqueous solutions for calibration in the slurry analysis has been investigated by Ebdon and his associates in the UK. According to their results the most suitable particle size of solid sample can be calculated as a function of its density. Unfortunately, for the vast majority of solid samples the calculated particle size is very small. Thus additional sample preparation (milling) is required.

In this work a slurry method was developed to analyse various fly ash samples. Optimal conditions were achieved for the flow rate and the concentration of the slurry, the sample particle size as well as the rotation of the stirrer. Copper, Mn, Pb and Zn were determined in powdered fly ash samples. The solid Certified Reference Material (CRM) BCR 038 was used to check the accuracy of measurements. Results were compared with data obtained by wet digestion Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES) and X-Ray Fluorescence Spectrometry (X-RFS). Powdered cement samples were also tested to ascertain their suitability as calibrants for the slurry method with ICP-AES.

COMPARISON OF NUCLEAR AND X-RAY TECHNIQUES FOR ACTINIDE ANALYSIS OF ENVIRONMENTAL HOT PARTICLES

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Actinide-containing radioactive hot particles have been dispersed into the environment during atmospheric nuclear tests, accidents due to the nuclear fuel cycle and authorized discharges from nuclear reprocessing plants. Several other activities like illicit traffic of radioactive material or the use of depleted U in shielding and weapons can also be considered as possible sources of contamination by actinides. Limits of Detection (LoDs) for actinide analysis by nuclear spectrometry as well as by various micro X-Ray Fuorescence (μ-XRF) and absorption techniques were ascertained using laboratory and synchrotron sources. The detection limits for X-ray techniques were calculated by Monte Carlo simulation. On the other hand, the detection limits obtained for X-ray microanalysis using synchrotron sources were close to that of nuclear analysis.

For long half-life nuclides (more than 10^5 years), X-ray spectrometry was more sensitive, while being nondestructive and offering additional information on oxidation states through X-ray absorption. For U, γ spectrometry resulted only in 10^{-7} g (^{238}U) *vs.* 10^{-13} g obtained with monochromatic beam μ-XRF at HASYLAB Beamline L. Using the combination of autoradiography and μ-XRF, identification and quantitative analysis of individual radioactive particles of 20 μm diameter were possible. Despite the strong spectral overlap with the Rb-K_α characteristic line, with micro X-ray absorption near-edge structure it was possible to determine the oxidation state of 15 μg g^{-1} U in a single hot particle. The applicability of X-ray microanalysis is presented through examples of hot particle identification from nuclear accidents in Thule and dispersed depleted U particles from ammunition in Kosovo.

TERMINOLOGY CONCERNING RADIOANALYTICAL CHEMISTRY OF “HIGH SPECIFIC ACTIVITY” RADIONUCLIDES AND LABELLED COMPOUNDS

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In nuclear chemistry and radiochemistry, the concept of carrier (isotopic and non-isotopic) plays a crucial role. There is an increasing need for high to very high specific activities, *e.g.*, the requirement for a minimum amount of isotopic carrier present in the Radionuclide (RN) preparation, often in combination with a half-life of RN as short as possible. The specific activity (A_S) of an RN is defined quantitatively as the activity of RN to the total mass of both radioactive and stable nuclides of the same element (compound) present in the radioactive preparation, under the assumption that a free isotopic exchange takes place. In a few cases an RN can be considered absolutely free of isotopic carrier. In this case the RN (or labelled compound) is named carrier-free. The A_S(CF) is a specific physical constant; it is an intensive parameter that cannot depend on the substrate or solvent which the RN is diluted in. In order to reach the maximum values of A_S, the radiochemical processing of radioactive material is carried out with no intentional addition of isotopic carrier; the radionuclide (labelled compound) obtained in this way is named No-Carrier-Added (NCA). Conversely, the activity concentration $C_A(t)$ of an RN is the ratio between its activity and the mass (or volume) of substrate or solvent in which the RN is diluted. Many techniques of nuclear and radioanalytical chemistry are based on high values of $A_S(t)$ and their variations during the radiochemical or radioanalytical procedure, while the activity concentration $C_A(t)$ is normally less relevant in this context.

ORGANIC RESIDUES IN ARCHEOLOGICAL OBJECTS

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The chemical analysis of organic residues in association with archaeological potteries and vessels is a precious source of information of archaeological interest. These organic residues can occur as bulks of ancient natural substances, as surface internal coatings or as organic materials adsorbed onto ceramics. The chemical characterisation of raw and man-treated materials provides information on the use of original vessels, diet and technology. Organic natural substances constituted by complex mixtures of chemical components, such as plant resins, waxes and animal fats, are the main materials encountered in this archaeological field. The difficulties of their determination is due not only to the complexity of the natural mixtures, but also to changes in the chemical composition in consequence of human activities and treatments as cooking, heating, extracting or mixing materials aimed at changing their properties for use in art and craft. Moreover, degradation occurring in the course of ageing under the influence of different burial circumstances induces further changes in the composition of the original materials.

For all these reasons, chromatographic techniques coupled with mass spectrometry appear to be the most suitable and used analytical techniques by which to gain information on the presence of specific biomolecular markers of assistance in the identification of materials. This work describes the development of an analytical procedure based on Gas Chromatography Mass Spectrometry (GC-MS) and its application to the characterisation of organic residues adsorbed on potteries. The results obtained for a series of samples from buccaros (Orvieto, Italy, V-VI century BC) and from fragments of ointment jars (Antinoe, Egypt, V-VII century AD) are discussed. The presence of fatty acids, long-chain alcohols and terpenoid compounds as well as their degradation products provide information on the natural substances once stored therein.

CHROMOTROPIC GUAIAZULENE-DERIVED RADICAL SCAVENGERS FOR THE DETECTION OF OXYGEN-CENTRED RADICALS IN MICELLAR MEDIA

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Increasing attention is devoted to minimise biological and non-biological damages that can be associated with oxidative chain reactions induced by free radicals. Such processes can be prevented, inhibited or retarded by the addition of certain compounds known as antioxidants. The radical scavengers are a particular class of antioxidants able to react with a free radical giving rise to a new radical species much less reactive than its precursor, the original radical being transformed into a non-radicalic species. In this connection, sterically hindered phenols play a very important role, their reaction with radicals implying a hydrogen transfer to the reactive radical with formation of the less reactive phenoxyl radical.

The electronic structure of the phenoxyl radical is of course different from that of the starting phenol. Consequently, the electronic properties of a chromophore attached to the phenol skeleton can be markedly modified on passing from phenol to the corresponding phenoxyl radical. Thus, whenever the chromophore absorbs in the visible region, the phenol → phenoxyl radical transformation is accompanied by a significant colour variation. Radical scavengers of this type should then exhibit chromotropic behavior when reacting with free radicals. A variety of phenolic derivatives carrying a guaiazulene moiety 1 have now been prepared starting from guaiazulene. These compounds react with oxygen-centred radicals exhibiting chromotropic behavior. On this basis, a simple colorimetric approach to the detection of oxygen-centred radicals was set up. The corresponding phenoxyl radicals were detected and characterised by EPR.

A CHEMICAL APPROACH TO THE ENVIRONMENTAL IMPACT ASSESSMENT OF ENERGY PRODUCTION

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The chemical approach to the assessment of the impact of energy production on ecosystems and mankind is an important way to assist safety and ecology politics in assuming fit-for-purpose regulations and laws. The new approaches in this context refer to: *i)* radicals production in energy processes; *ii)* integral toxicity following energy reactions; *iii)* degradability of chemicals (reagents and products).

As regards the first point, in a reaction producing energy there are also secondary pathways that can assume significant roles in keeping part of the energy latent and thus dangerously waiting for being delivered. These secondary pathways generally produce radicals, *i.e.*, very reactive chemical species able to react with practically all the substrates and able to damage and alter them. The measurement of their concentration can be assumed as a key piece of information to evaluate the impact of some reactions on ecosystems and mankind. Concerning the second aspect, during and following an energy production reaction different chemicals are formed able, each one and all together with synergic action, to impact on ecosystems. The impact can be thus assessed not on the basis of the causes, but rather of the effects, first of all toxicity to biosystems. The search for a biological monitoring approach able to well represent this impact is more than ever a challenge to the scientific community. From this standpoint, yeasts and algae seem promising biological systems, the impact being measured on the basis of respiratory and photosynthetic activity, respectively. The third point implies that fuels able to be completely degraded to water and CO_2 are much less dangerous than those which produce several different substances each one able to react with ecosystems. The ability to be completely degraded is not an easily measured property. The development of photosensors based on TiO_2 (as anatase) allows this kind of information to be easily obtained by exploiting the property of TiO_2 to simultaneously act as a catalyst and as a pH indicator.

Session 3
Development in analytical instrumentation

DIRECT Hg ANALYSIS BY MEANS OF SOLID SAMPLE ATOMIC ABSORPTION SPECTROMETRY

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Rapid analysis of Hg traces directly on sample as it is can now be performed without any sample preparation. DMA-80 is an Hg analyzer that allows the Hg content to be directly quantified in any kind of samples, either solid or liquid. The instrument does not require any preliminary sample digestion. Controlled heating in an oxygenated decomposition furnace is used to dry and then ash the sample in order to free Hg. Vapors of Hg are reduced to the elemental status and then are trapped by forming an amalgam on an Au support. At the end of the analytical cycle, Hg is rapidly released and conveyed through the reading cells. Absorbance is measured by means of Atomic Absorption Spectrometry at 253.7 nm as a function of Hg concentration. Analytical data obtained in the case of several matrices are presented in order to estimate the accuracy and precision afforded by this approach. The usual working range is between 0 and 3 mg kg^{-1}.

TRACE ANALYSIS OF HYDRIDE FORMING ELEMENTS AND OTHER ELEMENTS BY ICP-AES IN COMPLEX SAMPLES

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The Concomitant Metals Analyser (CMA) is a versatile device for use in Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES) by which a variety of samples can be analysed. A number of examples are given for the quantification of trace elements, including hydride forming elements, by CMA in various matrices. Sample preparation presents some analytical problems for hydride formation of some elements as the oxidation state can affect the final result. Analysis of samples such as cement can be performed and the determination of Te can be carried out, an element rarely determined by hydride generation systems due to its reluctance to form hydrides.

The determination of Hg by CMA in various matrices from waters to soils and ash samples is also discussed. This approach compares well with other accepted methods for Hg, even in the presence of up to 100 µg g^{-1} of Au. This provides good evidence of the fact that the CMA method is plagued by only a few interferences. The CMA system has been applied to clean waters, waste waters and geological samples and proves fit for routine analysis of various sample types. Analysis time is also saved as only one analytical run is sufficient for most elements.

DRC-ICP-MS FOR TRACE ELEMENT ANALYSIS OF ENVIRONMENTAL AND CLINICAL SAMPLES

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The development of ICP-MS instruments with gas-filled cells between the plasma and analyser quadrupoles has shown much promise in reducing polyatomic interferences. Current cell-based ICP-MS systems can be categorised into two classes, depending on the configuration and operating conditions of the cell. The first type of cell system that was developed was the collision cell system. This system evolved from the collision cells that were conceived in the early 1980's for organic mass spectrometry. The second type of system is the so-called Dynamic Reaction Cell (DRC).

An overview is given of performances and advantages of a PerkinElmer DRC-ICP-MS system for trace elements analysis of environmental and clinical samples. A DRC system is one where an active mass-filtering device is placed inside the reaction cell. In the case of the DRC, an active quadrupole is used inside the cell and is controlled to act as a mass filter. The DRC eliminates interferences through two mechanisms, *i.e.*, chemical resolution and Dynamic Bandpass Tuning (DBT). Chemical resolution uses the chemical reactions between the interfering species and the reaction gas to create products that do not interfere with the analytes of interest. The chemical reactions occurring inside the DRC are between ions that are essentially at the thermodynamic equilibrium (also call thermalised ions). This results only in predictable exothermic reactions taking place within the cell. As a consequence, in the DRC the obtainable chemical species are predictable using gas-phase kinetic and thermodynamic concepts and such knowledge is transferable from instrument to instrument.

DBT uses the application of a precisely controlled bandpass mass filter inside the DRC to exclude and eject undesirable species from the reaction cell, preventing the formation of new interferences. The use of an active quadrupole inside the DRC allows a mass bandpass window with both low-mass and high-mass cutoff regions to be established. This mass bandpass window is tunable and changes appropriately with the analyte masses being passed through to the analyser quadrupole. Because undesirable multiple ions can be expelled from the reaction cell, highly reactive gases, such as ammonia, oxygen, methane and others can be used. Applications are described to show how a DRC system allows better Limits of Detection (LoDs) to be obtained for those elements (*e.g.*, As, Cr, Fe, Se) which suffer from spectral interferences in the ICP-MS analysis of complex matrices. Improvement in precision and accuracy of isotope ratio measurements is also discussed.

STATE-OF-THE-ART ICP-MS: A TECHNOLOGY EVALUATION

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Inductively Coupled Plasma Mass Spectrochemistry (ICP-MS) is a multi-element trace and ultra-trace level analytical technique that has been widely applied to environmental monitoring since its development in the early 1980's. Some problems with the use of the technique for environmental analysis include the possibility of interferences derived from the products of chemical reactions in the plasma ion source and sampling interface, *e.g.*, polyatomic interferences. Interference correction techniques have been successfully employed to remove the effects of such problems, but have limitations. Recent instrument developments have given rise to a variety of hardware-based methods of interference avoidance. Such technologies include cool plasma, collision or reaction cells and sector-field (high resolution) mass spectrometry.

The approaches of these techniques are reviewed and examples are given of the advantageous use of each method in order to answer questions such as: *i)* how does each technology work? *ii)* what are the advantages/disadvantages of each? *iii)* where does each technology fit in with environmental monitoring? Data are presented showing that polyatomic interferences on environmentally significant analytes can be removed or resolved using each of the above technologies and that each method can be advantageous in its own right due to preferable removal/resolving characteristics for a particular interferent. In conclusion, high resolution is strictly-speaking the best approach for interference removal, while collision and reaction cells provide a lower cost alternative and some specific advantages.

NEW APPLICATIONS OF LC-ICP-MS IN ENVIRONMENTAL ANALYSIS

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Since its introduction, Inductively Coupled Plasma Mass Spectrometry (ICP-MS) has become rapidly accepted as a sensitive, selective detector for inorganic constituents in varied application areas such as environmental, semiconductor, clinical and geological sample types. These properties makes it an ideal detector for chemical speciation measurements. The application of liquid and gas chromatographic separation of traditional and non-traditional ICP-MS elements, such as As, Sn and P, is illustrated.

Session 4
Residues and contaminants in food

DETERMINATION OF METALS IN SOILS, SEDIMENTS AND MARINE LIFE IN SOUTHWEST LOUISIANA

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Southwest Louisiana has large-scale oil and gas drilling facilities and large chemical industries. The need for such products and the lax or absence of environmental regulations until the late 1960's - early 1970's, has led to widespread introduction of pollutants, particularly metals, in this area. This is also a productive area for shrimps, fish, oysters and other marine species. Soils and sediments represent concentrated reservoirs for metals that serve as sinks for introduced trace metals or can become environmental sources.

The area provides a "living laboratory" to investigate the transport, deposition and dissolution of metals into this fragile environment. Results of previous studies and ongoing studies on selected metals, notably Cr, Cu, Fe, Mn, Pb and Zn in soils and sediments as well as marine life in Southwest Louisiana, as determined by various atomic spectroscopic techniques, are presented.

PERSISTENT ORGANIC POLLUTANTS IN EDIBLE FISH: A HUMAN AND ENVIRONMENTAL HEALTH PROBLEM

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There is an important relationship between human and environmental health. Many Persistent Organic Pollutants (POPs) pose serious health risk to the environment and mankind. Among them, Polychlorobiphenyls (PCBs) are probably human carcinogens and can also pose non-cancer health hazards to brain functions and the nervous, immune and reproductive systems. Polychlorodibenzo-*p*-dioxins (PCDDs) and Polychlorodibenzofurans (PCDFs) can also cause severe reproductive and developmental problems (at a level two orders of magnitude lower than those associated with its cancer causing effects). PCDDs can cause immune system damage and interfere with regulatory hormones. The Environmental Protection Agency (EPA) confirmed that these substances are a cancer hazard to people. The International Agency for Research on Cancer (IARC) announced on February 14, 1997, that the most potent compound of this type, *i.e.*, 2,3,7,8-TCDD, was to be considered a Class 1 carcinogen, meaning by this a "known human carcinogen".

The risks associated with residues of POPs in tissues are a function of toxicity and individual exposure. Fish consumption might become a serious problem because of bioaccumulation phenomena, as reported by many studies worldwide. Data concerning POPs accumulation and patterns in edible tissues of several commercial fish species from the Mediterranean Sea and in *Dissostychus mawsoni* (toothfish) from the Ross Sea (Antarctica) have been obtained. The species analysed are part of the human diet (even if the Antarctic toothfish is not yet consumed in Italy at the moment). 2,3,7,8-TCDD toxic equivalents (TEQs) were also calculated to evaluate the toxic hazard to the consumer.

A CRL-IRMM JOINT PROFICIENCY TEST FOR TRACE ELEMENTS IN FISH TISSUE

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The Community Reference Laboratory (CRL) for residues and contaminants in food of animal origin at the Istituto Superiore di Sanità (ISS) plans and undertakes on a regular basis Proficiency Tests Schemes (PTSs) focused on the residues under its responsibility, as prescribed by the Council Directive 96/23/EC of 29 April 1996. In consideration of the benefits ensuing from a constant monitoring of the daily activities of the National Reference Laboratories (NRLs) for residues in the Member States, the ISS-CRL frequently prepares test materials in order to promote comparability of data and support harmonisation of routine analytical procedures. When an assigned value is available, the PTSs also provide objective assessment and improvement of the analytical trueness in the daily work.

In this context, an intercomparison exercise for trace elements in tuna fish matrix was undertaken in cooperation with the Institute for Reference Materials and Measurements, Joint Research Centre, European Commission (IRMM-JRC-EC). The goal of this PTS was to check the analytical performance of the NRLs in the case of real-world matrices. Approximately 360 kg of tuna fish, collected 40 miles off Faial Island (Horta, Portugal), were freeze-dried, ground, sieved, homogenised and bottled under argon atmosphere by the IRMM. Bottles containing each 15 g of freeze-dried material were sent out to the NRLs for chemical elements in the Member States and also to some voluntary public laboratories. Participants were requested to carry out at least three independent measurements, using the same calibration curve, of the elements As, Cd, Cr, Cu, Fe, Hg, Pb and Zn. The assigned value was obtained by agreement among results provided by a number of expert laboratories selected by the IRMM. The assessment of the performance was based on the *z*-score approach and the 10 % standard deviation was deemed to be a reasonable uncertainty for this kind of measurements.

EFFECTS OF PROCESSING ON THE CONTENT OF METAL CONTAMINANTS IN FOOD: THE CASE OF PASTA PRODUCTION

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The increasing demand for pasta and the growth of production and marketing call for strengthening of industry quality control programmes to ensure food quality and safety. As regards safety, one critical issue is the extent of possible contamination by heavy metals that are able to exert toxic effects following prolonged chronic exposure. The European regulation on contaminants in foodstuffs sets statutory limits for those elements that on the basis of the available knowledge most likely represent a potential threat to the public health. These limits apply to selected staple foods, whilst for final products the allowable levels must be derived taking into account the changes of the contaminant concentration caused by processing. However, information on the latter point is still inadequate.

In this frame, the effect of milling and pasta processing on the concentration of selected metal contaminants in pasta was studied. Five metals, namely Cd, Cr, Fe, Ni and Pb, were quantified along the pasta processing chain, from durum wheat grain to the final product. Cadmium and Pb are well-known toxic elements and the above mentioned European regulation established maximum levels for these metals in wheat grain. Chromium, Fe and Ni were included in the study as markers of metal release from equipment during processing. Durum wheat grain, semolina and pasta were sampled at an industrial plant for milling and pasta making. Samples were taken at different stages along processing in order to elucidate the influence of each stage on the element content. Samples of the water used for grain tempering and dough preparation were also collected. The entire procedure was performed according to a pre-established quality assurance scheme.

Grain and pasta were homogenised for subsampling and submitted to closed vessel Microwave (MW) digestion. The same dissolution technique was used for semolina. Analyses were performed by Inductively Coupled Plasma Mass Spectrometry (ICP-MS) resorting to both pneumatic and ultrasonic nebulisation for sample introduction. Milling was the key process influencing the concentrations of the studied elements and reduced the metal levels according to a definite element-specific pattern. For a given extraction rate, the percentage decrease in concentration was also dependent on the metal amount originally present in the grain. Purity of the water used as ingredient, element deposition from plant air and metal release from equipment were identified as critical issues in contamination control during processing. The effect of all these sources can be easily minimised in modern plants thus ensuring the highest safety of pasta from the standpoint of metal contamination.

CHEMICAL SPECIATION OF As IN RICE

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Relatively high amounts of As are contained in rice when compared to other foodstuffs. The identification and quantification of the various chemical species that may occur in rice and that possess different toxicity can provide an insight into the actual safety of its consumption, in particular from a regulatory point of view. The accuracy of measurement of As chemical species in rice would greatly benefit from the availability of fit-for-purpose Certified Reference Materials (CRMs). A study was thus undertaken to develop a method for the chemical speciation of As in rice on the basis of current knowledge in this field that might be exploited for preparing a CRM of this kind.

Samples of the Arborio rice variety were finely ground and the powder thus obtained was in turn extracted under sonication with a 1:1 (v/v) water-methanol mixture. The resulting solutions were separated by High Performance Liquid Chromatography (HPLC) and their concentrations determined by Quadrupole Inductively Coupled Plasma Mass Spectrometry (Q-ICP-MS), combined on-line with the former technique. This hyphenated system allowed for the quantification of As species in one analytical step. Four forms of As could be detected, *i.e.*, inorganic As (III), inorganic As (V), dimethylarsinic acid and monomethylarsonic acid at concentrations of 88.2 ± 7.1, 51.2 ± 3.5, 50.8 ± 5.0 and 15.2 ± 1.7 ng g^{-1}, respectively. The concentration of total As was found to be 211 ± 7 ng g^{-1}. This investigation was carried out in the frame of an EC feasibility project on CRMs for As and Se species.

DETERMINATION OF TRACE ELEMENTS IN OLIVE OIL BY ICP-AES AND ETA-AAS

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The determination of trace elements in edible oils is important because of the metabolic role of metals as well as for adulteration detection and oil characterisation. The most commonly used techniques for the determination of metals in oil samples are Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES) and Electrothermal Atomisation Atomic Absorption Spectrometry (ETA-AAS).

Among the different methods of sample preparation, Microwave (MW) digestion in a closed system is the most accurate procedure for the total recovery of the elements. An MW decomposition method of the edible oils in closed vessels was developed using a mixture of HNO_3 and H_2O_2. This digestion method effectively destroys the organic matrix of the samples. The procedure is simple, repeatable and relatively fast and no significant losses of the analytes are observed during the digestion step. The Limits of Detection (LoDs) achievable enable the determination by ICP-AES of even very low concentrations of most elements of interest in samples of olive oil. The proposed ICP-AES method permits the determination of Ca, Fe, Mg, Na and Zn. By this method the results for olive oil were (in $\mu g\ g^{-1}$) 2.1, 15.2, 3.3, 33.9 and 3.5 for the above elements, respectively. Elements present at small concentrations can be measured by ETA-AAS in the same sample digest. The concentrations of Al, Co, Cu, K and Ni measured by ETA-AAS in olive oil were in the range 0.15 - 1.5 $\mu g\ g^{-1}$. These results can be used for further evaluation of edible oils.

ASSESSMENT OF DIETARY INTAKE OF OCHRATOXIN A BY THE POPULATION OF EU MEMBER STATES: SCOOP TASK 3.2.7.

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According to Council Directive 93/5/EEC Member States of the European Union can cooperate on problems challenging the Commission in the area of food through the development of specific tasks. Commission Decision 1999/143/EC established Task 3.2.7 *Assessment of dietary intake of Ochratoxin A (OA) by the population of EU Member States*. Italy was designated as Coordinator. The aim of Task 3.2.7 was to collect and critically evaluate information available at European level both on the OA occurrence in susceptible food and on consumption of such food, in order to draw conclusions on the best estimate of dietary intake for OA by the population of EU Member States.

A total of 18,599 occurrence data were gathered and processed (positive food samples, 48 %) in order to obtain information on the food items more relevant for the OA intake both from general population and from specific groups of consumers. The contribution of each food group to the total dietary intake was as follows: cereals (50 %), wine (13 %), coffee (10 %), spices (8 %), meat (1 %), beer (5 %), cocoa (4 %), dried fruits (3 %) and others (6 %). As for the exposure assessment, the OA intake for general population and for specific groups of population in each participating Member State was evaluated. By comparing the suggested maximum TDI of 5 ng kg^{-1} (body weight) day^{-1}, provided by the Scientific Committee for Food (EU), with the results of this study, the mean dietary intake of the European population was below the indicated value, even though in some countries a high level close to TDI was observed for specific groups of population. In addition, although many data were available, no participating country could provide data on all the interested commodities, therefore leading to a potential underestimation of the overall dietary intake. The full report of Task 3.2.7 is available on Internet.

DETERMINATION OF OCHRATOXIN A IN HUNGARIAN WINES

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Ochratoxin A (OA) is a mycotoxin produced by several fungi (*Penicillium* and *Aspergillus* species) with carcinogenic, nephrotoxic, teratogenic, immunotoxic and possibly neurotoxic properties. It occurs naturally in a variety of plant products, such as cereals, coffee beans, cocoa beans and dried fruit. It has been detected in many commodities, *e.g.*, cereals, coffee, wine, beer, spices and grape juice and also in products of animal origin. Investigations of the frequency and levels of occurrence of OA in food and human blood samples indicate that foodstuffs are frequently contaminated. OA may also have a long half-life in humans. The European Commission has already fixed maximum levels for OA in raw cereal grains, cereal products and dried vine products. Furthermore, maximum levels for coffee, wine, beer, grape juice, cocoa and spices shall also be introduced in the near future. (EC Regulation No. 472/2002 of 12 March 2002).

Up to date there are no representative data sets available on the OA content of Hungarian wines. Therefore, the aim of this work was the determination of OA in Hungarian wines to evaluate their conformity with EU regulations after the introduction of maximum levels for OA. Considering the forthcoming accession of Hungary to the EU this aspect has become even more important. High Performance Liquid Chromatography (HPLC) with fluorescence detection preceded by extraction of OA using a commercially available immunoaffinity column has been quite popular so far, but the method is too slow and too expensive for large sample batches, not to speak of its often poor reproducibility. The applicability of common C18-SPE for sample clean-up and concentration followed by HPLC analysis is discussed.

OCHRATOXIN A OCCURRENCE IN HUNGARIAN AND ITALIAN RED WINES

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It is well recognised that the occurrence of Ochratoxin A (OA) in food can seriously impair human health. According to surveys carried out in many countries world-wide, OA can contaminate many agricultural commodities including maize, wheat, barley, beans, coffee, beer and cocoa. However, because of many possible sources of errors or lack of information (reliability of sampling procedures and of analytical data, influence of technological procedures, lack of consumption data) the major food sources of OA intake for humans are still controversial. More recently the presence of OA in wine has received increasing attention, since it is considered to be an additional source of OA for those countries characterised by large consumption of this beverage. This study was carried out with the aim of obtaining information on the exposure of the Italian population to this source of OA.

Two hundred red wines and one hundred Hungarian red wines were collected in different geographic areas of the two countries. All samples were analysed by adopting an in-house validated method using High Performance Liquid Chromatography (HPLC) with fluorescence detection for the quantification step. Recovery factors were calculated at 0.1, 0.5 and 1 ng ml^{-1} spiking levels. The Limit of Detection (LoD) of the method was 0.01 ng ml^{-1}. Calculation of the results was made by linear regression analysis interpolating experimental data with a calibration curve. A confirmatory step was used to assess the identity of OA peaks by the formation of OA methyl ester derivative. The output of the study provides direct information on the efficiency of Good Agricultural Practice (GAP) and Good Manufacturing Practice (GMP), these being the pivotal starting point for achieving hygienic quality of food products. From a general viewpoint, a number of issues are still open to debate, *i.e.*: *i)* setting up of monitoring plans for the risk characterisation of OA in wine; *ii)* identification of geographical areas at risk in both countries for a more accurate implementation of surveillance plans; *iii)* performance of the analytical methodology for OA determination in wine samples; *iv)* thorough assessment of the exposure of the consumers.

A METHODOLOGICAL APPROACH FOR THE DETECTION AND DETERMINATION OF ANTIBACTERIAL DRUG RESIDUES IN ANIMAL FOODS

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Antimicrobial drugs are widely employed in the treatment of food producing animals and as nutrition additives. This massive use inevitably leads to residues in food. The presence of antimicrobial drug residues causes concerns for the consumer's health. Thus, the UE has introduced in its legislation the concept of maximum tolerable concentrations of residues in foods, *i.e.*, the Maximum Residue Levels (MRLs). In this context, major concerns are the possible allergic phenomena for exposed individuals, the risk of selecting antibiotic-resistant bacteria and the selective pressure that drug residues may exert over human gut microflora. For an accurate risk assessment of eating food containing antimicrobial drug residues it is therefore necessary to have suitable methods for monitoring residues in food.

Only a few years ago, food control for antimicrobial residues in most countries was based almost exclusively on microbiological methods. More recently, several sensitive, accurate and automatable analytical methods have become available for routine monitoring programmes. Suitable spectrometric confirmation methods, which are useful for unambiguous identification are also more and more being developed. At present the analytical approach adopted in the UE for the detection and determination of antimicrobial residues in foodstuffs includes three sequential steps, *i.e.*, screening, post-screening and confirmation. A screening method is defined as the procedure that is applied to sample analysis, the purpose being to establish the presence or absence of residues of veterinary drugs. When a positive result is obtained with the screening method, the post-screening method should be applied to identify specific antibiotics or antibiotic groups before a confirmatory method, usually a physical-chemical technique, is used for full identification and determination.

NATURAL PRESENCE OF NIACIN IN RAW AND CURED MEAT

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The amount of niacin in samples of raw and cured meat was quantified in order to ascertain the baseline levels of this substance in the various organs and tissues of pigs. At the preliminary stage, analytical methods were reviewed and those fit-for-purpose were validated. Sampling criteria were then set and slaughterhouses were selected from which meat should be sampled.

It was thus possible to achieve a reference range for the content of niacin in cured pork meat on the basis of which conformity of meat products with current legal provisions can be checked.

Session 5

Pollution monitoring in urban and suburban settings

MONITORING OF SURFACE WATERS BY BIOFILMS

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Biofilms are formed on the surface of artificial or natural substrates located in the photolytic layer of surface waters. The main components of biofilms are bacteria, algae and their metabolic products (*e.g.*, polysaccharides, lipids, proteins *etc.*). These last compounds form the so-called Extracellular Polymeric Substance (EPS) matrix. Due to the large number of functional groups (carboxyl, hydroxyl *etc.*) the EPS matrix has an excellent chelate-forming ability. Metal ions and different organic residues (*e.g.*, pesticides, herbicides) can bind to the biofilms. It should be emphasised, however, that not only the EPS matrix, but also microorganisms are able to accumulate various contaminants from the surface waters.

In order to use biofilms for monitoring of water quality of lakes or rivers, it is necessary to understand their formation and the colonization processes of microorganisms and to know exactly what properties of the substrates can influence the colonization and the biomass production of the microorganisms. From a biological point of view the biofilm formation is successful provided that the microorganisms living in the surface water are substantially present in the biofilm. In this case the algological and bacteriological investigations result in reliable biological information about the possible ecological changes. In this context, chemical investigations of biofilms are useful to find the critical impurities through the application of modern analytical techniques. For trace metal determination Total-Reflection X-Ray Fluorescence Spectrometry (TRXRFS) and Inductively Coupled Plasma Mass Spectrometry (ICP-MS) are recommended due to their excellent analytical capabilities, *i.e.*, fit-for-purpose Limits of Detection (LoDs) and multielemental ability. Organic contaminants need more sophisticated analytical procedures, their separation from the matrix being a critical step. Their determination can be carried out by Gas Chromatography-Mass Spectrometry (GC-MS) or Liquid Chromatography Mass Spectrometry (LC-MS).

The results of the Velence lake project are presented and discussed. The biofilms were grown on a polycarbonate substrate at a depth of 20-30 cm. During a nine weeks-long growing period, two substrates were removed weekly from the lake. The total biomass production achieved its highest value after seven weeks. Calcium, Sr and Ti, as well as Fe, K, Mn and Zn showed their maximum concentrations in the biofilms after five and six-seven weeks, respectively. The enrichment factor of the six weeks-old biofilm for the said elements amounted to 103-104. The recommended colonization time for biomonitoring of the lake Velence is six weeks when applying polycarbonate substrates. The dominant algal species were found to be: *Achnantes minutissima*, *Entomoneis costata*, *Amphora pediculus* and *Entomoneis alata*. In the second phase, four weeks-old biofilms grown in the lake on polycarbonate substrates were transported to the laboratory and their growth went on under controlled conditions in Ni and Pb contaminated (10^{-5} *M*) lake water. Nickel resulted in about 14 % reduction in the biomass production, while the effect of Pb was negligible. The concentration of Zn in the biofilm decreased by about 20 % in presence of Ni or Pb, whereas the concentration of other essential elements remained unaltered.

The effect of the substrate on the colonization processes of microorganisms and the biomass production was also studied. Granite, andesite, plexiglas, polycarbonate and old reed were investigated. The total biomass production achieved its highest value in the case of andesite. On the other hand, the abundance of algae was the highest on the surface of polycarbonate films. The concentrations of C, Fe, K, Mn, Rb, Ti and Zn were very high also in case of andesite. The change in element concentrations related to biofilms on old reed surfaces ranged from – 2 and + 25 %. Since the biodiversity of bacteria in the biofilms in the case of granite was the highest and the differences in element concentrations for biofilms grown in granite and andesite were relatively low, granite substrates were selected for future investigations.

CHLORITE AND CHLORATE IN WATERS DISINFECTED WITH CHLORINE DIOXIDE

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The continuing diminishing sources of fresh waters has stimulated the search for unconventional water resources, such as effluents from municipal sewage treatment plants, which can be reused for purposes of irrigation in agriculture, cooling water in industry, groundwater aquifer recharge and, in the long term, even for drinking water. The main problem of using effluents is the presence of pathogenic bacteria and viruses that can affect human and animal health. Therefore, disinfection has been used for many years to control and reduce waterborne diseases.

At the moment, most water treatment plants use NaClO as their primary biocide. However, the toxicity of chlorinated organic compounds produced during the treatment has led to increased interest in the use of alternative agents. One possible candidate as viable substitute of free Cl_2 is ClO_2, which is not expected to produce trihalomethanes and other chlorinated organics. Before this disinfectant can be recommended for routinary use, it is imperative that its safety be assessed. In particular, more data on formation and persistence of its inorganic by-products (chlorite and chlorate) are needed to foresee further potential health hazards. In this research the presence of chlorite and chlorate in sewage waters disinfected with ClO_2 has been investigated. The effect of initial concentration of biocide and contact time was evaluated using a pilot plant fed with the effluent of a municipal treatment plant. Moreover, the influence of the ClO_2 generator performance was assessed.

DETERMINATION OF EPICHLOROHYDRIN IN WATERS INTENDED FOR HUMAN CONSUMPTION

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According to the latest European Directive on the quality of waters intended for human consumption, the maximum concentration of epichlorohydrin (ECH) in drinking water cannot exceed 0.1 mg l^{-1}. Its presence in drinking water has become a concern since toxicological studies showed its adverse effect on skin, liver, kidneys and the central nervous system. It has recently been supposed that ECH may cause chromosome aberration and cancer. A possible route by which epichlorohydrin may reach drinking water is *via* epoxy resins currently used to shield tanks and to repair plastic pipes. Moreover, ECH can be found in waters treated with hydrophobically modified cationic polyelectrolytes if complete coagulation does not occur.

Few methods for ECH determination in aqueous solutions have been described in the literature. None of them seems adequate to achieve the necessary limit of quantification without resorting to preconcentration techniques that can introduce contaminants and artifacts or cause analyte losses. This study has assessed the analytical performance of a dynamic headspace-sampling device coupled to Gas Chromatography with Electron Capture Detection (ECD-GC). The effect of different parameters that control the detector response (make-up gas flow, temperature and anode gas flow) and purge-and-trap sampler performances (sample temperature and salinity, purge pressure and flow, purge and desorb times) on ECH response have been investigated and discussed. The proposed procedure enables the quick quantification of ECH in concentrations lower than the European legal limit and does not require large sample volumes.

FRACTIONATION OF ENVIRONMENTALLY MOBILE HEAVY METALS IN SEDIMENTS BY MEANS OF SEQUENTIAL EXTRACTION WITH SUPERCRITICAL CO_2 AND SUBCRITICAL H_2O

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The toxicity of heavy metals accumulated in surface water sediments is strongly influenced by the chemical form under which they occur. Sequential extraction procedures which are applied for the fractionation of trace metals generally are not suitable to extract the intact species as necessary for further ecotoxicological tests. A new sequential extraction scheme is reported which is based on the application of supercritical CO_2, subcritical H_2O and subcritical mixture of H_2O and CO_2. This is expected to have a potential also for the extraction of intact species forms. The performance of this procedure has been compared with that of the BCR-recommended three-steps sequential extraction procedure; this last is practically a stepwise decomposition procedure and therefore the extracts cannot be used for further ecotoxicological testing. The new procedure gives more detailed information about environmentally mobile (water-soluble, bicarbonate-forming) fractions and the extracts can be used for ecotoxicological studies.

Environmental Stable Isotope Metabolic Assay (ESIMA) and Pollen Tube Growth (PTG) ecotoxicological tests were applied to extracts obtained from river (Saale, Tisza) and lake sediment samples. According to the preliminary results the pore water extracts in the sediments polluted by heavy metals have been shown to be significantly toxic. It is expected that in extracts obtained by subcritical water these effects can also be detected. Subcritical water extracts has shown similar ecotoxicity in the PTG test, but the effects of different pollen charges were significantly different. By the ESIMA test the ecotoxicity of water extracts could be detected directly in hydrocultures and sediment. These results allow the conclusion to be drawn that the BCR fractionation procedure overestimates the risk caused by mobilization of heavy metals in the aquatic environment, whereas the new fractionation procedure better highlights the ecotoxicological potential due to heavy metal mobilization.

As, Hg, Tl AND Zn CONTAMINATION OF STREAM SEDIMENTS AND RESIDUAL SOILS IN SUBURBAN AND TRANSITIONAL AREAS OF CENTRAL ITALY (MIGNONE RIVER BASIN, LATIUM)

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Geochemical mapping of 37 elements (*aqua regia* extraction and Inductively Coupled Plasma-Mass Spectrometry, ICP-MS) determined on samples of stream sediments (fraction <150 mm) from the basin of the Mignone river (Latium, Italy) has shown, in the area close to the towns of Tolfa and Allumiere, high levels of As, Hg, Tl and Zn which exceed the threshold values fixed by the Italian Law for contaminated soils. Sulphides mineralizations, exploited in this area since the Etruscan age, should be considered as the main sources of sediment contamination. On the other hand, local anthropic activity (*e.g.*, tanning factories using As-enriched chemicals) could also contribute to the levels observed in stream sediments.

By considering the extension of the basin from which the samples were taken, a further survey was focused on residual and sedimentary soils of the Tolfa-Allumiere area. Soil sampling was based on the physiographic and the geological units and took into account land use instead of geostatistical approach based on a regular grid. Topsoil (0-2 cm) and subsoil (>30 cm) were collected and analysed in order to identify local anomalies and background components whereas air-mobilised soil dust was sampled to assess potential hazard deriving from inhalation and ingestion of soil particles containing As, Hg, Tl and Zn. Local administrations can use the results of this research to correctly plan land management in order to minimize the local intake of potentially toxic elements which should be considered among the environmental factors responsible for the quite high rate of mortality in the area due to respiratory tract and lung cancer.

MATERIAL TRANSPORT BETWEEN THE ATMOSPHERE AND SEDIMENT OF THE LAKE BALATON

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A monitoring system has been developed to gain information on the present level of harmful or potentially harmful pollutants in discharges to the Lake Balaton, or within the lake itself. Determination of 15 organic pollutants (PAHs) and inorganic pollutants (mostly toxic metals) in aerosol, precipitation, water and sediment samples collected at and around the Lake Balaton was carried out. The aim of collecting aerosol and precipitate samples in the same site at the same period was to determine the distribution of elements in two depositions. For fractionation by particle size, aerosols were sampled by a cascade impactor. A simple three-stages sequential leaching procedure was applied to establish the distribution of metals among environmentally mobile (1), bound to carbonates and oxides (2), and environmentally immobile, (bound to silicates) (3), fractions in aerosols. The comparison of dry and wet depositions showed that the ratio of D_{dry}/D_{wet} is significant, in particular, for Al, Cu and Fe, indicating that the dry deposition plays an important role. The soluble fractions of depositions ($D_{drymobile}+D_{wet}$) were compared to the total depositions ($D_{dry}+D_{wet}$) and it was found that 85-94 % of toxic elements could be dissolved in the water. Seasonal changes of the concentration of PAHs in aerosols can be observed. Samples collected during the winter contained the highest values.

Sediment samples were collected from the top 10 cm layer of the bottom of lakes. In a special sampling programme core samples were collected from 15 different sites inside the lake and 10 sites in harbors at a depth of 60-70 cm. Core samples were cut into 10 cm pieces, dried at room temperature, then stones and plant fragments were removed by passing the dried sample through a 2 mm sieve. The sieved sample was powdered and finally passed through a 63 μm sieve. A four-steps sequential leaching procedure was applied for the determination of the distribution of the elements. Particular attention was paid to distinguish between environmentally mobile and environmentally immobile fractions. The results of the sum of four fractions of bottom sediments of the Lake Balaton, rivers on its catchment's area and harbors were compared to Sediment Quality Values (SQVs) and Sediment Background Values (SBVs). Data showed that the average concentration of elements was usually less than that of SQVs and other background data for soils and geochemical values. The sediment is therefore unpolluted and its disposal on the soil is feasible. The low metal concentration of sediments correlates well with the finding that the major part of the dry and wet deposition is water-soluble. On the basis of these results, it can be definitely confirmed that the quality of the water and sediment of the Lake Balaton is satisfactory.

TWO-YEARS MEASUREMENTS OF PM10, PM2.5 AND ULTRAFINE PARTICLES AT TWO SITES IN MUNICH

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Various epidemiological studies have shown associations between daily ambient concentrations of particles and mortality. There seem to be stronger associations with particle size PM2.5 compared to PM10, but ultrafine particles (diameter less than 0.1 µm) may be also important. In order to ascertain potential health effects of different PM size fractions a longitudinal study (CorPuScula) was conducted with a group of 50 elderly persons and 50 children in Munich (Germany). Concentrations of PM10 and PM2.5 (9 am - 9 pm means) were measured gravimetrically with low volume samplers at two sites. One site (June 2000 till July 2001) was located in a northern part of Munich, the other site (September 2001 till August 2002) in the East. Ultrafines were measured with a particle counter (TSI) at a distance of about 3 km from the first site and directly at the second one.

PM10 concentrations ranged between 1.8 and 92.4 µg m^{-3} at the first site and between 1.9 and 102.9 µg m^{-3} at the second one. The median value was 17.0 µg m^{-3} at both locations. For particle fraction PM2.5 the ranges were 1.1 – 81.2 µg m^{-3} (median 11.6 µg m^{-3}) and 0.4 – 94.2 µg m^{-3} (median 12.0 µg m^{-3}). At both sites PM10 and PM2.5 were significantly correlated ($r = 0.90$ and $r = 0.93$, respectively) with PM2.5 accounting for 76 % (respectively 79 %) of PM10. Correlations of the PM10 fraction with a network station of the Bavarian State at a distance of 7 km were highly significant as well ($r = 0.94$ and 0.91). Measurements of total particle numbers, which are mainly represented by ultrafine particles, were correlated weakly with PM10 or PM2.5 ($r = 0.57$) at the first site, but not correlated ($r < 0.1$) at the second one. The range of particle counts was 5500 to 86,000 per cm^3 for the 24 hr average at both sites. The median values (24 hr) were 19,930 and 20,553 cm^{-3}. The maximum number for one minute measurements reached 115,000 cm^{-3}. The major conclusion of these data is that concentrations of particle fractions PM10 and PM2.5 are not clearly correlated with concentrations of ultrafine fractions. This suggests that there are different sources of these particle fractions.

TRACE ELEMENT ANALYSIS OF AIRBORNE DUST AND OTHER SOLID SAMPLES IN SLURRY FORM BY ELECTROTHERMAL ATOMISATION ATOMIC ABSORPTION SPECTROMETRY

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To avoid time consuming sample preparation, risk of contamination and dilution of samples an Electrothermal Atomisation Atomic Absorption Spectrometry (ETA-AAS) method has been elaborated for the direct analysis of powdered solids. For exact weighing of solids in the graphite furnace, the powdered samples were converted into a stable slurry form. Automatic sampling and dilution of slurries were carried out by means of the USS-800 Ultrasonic Slurry Sampler, which is fitted to the PerkinElmer AAnalyst 600 Transversely Heated Graphite Atomiser (THGA) with Zeeman background correction. The samples studied were marine sediments, airborne dusts and rice powder. These samples contain inorganic, mixed and organic matrices. The particle size distributions are also different. Marine sediments pretreated to be a candidate Certified Reference Material (CRM) are ideal for solid sampling analysis because they are a very fine grain powder. The average diameter of the particles are less than 10 μm. A 1:1 ethanol-water mixture was found to be a useful medium to form a stable slurry from all three type of powders.

To assure the accuracy of slurry analysis, the samples were also digested in Microwave (MW) system. Calibration for slurry analysis was carried out with CRMs as well as with plain nitrate solutions. Furnace heating parameters, rate of slurry and dilution sample volume were optimised by checking the accuracy and precision of the analysis for Ag, Ba, Cd, Co, Cr, Cu, Pb, Sr and Zn. The optimal volume of the slurry for the analysis depends on the analyte concentration of the original sample. For the major components this is about 15 μl, whereas for trace components 35-40 μl are preferred. The stability and lifetime of slurries significantly increased with their dilution. The shape of absorbance signals of analytes has been studied and compared for a variety of samples, in different matrices. In some cases these shapes were similar for the nitrate solution and for the slurry. This fact explains the good analytical results obtained for some elements in the slurry after calibration with nitrate solution.

INNOVATIVE STABILIZATION-SOLIDIFICATION PROCESSES OF SOLID RESIDUES PRODUCED BY AN INCINERATOR PLANT OF URBAN SOLID WASTE

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Incineration is a suitable and effective procedure for the treatment of Urban Solid Waste (USW) since it allows USW to be reduced in volume and weight by a factor of about three. Moreover, the coupled energy recovery unit which is mandatory in modern plants makes them economically almost self-sustained, once the plant has been established. In this respect, it is also worth noting that modern incinerator plants are very effective in reducing the content of unwanted chemicals in the fumes well below the law limits. However, fly ash and a limited amount of sludge are produced in this process. These residues are classified as hazardous waste owing to the content of heavy metals and, to a lesser extent, of organic pollutants.

Over the past few years, various Stabilization/Solidification (S/S) processes of fly-ashes have been developed in order to obtain materials that might be disposed of in ordinary landfills. These procedures, however, have proven to substantially increase the volume and the weight of the waste, causing disposal to be again expensive and to produce a material that might still be very hazardous for the environment. Consequently, the primary objective is to define innovative formulations that succeed in assuring the reduction of pollutant concentration in the leaching solution below the regulation limits without losing the advantages of the incinerator process in terms of weight and volume. They should also possibly provide a better compressive strength of the final material, which is critical for its beneficial recycling instead of landfill disposal. In this study, the optimised formulation of the classical Portland cement-based process of fly ash S/S is presented, along with a very innovative formulation based on a polymer incapsulation process which allows the release of toxic metals, *e.g.* Cd, Cu and Pb, to be reduced by a factor of ten and the compressive strength to be increased by the same factor.

OCCURRENCE OF ATMOSPHERIC PCDDs AND PCDFs IN ROME BEFORE AND AFTER THE BAN OF LEADED GASOLINE

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The source of Polychlorodibenzo-*p*-dioxins and Polychlorodibenzofurans (PCDDs, PCDFs) in automotive exhaust is not yet fully explained. The chlorinated hydrocarbons used in the formulation of Pb-alkyl additives have been indicated as a possible major source. Based on this, the decreasing use of leaded gasoline followed by its final ban (enforced since 1 January 2002 in Italy) should have implied a decreasing presence of PCDDs and PCDFs in urban air and possibly some difference in their profile. To investigate this aspect, particulate phase PCDDs and PCDFs were monitored during one year since September 2001 at a medium-traffic road site in Rome at a weekly frequency. Results were then compared with those obtained in a previous study performed before the ban (from February 2000 to January 2001) at the same site.

The yearly-averaged overall PCDDs and PCDFs concentration, expressed as Toxic Equivalents (TEs) of 2,3,7,8-TCDD, resulted in a small decrease as compared to the previous study (TEs, 53 *vs*. 60 fg m^{-3}), compatible with the expected interannual variability. The monthly trend confirmed the one found in the former study. On an annual basis, the two contamination profiles were almost identical, exhibiting a typical particulate congener distribution in urban air. The similarity of concentration levels and profiles between the two periods may be due to the predominant use of unleaded gasoline already occurring before the ban of leaded gasoline, which implies a small or not detectable variation in PCDDs and PCDFs presence in air before and after the ban, or to a minor role of Pb-alkyl additives in the air pollution by PCDDs and PCDFs.

DEVELOPMENT OF AN X-RAY FLUORESCENCE METHOD FOR THE ANALYSIS OF ATMOSPHERIC AEROSOL SAMPLES

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Appropriate techniques for direct determination of the inorganic components of atmospheric aerosols are Proton Induced X-Ray Emission (PIXE), Total X-Ray Fluorescence (TXRF), X-Ray Fuorescence (XRF) and Instrumental Neutron Activation Analysis (INAA) Morphology of airborne particulate could be determined by X-Ray Diffraction (XRD), Area Source Emission Model (ASEM) and Analytical Transmission Electron Microscope (ATEM). In general, Nuclepore filters were used for PIXE analysis and cellulose nitrate filters for TXRF. Whatman and teflon filters were used for other analyses. Also Inductively Coupled Plasma (ICP) techniques and Atomic Absorption Spectrometry (AAS) allowed the elemental composition of airborne particulate to be determined, but sample preparation is unavoidable. The greatest advantage of the direct determination is that sample preparation is not necessary in the case of small amounts of sample, thus minimising errors. Moreover, depending on the concentration, a wide range of elements (from O to U) can be determined by these methods. Nowadays, the XRF methods can quantify small amounts of sample and also thin samples in consequence of the smaller distance between the X-ray tube and the sample and of improved hardware and X-ray tube performance.

A simple and rapid method was development for the analysis of aerosol samples by XRF. The instrument employed was a PHILIPS PW 2404 type XRF spectrometer equipped with a Rh (4 kW) tube. Two different filters (Whatman, Teflon) and a Prolene® foil, developed by Philips, were used. The calibration procedure was carried out with standard multielemental solutions. 500 µl of solution were dropped onto the sample supports and dried at ambient temperature. The elements measured were Al, Ca, Co, Cr, Cu, Fe, K, Mn, Na, Ni, Pb, Sr and Zn. Blank values and the intensity of signals were measured in order to optimise the working parameters (excitation conditions, measurement time). The filter samples were coated by a Re or Ta layer so as to make them of *infinite thickness* as regards the penetration depth of the X-ray beam. The Re and Ta plates served as secondary targets as well. The accuracy, precision and detection limits (0.01-0.18 µg g^{-1}) were better in the case of the Teflon filter and the Prolene® foil rather than for the Whatman filter.

HEAVY METALS AS TOXICANTS IN BIG CITIES

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Heavy Metals (HMs) can cause very detrimental effects on human health and the environment. Their ecotoxicological properties are in general well known. On the other hand, as regards human toxicology, new aspects should be taken into account, such as gender and age dependence. The chemical risk posed by HMs can be expediently estimated through the scheme of J. Morgan. In this context, the importance of the accurate determination of HMs cannot be overemphasised.

As regards urban atmosphere, motor vehicles and industry exert the greatest influence. Water, soil and vegetation also experience adverse effects caused by HMs. Home and working environments should be protected against contamination by such toxicants, also from the point of view of waste disposal. The health status of urban settings is based, among others, on an adequate and safe supply of water and food. Vegetation also plays a key role in reducing the contents of HMs in the atmosphere and soil. Rather important in this respect is the awareness of people living in big cities of the risks posed by HMs. Scandinavian countries and Japan can be taken as good examples of the way the concept of clean territory is being implemented at the beginning of the new century.

A PRELIMINARY INVESTIGATION ON PLATINUM-GROUP ELEMENTS IN DUST AND GRASS OF THE URBAN AREA OF BIAŁYSTOK (POLAND)

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Palladium, Pt and Rh, *i.e.*, the so-called Platinum-Group Elements (PGEs) are released by catalytic converters for automotive traction. There is growing concern on the effects of these emerging pollutants for people living in urban areas. In this study, PGEs contents were determined in samples of road dust, tunnel dust, common grass as well as pine needles collected from residential areas of Białystok (northeast Poland). High Resolution (HR) and Quadrupole (Q) Inductively Coupled Plasma Mass Spectrometry (ICP-MS) were compared for their performance in the environmental analysis of Pt and Rh. Palladium was determined by Total X-Ray Fluorescence (TXRF) and HR-ICP-MS after matrix separation by reductive coprecipitation with Hg.

The highest PGEs concentration was found in road dust samples. Platinum content in road dust ranged from 34.2 - 110.9 ng g^{-1}, while that of Rh from 6.0 - 19.7 ng g^{-1}. The mean concentration of Pd in this matrix was 32.8 ng g^{-1} as determined by TXRF analysis and 42.2 ng g^{-1} as quantified by HR-ICP-MS, respectively. The highest Pt concentration in tunnel dust was found in the fraction of size below 75 mm (22.3-23.3 ng g^{-1}). The mean concentrations of PGEs in grass were 8.63 ng g^{-1} for Pt, 0.65 ng g^{-1} for Rh and 3.2 ng g^{-1} for Pd. The concentration of PGEs in pine needles was below the Limits of Detection (LoDs) of the methods employed.

INVESTIGATION OF TRACE ELEMENTS IN A NEW CERTIFIED REFERENCE MATERIAL (ROAD DUST) FOR PGEs

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The use of car catalytic converters results in lower emission of CO, NO_x and unburned hydrocarbons into the environment, but at the same time caused the emission of Pt, Pd and Rh (Platinum Group Elements, PGEs) due to the surface abrasion of the catalytic converters during the car operation. Until the end of the last year there was no environmentally relevant standard reference material commercially available for the analysis of PGEs in aerosol or airborne dust samples. This year a new certified reference material (BCR 723 Road Dust) was produced with certified values for Pt, Pd and Rh.

In the determination of these elements by Inductively Coupled Plasma Mass Spectrometry (ICP-MS), the spectral interferences caused by the other trace elements present in the sample is a major problem. The contribution of the interferent species on the analyte signal depends on the concentration of the interfering element. The aim of this work was to determine the concentrations of the interfering elements as well as of other trace metals. Different digestion procedures were applied, *i.e.*: *i)* ashed samples were digested using *aqua regia* plus HF; *ii)* Microwave (MW) digestion was resorted to after addition of a mixture of HNO_3, H_2O_2 and HF; *iii)* MW digestion was carried out using *aqua regia* with HF. For quantitative analysis the concentrations were determined by means of both the external calibration and the standard addition method. As the concentrations of the other trace elements in the BCR 723 Road Dust sample are given only as indicative values, another standard reference material (BCR 1648 Urban Particulate Matter) was used to check the accuracy of the procedure.

PLATINUM DETERMINATION BY NAA IN TWO ROAD DUST MATRICES PROPOSED AS CERTIFIED REFERENCE MATERIALS

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Platinum determination in various matrices at the environmentally relevant concentrations (ng g^{-1}) is not an easy task. Inductively Coupled Plasma Mass Spectrometry (ICP-MS), Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES), Differential Pulse Voltammetry (DPV), Neutron Activation Analysis (NAA) and Atomic Absorption Spectrometry (AAS) are considered the most sensitive and theoretically reliable analytical techniques for the determination of Pt at the trace level. Unfortunately, none of them can be employed without preanalytical treatment because of the severe interferences that can considerably affect the final results. Until now, there has been no Certified Reference Materials (CRMs) available for Pt content at the levels of interest. The environmental impact of the Pt Group Elements (PGEs) is mainly due to their use in car catalytic converters with the ensuing highly remarkable increase, in recent years, of their concentration in traffic-exposed areas.

In this work, a method for Pt determination was developed. The method is based on NAA coupled with a preirradiation concentration-separation procedure employing a Dowex ion-exchange chromatographic column to overcome serious interferences from other elements. Two environmental matrices, Road Dust CW7 and Road Dust CW8, collected and prepared by the Institute for Reference Materials and Measurements as candidate CRMs, have been analysed. The results are compared with data obtained by other laboratories with various techniques.

ANTHROPIC IMPACT ASSESSMENT ON GREEN URBAN AREAS BY ANALYSIS OF INORGANIC MICROPOLLUTANTS IN MOSSES. THE CASE STUDY OF ROME

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From a sanitary point of view, sources of potential contamination for an urban soil are basically due to atmospheric fall-out of pollutants produced by domestic heating systems and vehicular traffic. Among such pollutants it is possible to find heavy metals, suspended dusts, polycyclic aromatic hydrocarbons and volatile organic compounds. Taking into account the recent use of car catalytic converters, persistent inorganic micropollutants like Pd, Pt and Rh must be taken into account as these metals show a not negligible toxic potential.

This study is based on the use of bioindicators (mosses and top soils) to assess the concentration distribution of pollutants such as Pd, Pt and Rh as well as Al, Cd, Cu, Cr, Hg, Ni, Pb, V and Zn. The urban areas monitored were Villa Borghese, Villa Ada and Villa Doria Pamphili. Twelve stations were set up altogether. Two more sites (Villa Celimontana and the garden of the Istituto Superiore di Sanità) were investigated to achieve a more complete survey of the entire area. The values obtained can be used to evaluate the deposition rate of the investigated elements in order to assess the enrichment factors in soil over the past few years.

POLLUTANT EMISSION AND REMOVAL IN A RENEWED URBAN CREMATORIUM

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The acquisition of data and information on urban crematoria emissions, as they stand with current cremation practice, is essential to develop and validate methods for reducing the release of pollutants, to set up process optimization techniques which can reduce pollutant formation and to assess the performance of end-of-pipe flue gas cleaning systems in existing crematoria. Urban crematoria emission is of growing interest in Italy as a consequence of the currently increasing demand for cremation, not only as a system of burial, but also as a system of disposal of non-decomposed human remains from operations of exhumation (as prescribed by the Circular of the Ministry of Health No. 10 of 31 July 1998).

Preliminary results from a testing programme in progress on an urban crematorium emission are reported. This crematorium recently was equipped with a new end-of-pipe flue gas cleaning system. The results obtained indicate a close connection between concentrations of pollutants and the related system of abatement as well as the combustion process. In the cremation process, combustion, incomplete combustion and the volatilization of metals cause air pollution. Combustion is responsible for the emission of particulate matter, hydrogen chloride, dioxins and other pollutants that can form in the atmosphere. Hydrogen chloride is produced when plastics containing chlorine are combusted. Incomplete combustion during cremation, as with any incomplete combustion process, will produce CO. It is very difficult to control the emission limit of this gas. Results show that there is a relationship between CO emission and different periods of cremation process. Volatilization of Cd, Hg and Pb is also a source of great concern in that Cd and Pb may be present as components of the coffin and Hg is contained in dental fillings.

ASSESSMENT OF THE POLLUTANT LOAD FROM CREMATORIA IN URBAN AREAS

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In order to develop specific legislation on crematoria in Italy, a study was carried out to assess the acceptability of the installation of such plants in urban cemeteries. Countries with area constraints for existing cemeteries and difficulties in finding new suitable areas for cemetery use have to reconsider all the parameters. These include the siting and the operability of crematoria in existing cemeteries, in particular design, process, flue gas cleaning systems and assessment plant operation (hours of operation, number of days per week and special safety procedures), *i.e.*, all those factors through which the pollutant load from the stack can be minimised. In this context the feasibility of the installation of a crematorium in a cemetery of a town in northern Italy that could operate at a rate of 1000 cremations per year was investigated. It is assumed that the proposed crematorium releases gases and small particles, including potentially toxic substances such as heavy metals (in particular Hg), Polychlorodibenzo-*p*-dioxins (PCDDs) and Polychlorodibenzofurans (PCDFs). The emitted substances are transported downwind and dispersed depending on local weather conditions and soil type. However, some of the emitted substances reach ground level within a few kilometers from the stack, thus giving place to an area of concentration of maximum ground-level pollutants. This area of maximum exposure includes communities and residents living near the facilities who can be adversely affected by the emissions.

To identify the nature of the pollutants released and their ground-level concentrations, stack, meteorological and site data were collected to run a pollution dispersion model. Pollutant concentrations in the environment were assessed using the air dispersion model ISCST3 of the US Environmental Protection Agency (EPA). The results obtained show very low concentrations of pollutants at the ground level (in the order of magnitude of ng m^{-3}) and even less for Cd, Hg and Pb. In the case of PCDDs and PCDFs, concentrations were below the fg m^{-3} level. In all cases, the detected levels were much lower than the limits prescribed by national, European and international guidelines and legal provisions on emissions. However, the long-term effects of the emitted pollutants must be considered in the overall assessment, since there are pollutants (*e.g.*, Hg, PCDDs and PCDFs) which can bioaccumulate. The crucial question in the installation of crematoria in urban areas is not only concerned with the emission of very small amounts of pollutants, but also with their long-term effects on human beings. The crematorium studied may well meet the limits in force for pollutants, but this is not a guarantee that the pollutants will be not harmful. In fact, many of the key toxicants involved, such as Hg, Pb and dioxins, do not break down in the environment and give place to bioaccumulation.

AN ICP-MS STUDY OF THE ABUNDANCE OF As, Hg, Pb AND Sb IN A CONTAMINATED AREA OF CENTRAL ITALY

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A study on metal contamination in an abandoned mining area in Tuscany (Italy) was carried out. Particular attention was devoted to As, Hg, Pb and Sb because they are not only environmental contaminants, but they are also very difficult to detect and to eliminate being long-lasting pollutants toxic to most forms of life. An improved method for reliably monitoring these elements even at very low concentrations was developed and tested.

The method is based on analytical determinations by Inductively Coupled Plasma Mass Spectrometry (ICP-MS) and is primarily focused on analysis of soils, but also air and waters components were investigated. Results showed that, although the industrial activity of mining and processing of cinnabar in this zone was discontinued more than ten years ago, the contamination level is still rather high. The health hazard and possible epidemiological effects of contamination in this area are assessed.

Session 6
The Venice Lagoon

SCIENTIFIC RESEARCH ON THE VENICE LAGOON: THE RESEARCH PROGRAMME 2000-2004

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The *Consorzio per la Gestione del Centro di Coordinamento delle Attività di Ricerca Inerenti il Sistema Lagunare di Venezia* (Consortium for Coordination of Research Activities Concerning the Venice Lagoon System, CORILA) is an association between the Ca' Foscari University and the University Institute of Architecture of Venice, the University of Padua and the Italian National Research Council. A non-profit organisation, it is supervised by the Ministry of Higher Education and Research. CORILA promotes and coordinates research on the Venice Lagoon also at the international level. The CORILA research programme for the period 2000-2004 is based upon four thematic areas, *i.e.*, economics and social aspects, architecture and cultural heritage, environmental processes and data management. It is subdivided into ten research lines. These have been assigned to research groups *via* a selection process which identifies the best local scientific resources as well as capacity for collaboration with international scientific institutions.

The programme aims at providing concrete results and scientific excellence as well as response to specific queries emerging from local administrations. Seventy institutions and organisations are involved, eighteen of which are foreign institutions. Human resources equate to 3000 man-months over three years. The programme costs approximately € 10,8 million of which € 6,2 million comes from funds allocated through the Special Law for Venice, while the rest comes from other administrations and from the partners themselves (more than 40 % of Special Law funds are matched by cofinancing). CORILA coordinates the research work and promotes effective interdisciplinary scientific exchange.

THE PROFICIENCY TESTING PROGRAMME FOR TRACE ELEMENTS OF THE CORILA PROJECT

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Harmonised quality schemes are being implemented in the framework of the thematic area Organisation and Dissemination of Data of the *Consorzio per la Gestione del Centro di Coordinamento delle Attività di Ricerca Inerenti il Sistema Lagunare di Venezia* (Consortium for the Management of the Coordination Centre of Research Activities on the Venice Lagoon System, CORILA). Over the last few months, two proficiency tests were launched to assess the capabilities of the analytical laboratories involved in the determination of trace elements in environmental inorganic matrices from the Lagoon of Venice.

Both interlaboratorial trials were based on the determination of As, Cd, Cr, Cu, Fe, Hg, Pb and Zn in aqueous acidic, matrix-enriched solutions at concentrations within the ranges generally found either in marine water or in sediment after chemical digestion. The proficiency of participants was assessed on the basis of the z-score criterion ($z \leq 2$, good results; $2 < z \leq 3$, questionable results; $z > 3$, unacceptable results). In the first two runs, the relevant percentages for the laboratories scoring $z \leq 2$ and $z \leq 3$ were 61 % and 71 % and 65 % and 77 %, respectively. These first two proficiency tests, on the one hand, clearly pointed to the benefits the laboratories had from their participation in these exercises, on the other hand provided sound evidence of the need for further trials based on real environmental matrices.

TRACE METAL BENTHIC FLUXES IN THE VENICE LAGOON

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To assess the exchange of trace metals from sediment and water in the Venice Lagoon, a study was carried out based on a benthic chamber experiment in one site of the central basin of the lagoon located close to the industrial area of Porto Marghera. The chamber was monitored for pH, dissolved oxygen, Eh, salinity and temperature by a multiparametric probe and for trace elements by collecting samples every 3-4 hr, for approximately 57 hr. The concentration of Ag, Al, As, Cd, Co, Cu, Fe, Mn, Mo, Pb, Sb, U, V and Zn were determined by Sector Field Inductively Coupled Plasma Mass Spectrometry (SF-ICP-MS) coupled with a desolvation unit through direct injection of diluted (1:10 with ultrapure water) aliquots of samples. The accuracy was tested by the Certified Reference Material (CRM) CASS-4 Coastal Seawater. Experimental results were always within the certified intervals. For Ag, Al and Sb, the values were in excellent agreement with concentrations reported in the literature.

The concentrations determined in the seawater samples were in agreement with previous concentrations determined in samples collected in the same area. The range of concentrations (in ng g^{-1}) for the elements were: Ag, 0.007-0.031; Al, 0.24-0.61; As, 1.42-2.27; Cd, 0.050-0.182; Co, 0.440-1.461; Cr, 0.15-0.34; Cu, 0.81-2.46; Fe, 0.25-1.66; Mn, 11.59-31.66; Mo, 6.50-10.62; Pb, 0.047-0.225; Sb, 0.240-0.492; U, 1.7-3.3; V, 1.3-2.8; and Zn, 5.20-21.51. During the experiment the oxygen content decreased until a suboxic condition was reached (the final percentage of saturation was 12 %). At the same time, the concentrations of metals changed and fluxes were calculated. Some elements showed a positive flux from the sediment to the water column (Cd, Co, Sb and Mn), while for other elements (Cu, Fe) an initial negative flux (0-15 hr) was evident. This was followed by a null flux until the end of the experiment. Results are discussed also taking into account oxygen concentration and Eh value.

POLYCYCLIC AROMATIC HYDROCARBONS IN THE ATMOSPHERE OF THE VENICE LAGOON

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Polycyclic Aromatic Hydrocarbons (PAHs) are ubiquitous and hazardous pollutants released into the atmosphere from anthropogenic and natural sources. PAHs are formed primarily during incomplete combustion of fossil fuels and wood. In this work, the role of the aerosol in the transport of pollutants into the Venice Lagoon area was investigated. Dissolved and particulate-bound PAHs were collected at three different sites around the lagoon. Sampling was performed from March to December 2002 by a high volume sampler equipped with a Quartz Filter (QF) coupled with a Polyurethane Foam Plug (PUF). On the basis of the speed and the direction of the wind, it was possible to evaluate the input of pollutants from the different sources (urban and industrial sources, Moranzani site; no direct source, Teolo site; marine sources, P. Sabbioni site). Filters and PUF samples were Soxhlet extracted for 24 hr with a *n*-pentane - dichloromethane (2:1 v/v) mixture. The extracts were purified on a column containing activated alumina and florisil. The PAHs were eluted with *n*-hexane and determined by Gas Chromatography Mass Spectrometry (GC-MS).

Results showed that the lowest concentration is at P. Sabbioni with 0.4 ng m^{-3}, whereas the highest one is at Teolo with 15.2 ng m^{-3}. Phenantrene is the most abundant compound in the gas phase of the aerosol at all sites. Broad seasonal variations in PAH concentrations were noted during the study with autumn concentrations tending to be higher than spring and summer ones. This has been noted primarily at the Moranzani and P. Sabbioni stations, whereas at the Teolo station the summer concentrations were higher than spring and autumn values.

Session 7
The extreme environment of Antarctica

CHEMISTRY IN ANTARCTICA: LOCAL, REGIONAL AND GLOBAL IMPLICATIONS

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Chemistry has a relatively short history in Antarctica and its surrounding ocean. This presentation briefly outlines its development from the Heroic Age onwards in support of other sciences. Examples of its key contributions to recent science areas are discussed at three levels: monitoring of local impacts of human activities; regional science on Antarctic organisms and the Southern Ocean; and contributions to global science in terms of climate change and pollution.

It is concluded that chemistry is fundamental to much of the present and future science in Antarctica, that there are still considerable challenges in understanding chemistry at low temperatures and that improved levels of collaboration and facilities are needed to maximise opportunities.

TEMPORAL VARIABILITY OF TRACE ELEMENTS IN ANTARCTIC (DOME C) ICE OVER THE LAST 45,000 YEARS

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Climate changes, on all time scales as well as on all spatial scales, have occurred in the past as a result of various natural influences. To quantify the response of the climate system to forcing, it is essential to account for all the complex interactions and feedbacks among the climatic system components, as they are the background upon which the now confirmed global warming of the planet is based. The role of trace elements in the biosphere is relatively unknown. The more abundant first row transition metals (Co), Cu, Fe, Mn, (Ni) and Zn play a key role in biological evolution and are present in every cell of every living organism. Given their importance in phytoplankton production and in marine cycles of C, N, Si and P, changes in the abundance of Fe and other bioactive trace elements are supposed to have been substantially involved in the glacial-interglacial exchange of atmospheric CO_2.

Ice core records, unique in documenting the Earth's past atmosphere, show large and regular climate-related changes in atmospheric CO_2 with minimum values during glacial periods that have been associated with increased oceanic C uptake, particularly in the Southern Ocean. However, the mechanism involved remains unclear. With adequate Fe, it is assumed that there are massive phytoplankton blooms which give rise to increased uptake of CO_2, thus enhancing the efficiency of the "biological pump" in the Southern Ocean, one of the high-nutrient, low-chlorophyll zones. The atmospheric Fe source is overwhelmingly associated with the deposition of dust, but all attempts to estimate dust inputs into the oceans have been hindered by the limited availability of long-term data sets.

This study presents the records of Al, Fe, Mn, U and V concentrations measured during the European Project for Ice Coring in Antarctica (EPICA) in ice cores sampled at Dome C. These analyses have provided information on the atmospheric deposition over the past 45,000 years, with some evidence of the dramatic decrease in trace metal concentrations from the Last Glacial Maximum (LGM) to the Holocene and of higher concentrations during the Antarctic Cold Reversal (ACR) with respect to the Holocene average. These trends correlate well with dust content, thus supporting the assumption that there was an enhanced terrestrial input during the LGM with the ensuing higher availability of essential trace elements.

THE PRESENCE OF ORGANIC MICROPOLLUTANTS IN ENVIRONMENTAL MATRICES FROM VICTORIA LAND AND ROSS SEA (ANTARCTICA)

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Polychlorobiphenyls (PCBs) and Polycyclic Aromatic Hydrocarbons (PAHs) are two of the most widespread classes of environmental persistent pollutants. They have been included in the list of priority pollutants, thus attaching priority to their monitoring in the environment as well as to studies of their toxic effects on living organisms. This presentation gives a concise overview of the most widely used analytical procedures for the determination of PCBs and PAHs in environmental matrices, covering also sample collection and storage, sample preparation, instrumental analysis and quality control of analytical data. The Italian contribution to this research areas is also illustrated.

The results of several Italian expeditions to the Ross Sea and Victoria Land are presented. In particular, seawater, pack ice, sediment, soil, snow/firn and ice were collected from several sampling sites and analysed. The results obtained highlight a low and quite homogeneous PCB contamination of the studied area which may rule out any direct source of PCB pollution in Antarctica. Seawater, marine sediment, lake sediment and soil samples showed a typical PCB concentration of about 130 pg l^{-1}, 150 (pg g^{-1})/(m^2 cm^{-3}), 240 (pg g^{-1})/(m^2 cm^{-3}) and 130 (pg g^{-1})/(m^2 cm^{-3}), respectively. All values but the first one are normalised with respect to the calculated surface of the sample which is expressed in m^2 cm^{-3}. A very peculiar effect of the pack-ice melting process on the PCB content in seawater was also discussed. Finally, snow-firn depth profiles of PCBs and PAHs seem to indicate that the amounts reaching the Antarctica *via* atmospheric transport have decreased over the last ten years.

PERSISTENT ORGANIC POLLUTANTS IN BENTHIC ORGANISMS FROM TERRA NOVA BAY (ANTARCTICA)

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Among Persistent Organic Pollutants (POPs), Polychlorobiphenyls (PCBs), Hexachlorobenzene (HCB), Dichlorodiphenyldichloro ethane (*pp'*-DDE), Polychlorodibenzodioxins (PCDDs) and Polychlorodibenzofurans (PCDFs) are known to elicit acute or toxic responses in organisms, including humans. The toxic potential of dioxin-like compounds was calculated by using the Toxic Equivalency Factor (TEF) approach. POPs were determined in various Antarctic benthic species, including the red algae *Iridaea cordata*, echinoderms (sea cucumbers, the sea star *Odontaster validus*, the sea urchin *Sterechinus neumayeri*), mollusks (the Antarctic scallop *Adamussium colbecki*, the Antarctic whelk *Neobuccinum eatoni*, the Antarctic yoldia *Yoldia eightsi*) and fish (the emerald rockcod *Trematomus bernacchii*) from Terra Nova Bay (Ross Sea).

Prey-predator relationships and other ecological relationships have been taken into account when discussing the results. High levels of POPs were found in emerald rockcod liver samples (6.4±6.2 ng g^{-1} wet weight for HCB, 0.42±0.1 ng g^{-1} wet weight for *pp'*-DDE, 22.7±18.6 ng g^{-1} wet weight for PCBs). Low levels of HCB and *pp'*-DDE were detected in Antarctic yoldia (0.035 ng g^{-1} wet weight and 0.016 ng g^{-1} wet weight, respectively). For most samples the concentration pattern was PCB > HCB > *pp'*-DDE. In the case of PCB congeners the sequence was hexa-CBs > penta-CBs > hepta-CBs > tri-CBs > tetra-CBs > octa-CBs > nona-CBs. Fingerprints showed different patterns, probably depending on species, sex, age and breeding activity. PCDDs and PCDFs were below the Limits of Detection (LoDs) (<0.001 ng g^{-1} wet weight) in all the analysed samples. The sum of non-ortho PCBs ranged from <0.001-0.198 ng g^{-1} wet weight and the sequence was PCB126 > PCB77 > PCB169. Toxicity, expressed as Toxic Equivalents (TEQs), was primarily due to PCB126, PCB118 and PCB105.

NUTRITION AND BODY COMPOSITION VARIATION OF MAN IN EXTREME ENVIRONMENT

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Nutrition is not only a vital necessity, but adequate food consumption also represents a fundamental step in order to assure a sound psycological and physical state. A correct balanced nutrition assures all the vital and physical processes. It is therefore essential that food be appetizing, hygienic and nutritionally correct. On the other, hand an inadequate diet for an extended period of time can adversely affect health. Given the influence of nutrition on man's state of health, the scientific community has turned its attention to the possible causes of malnutrition in extreme situations.

In this context a study was undertaken in 2002 about the biophysiological variations to which man is liable in extreme environments. The objective of this study was to ascertain whether researchers at the Terra Nova Bay in Antarctica assume food qualitatively and quantitatively balanced to sustain life in the best possible way in an extreme environment and to evaluate any behavioral changes toward food that might occur in consequence of low temperature, isolation and lack of the light-dark cycle with the attendant reduction in psycological and physiological efficiency.

Session 8
Medicine and human biology

APPLICATIONS OF DIODE LASER ATOMIC SPECTROSCOPY TO SAMPLES RELATED TO THE ENVIRONMENT AND HUMAN HEALTH

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Diode Laser (DL) light sources show much promise in atomic spectrometry. These compact and low cost semiconductor devices provide intense, tunable, very narrow-band light emission which can be modulated electronically. The benefits of using DLs as excitation light sources in Atomic Fluorescence Spectrometry (AFS) and Atomic Absorption Spectrometry (AAS) have been already demonstrated in several publications as regards flame or graphite furnace atom sources. The analytical benefits include: *i)* higher sensitivity for AFS measurements due to higher (by several orders of magnitude) emission intensity of DLs over hollow cathode lamps; *ii)* applicability of background correction techniques in AAS *via* the tunability of DL emission; *iii)* high resolution (isotope selective atomic spectrometry is possible); *iv)* extended multielement capabilities. It is now generally acknowledged that the widespread application of DLs in atomic spectroscopy is delayed only by technical difficulties involved with manufacturing diodes for the UV wavelength range. This practically limits the applications of DLs to the alkaline and alkaline-earth elements. Nevertheless, it is clear that these elements and their determination have great importance in many fields related to the human health and the environment.

The potential of DL atomic spectrometry as applied to Inductively Coupled Plasma (ICP) techniques was already demonstrated. The Diode Laser Atomic Absorption Spectrometry (DL-AAS) and Diode Laser Induced Fluorescence (DLIF) ICP experimental setup, already described, is centered around a commercial ICP atomic emission spectrometer. In this simple, but effective, unmodulated single beam setup, the ICP serves as the atom source and the spectrometer monochromator, photomultiplier detector and built-in data acquisition software are utilized to collect background-corrected signal intensities. A simple, three-step measurement procedure was devised that corrected for the contribution of the thermal emission and scattered laser light on analytical signals. Prior to the DL-AAS-ICP and DLIF-ICP measurements, the DL emission is finely tuned to the atomic transition of the element to be studied by precisely controlling the current and temperature of the diode. In the fluorescence setup, tuning is done by using a fiber optic bundle to lead the light into the monochromator. Reference wavelength for the tuning is provided by the peak position of the ICP thermal emission of the element under test. With this setup, and after optimisation of the ICP operating parameters (plasma radiofrequency, observation height, carrier gas flow rate), Limits of Detection (LoDs) of, *e.g.*, 150 μg l^{-1} (DL-AAS-ICP) and 8 μg l^{-1} (DLIF-ICP) for Li could be easily achieved. After replacing the DL with another one emitting at a different wavelength, other alkali and alkali-earth elements could be quantified. The effect of the presence of high salt concentrations (NaCl) on the analytical signals was also studied and no significant interferences were found for up to about 1 % (10,000 mg l^{-1}) salt concentration. This is one of the analytical benefits of the use of an ICP atom source over, *e.g.*, flame atom sources. This presentation reports further analytical results and figures of merit for the above methods when applied to the measurement of Li in different artesian and mineral waters.

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DEPLETED URANIUM: POSSIBLE HEALTH EFFECTS AND EXPERIMENTAL ISSUES

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In recent years cases of cancer have been reported among Italian troops involved in the peace-keeping mission in Bosnia and Kosovo. A Committee of Enquiry was set up to investigate on a possible etiologic role of potential exposures to Depleted Uranium (DU), although from the information available to date there are no data that confirm significant exposure to U compounds. The overall incidence of cancer was significantly lower than the expected incidence based on data from Italian cancer registers. The only type of cancer for which a statistically significant excess was observed was the Hodgkin's lymphoma, but up to this now several constraints have prevented from ascertaining whether lymphatic cancers are correlated or not with DU exposure. However, some radiation protection remarks emerge on the basis of biological and epidemiological evidence, not only concerning military personnel, but also Balkan population.

In this work, starting from the Italian troop epidemiological findings, a critical review of knowledge and postulates about U exposure is presented. Moreover, an evaluation of the dose to local population, particularly to embryo/foetus, due to environmental exposure is carried out. Results of improvement and specialisation of the gamma spectroscopic technique, implemented in order to assess DU activity concentration in environmental samples with a relatively manageable technique, are also discussed.

DETERMINATION OF ALKALI METALS IN CONTROL AND AD BRAIN SAMPLES BY DIFFERENT TECHNIQUES

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Several metals are suspected or known to play a key role in different neurological disorders, including the Alzheimer's Disease (AD). In spite of this fact, few concentration data can be found on the distribution of metals in human brain. The present study focused on a group of poorly covered elements, *i.e.*, the alkali metals. A fit-for-purpose Neutron Activation Analysis (NAA) procedure had been already developed for the determination of Cs, K, Na and Rb. Despite the merits of this technique, several inconveniences and difficulties arose, *e.g.*, low concentrations required hours of measuring time, a decrease in background caused by matrix constituents required several weeks of cooling. Therefore, more rapid spectrochemical methods were used after microwave digestion of samples.

Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES) was applied for the determination of K, Li and Na. No interferences were observed, but ultrasonic nebulisation was needed for Li quantification. Cesium and Rb were measured by Inductively Coupled Plasma Mass Spectrometry (ICP-MS) with In as the internal standard. Agreement between NAA, ICP-AES and ICP-MS was found to be good for K, Na and Rb, while for Cs somewhat higher differences were noted. Average values, distribution inhomogenity, interpersonal variability and possible correlation among elements were ascertained in both the control and the AD group.

IRON UPTAKE AND TOXICITY IN Caco-2 CELLS

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General toxicity *in vitro* is often tested by Microtiter (MTT) assay. Cell proliferation and viability is quantified by forming a blue formazan *via* intact mitochondria. For that reason cells are completely dissolved in DMSO and absorption is measured spectrophotometrically. Contrary to other tests used in cell culture after a MTT assay, no further toxicological and biochemical parameters can be measured. This has no influence on the analysis of inorganic compounds. Thus, the overall quantity of intracellular metals can be determined without further sample preparation.

The aim of the present study was to optimise the Fe determination in a human intestinal cell line (Caco-2) by Electrothermal Atomisation Atomic Absorption Spectrometry (ETA-AAS) subsequent to an MTT assay and to detect toxicity of different species of Fe. ETA-AAS measurements were optimised establishing the proper temperature programme and applying the standard addition method. The optimised temperatures are as follows: 600 °C (preashing), 1200 °C (pretreatment), 2100 °C (atomization). The Limit of Detection (LoD) was below 1.2 µg l^{-1}. Cells were incubated with 1.5 m*M* solutions of different species of Fe, *i.e.*, $FeCl_3$:NTA (1:2), $FeCl_3$:citric acid (1:2), $FeCl_3$ and $FeSO_4$ for about 22 hr. After the MTT assay, LDH release and intracellular Fe determinations were performed. The lowest membrane damage (measured by LDH release) was registered in cells treated with $FeCl_3$:citric acid (1:2) followed by $FeSO_4$, $FeCl_3$ and $FeCl_3$:NTA (1:2). The Fe content caused a decrease in the MTT signal. The highest Fe content of Caco-2 cells was detected after treatment with $FeCl_3$ and $FeCl_3$:NTA (1:2). The highest signal for cell viability was found after incubation with $FeCl_3$. The method presented simplifies the analysis of uptake experiments.

ICP-MS DETERMINATION OF PLATINUM IN BIOLOGICAL FLUIDS OF ADULT PATIENTS WITH SOLID TUMOURS

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Much is known about the role of the oral bis-(acetate) ammine-dichlorocyclohexylamine platinum (IV) analogue (BMS-182751, JM-216) in the clinical treatment of some human tumours due to its cytotoxic activity. In a previous work a clinical study was reported which dealt with pharmacokinetics and pharmacodynamics in patients treated with the Pt analogue JM-216 for a long period of time. Platinum concentration in urine, plasma and ultrafiltrate plasma of the patients was monitored daily by means of Inductively Coupled Plasma Mass Spectrometry (ICP-MS) Analyses were performed by simple dilution of the samples without any other pretreatment. The range of concentrations that occur in this type of study is extremely varying, depending on the nature of the matrix, the starting dose of the antitumoural agent, the time elapsed from the administration *etc*.

In this contribution the analytical aspects related to the determination of Pt in these matrices is reported with particular attention to the figures of merit of the adopted methods, *i.e.*, applicability, Limits of Detection (LoDs) and Limits of Quantification (LoQs), linearity *etc*. The methods were fully validated and the data have been used for the evaluation of the uncertainty of the measurement. It has been calculated that at 1-2 $\mu g\ l^{-1}$ levels the relative expanded uncertainty was in the order of 20-30 %, while at higher concentrations it became 1-5 % (independently of the matrix in which the determinations were made). For lower levels, typical of non-treated patients or of some ultrafiltrate plasma samples, the calculation of the uncertainty of measurement gave values in the range from 40 to 80 %, with a calculated limit of detection of 0.01 $\mu g\ l^{-1}$.

ANALYTICAL AND LC-MS CHARACTERISATION OF FRUIT-BASED NUTRACEUTICALS

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FLAVIN7 is a fruit-based new Hungarian nutraceutical, which contains a number of organic antioxidant and free radical scavenger compounds (like flavonoids, tannins *etc.*) with characteristic biological and pharmacological activities (*i.e.*, cardiovascular, cytotoxic, anticoagulant, hepatoprotective activities *etc.*). The quality control regulations of nutraceuticals in the USA and the EC countries are roughly the same as for pharmaceuticals.

A study was thus undertaken to investigate the properties of these very complex mixtures. The results obtained by different instrumental methods, *i.e.*, UV-VIS, High Performance Liquid Chromatography (HPLC), Liquid Chromatography Mass Spectrometry-Mass Spectrometry (LC-MS-MS) and free radical scavenger tests are discussed.

TRACEABILITY AND UNCERTAINTY OF MEASUREMENT IN LABORATORY MEDICINE: A NEW CHALLENGE

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According to the new standards for calibrating, testing and medical laboratories, the traceability of analytical results to stated references must be demonstrated and procedures must be in place to estimate the uncertainty of measurement. The European Council Directive 98/79/EC also requires the traceability of *in-vitro* diagnostic medical devices, including reference materials, to be assured. In analytical chemistry, and particularly in laboratory medicine, establishing a traceability chain to SI units can be difficult because of the lack of primary standards and primary methods and the complexity and variety of measurands.

International initiatives are currently in place to provide scientific and technical support to this task. In addition, specific initiatives at the local level and in specialised fields, such as the biological monitoring of occupational and environmental exposure, are necessary to provide the same level of education and technical support to analysts operating in routine laboratories throughout the European Union.

COMPETENCE ASSESSMENT OF FACILITIES AND LABORATORIES INVOLVED IN THE EVALUATION OF CHEMICAL COMPOUND SAFETY: CHALLENGES AND RECENT DEVELOPMENTS

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Many benefits of modern societies are warranted by the use of chemical compounds. On the other hand, increasing concern may raise from the lack of reliable information on the impact on human health deriving from the use of chemicals. Risk assessment, which in turn consists of hazard evaluation and exposure estimation, is mandatory in order to guarantee the safety of chemicals. Both activities are strictly dependent upon the availability of reliable data and information, produced by, *e.g.*, test facilities and testing laboratories, including clinical laboratories, the specific management and technical competence of which should be properly assessed. Auditing of the quality management system plays a key role in the evaluation of the adequacy of policies, processes and procedures to meet quality needs, but is not sufficient to fully evaluate technical competence.

The assessment of competence of test facilities and testing laboratories applies in the premarketing phase as well as after the chemical compounds are placed on the market. In the latter and, in some cases, long-lasting phase, it is necessary to carry out an appropriate monitoring of environment, food and, in specific situations, human beings (biological monitoring). In the field of chemical safety, standards, guidelines and legal and operative instruments are nowadays available. The availability of these tools makes it possible to assess both the comparability and reliability of data and the competence of facilities and laboratories involved in the production of the data themselves.

ANALYSIS OF HUMAN LIVER SAMPLES: ULTRASONOGRAPHY AND TRACE ELEMENT CONTENT OF THE LIVER IN CHRONIC DIFFUSE LIVER DISEASE

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Chronic Diffuse Liver Disease (CDLD) is very frequent in Hungary and its incidence is increasing continuously. Ultrasonography (US) is involved in the primary diagnostic approach of patients affected by this disease as well as in the follow-up of the patients. In CDLD the echogenicity and echodensity of the liver become higher than normal (bright liver). CDLD includes a variety of liver diseases with similar Ultrasonographic (US) signs. Nevertheless, two basic groups of bright liver can be differentiated according to attenuation, *i.e.*, the low and the high attenuation types. A quantitative attenuation procedure was elaborated based on a comparison of attenuation of the patient's liver with attenuation of homogeneous tissue-equivalent reference phantom. By this method, the correlation with other (*e.g.*, clinical and histopathological) parameters can be investigated.

The aim of the present study was to find some possible factors which can play a role in the formation of different liver structures as characterised by ultrasonic images. In the first step the water content of the liver samples was investigated, as calculated from the pre- and post-lyophilisation weights. No correlation was found between liver water content and attenuation. One key parameter might be the trace element contents of some characteristic samples. At the first stage pathological samples taken by autopsy were examined in order to choose prospective analyte elements and assess their concentration ranges. The analytical protocol thus developed can be applied also to biopsy samples. One major problem is the size of the samples as those obtainable from living organisms are obviously of reduced mass. This fact requires that analytical techniques be properly chosen. Total reflectance X-ray Fluorescence (TXRF) spectrometry is appropriate for this task because of its small sample consumption and very good Limits of Detection (LoDs). Inductively Coupled Plasma Mass Spectrometry (ICP-MS) exhibits favourable LoDs for numerous elements as well, but the technique requires larger sample volumes when using the solution nebulization sample introduction. A comparative study was performed on a series of selected samples which were analysed using both techniques. The possible correlation of experimental data with ultrasonic image types is also discussed.

Session 9
Occupational hygiene

EFFECT OF TIRE DUST ON THE LUNGS, PLEURA AND CONNECTIVE TISSUE

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Employment in the rubber industry has been associated with cancer of the lungs and many other organs. Airborne particulate material derived from tire debris and typical of heavy urban vehicle traffic might be an important factor in producing lung damages. In order to study the pathogenicity of urban tire dust, animal experiments have been performed. Wistar rats received a single instillation of a suspension of tire dust into the lower lobe of the right lung. At the same time, an intraperitoneal and subcutaneous injection of the suspension was given to study the reactions of the mesothelium and the connective tissue. The animals were sacrificed up six months after treatment. Lungs, abdominal organs and subcutaneous connective tissue were processed for light and electron microscopic examinations, as well as for energy dispersed X-ray- and IR-spectrometry.

Particles in the respirable size range accumulated in the terminal bronchi, inducing an increased secretion activity of the epithelium. As a sign of biosolubility alveolar macrophages fragmented the tire debris. Granulomas containing giant cells developed around the interstitial dust depositions in the lungs and induced microabscesses in the subcutaneous connective tissue. The mesothelial cells covered the dust depositions and showed local metaplasia. Epithelial dysplasia or fibrogenic effects were not observed during the experiments, even though infections might be transferred by tire particles.

RELATIONSHIP BETWEEN INDUSTRIAL ACTIVITY AND FREQUENCY OF RESPIRATORY SYSTEM DISEASES IN REGIONS OF REFINERY AND HEAVY OIL-FIRED POWER PLANTS

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According to epidemiological studies, exposure to Residual Oil Fly Ash (ROFA) is associated with adverse pulmonary health effects, respiratory effects, cardiovascular diseases and malignant neoplasms in humans. The bioavailable metal constituents (Ni, V) of ROFA are responsible, depending on their concentrations and chemical forms, for the occurrence of these diseases. Over the last forty years, the studied power plant has been burning the material remaining from the refining of crude oil, thus releasing ROFA into the environment. The settling of ROFA particles depends on their density and diameter, the wind, the stack height *etc*. The deposition of the particles reaches a maximum at about 10 km if an electrostatic precipitator is used; otherwise, at 2-3 km. As the chemical composition of the particles depends on their size and the quality and quantity of oil and gas burnt, the adverse effects affecting health of the inhabitants of the surrounding villages and towns are very complex.

The objective of this study was to verify whether respiratory diseases and malignant neoplasms were more frequent in the population of the settlements in the vicinity of the power plant as compared to properly chosen controls and to try to indicate a possible solution. The data received from the National Public Health and Medical Officer Services (NPHMOS), based on the reports of family doctors made on lst January 2000 and 2002, provided the number of the inhabitants that underwent medical treatment and suffered from chronic bronchitis, emphysema or other chronic lower respiratory system diseases. The data obtained from the National Cancer Registry of Hungary, based on the reports of the hospitals, gave the annual number of newly detected malignant neoplasms during the time period 2000 - 2001. The number of the patients and the number of the newly detected neoplasms were divided by the number of the individuals in the same age group in the investigated settlement, this information being used for prevalence and incidence rate calculations, respectively.

The prevalence rates of adult patients treated for chronic bronchitis, emphysema or other chronic lower respiratory diseases were divided by the prevalence rates in the control settlement. The obtained ratio was the highest (3 - 8) for villages situated 8-11 km far from the power station in the predominant direction of wind. The incidence rates of the newly detected malignant neoplasms of lip, oral cavity and pharynx registered in these villages were also high (4) compared with those of the control settlement. It can be stated that the emitted fly ash is responsible for the more frequent occurrence of the examined diseases in the investigated settlements. As a solution to the problem, it would be advisable to burn the residual oil using always an electrostatic precipitator of adequate efficiency. In order to avoid the high concentration of toxic metals, the burning of residual oil should as much as possible be evenly spread over time. It is highly recommended that NPHMOS, in cooperation with the power plant, collect aerosol samples in the villages more at health risk on a regular basis and carry out the determination of their heavy metal contents.

THE POSSIBILITIES OF ASSESSMENT OF WORKPLACE EXPOSURE TO WELDING FUMES

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Among the health damaging factors in the working environment much concern is nowadays due to toxic effects caused by welding fumes, primarily as regards: *i)* exposure to partly unknown toxic elements; *ii)* occurrence of toxic eements under different species with different physical and chemical properties (solubility in different media, oxidation state, *etc.*); *iii)* distribution of size fractions in welding aerosols in a very wide range. Therefore, selective determination of each size fraction cannot be performed on the basis of the standard EN 481 (inhalable, thoracic, respirable fraction); *iv)* depending on the welding process applied toxic elements can be distributed among different fractions. Moreover, there is a fraction in the size range of Ultrafine Particles (UFP) for which a sampling technique for the quantitave determination is currently under development.

The determination of exposure to welding fumes by air analysis is affected by much uncertainty as regards the risk posed to human health. Also biological monitoring offers in this context a good possibility for the assessment of the dose uptaken provided that there exists a linear relationship between external and internal exposure. The measure of internal exposure to welding fumes can be determined by biological monitoring for most toxic elements. The activities in progress in this framework are as follows: *i)* elaboration of measuring methods for toxic elements (Al, Co, Cr, hexavalent Cr, Mn, Ni) in air samples of welding fumes by different analytical techniques, *e.g.*, Atomic Absorption Spectrometry (AAS) and Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES). Inductively Coupled Plasma Mass Spectrometry (ICP-MS) was used for biological samples; *ii)* participation in European proficiency testing schemes for the above elements in workplace air samples (WASP, HSL, UK) and biological samples (Al. Worldwide, Poitiere, France; UK TEQAS, Guildford, UK; EQAS, Erlangen, Germany); *iii)* comparison of different methods allowing for an RSD < 10 %; *iv)* qualitative identification of components in welding fumes of unknown origin for the purpose of further investigation of their toxic effects; *v)* comparative investigation in a bus assembly plant with two type of sampling heads for inhalable fractions of air pollutants from welding processes with an RSD < 20 %.

OCCUPATIONAL EXPOSURE TO LOW LEVELS OF ORGANIC AND INORGANIC SUBSTANCES IN A CHEMICAL PLANT FOR THE PRODUCTION OF TEREPHTHALIC ACID DIMETHYL ESTER

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The aim of this study was the evaluation of personal exposure to chemical pollutants of workers employed in a chemical plant for the production of terephthalic acid dimethyl ester (DMT). Chemical agents have been included in the monitoring programme on the basis of the industrial process. In the plant the oxidation of *p*-xylene is performed by air and the resulting acids are esterified with methyl alcohol. Purified DMT is then utilised for the production of polyethylene terephthalate. The monitoring programme included terephthalic acid dimethyl ester (CAS no., 120-61-6), *p*-toluic acid methyl ester (CAS no., 99-75-2), terephtalic acid (CAS no., 100-21-0), *p*-xylene (CAS no., 106-42-3), acetic acid methyl ester (CAS no., 79-20-9), benzoic acid methyl ester (CAS no., 93-58-3), formic acid (CAS no., 64-18-6), methyl alcohol (CAS no., 67-56-1), acetic acid (CAS no., 64-19-7), cobalt acetate (CAS no., 71-48-7) and acetic acid Mn (II) salt tetrahydrate (CAS no., 6156-78-1).

Personal exposure measurements to the cited airborne substances were performed in the breathing zone of six workers. Air samplings were carried out by pumping air through glass fiber filters (for terephthalic acid dimethyl ester and *p*-toluic acid methyl ester aerosols), by adsorption on Anasorb 747 (SKC) (for methyl alcohol vapour) and on activated charcoal (SKC) sampling tubes (for formic and acetic acid vapours). *p*-Xylene, acetic acid methyl ester and benzoic acid methyl ester vapours were collected by passive sampling on charcoal bags. Cellulose nitrate filters (Sartorius) were used for Co and Mn sampling. Analyses were performed by Flame Ionization Detection Gas Chromatography (FID-GC) for *p*-xylene, acetic acid methyl ester and benzoic acid methyl ester, UV-detection High Performance Liquid Chromatography (HPLC) for terephthalic acid dimethyl ester and *p*-toluic acid methyl ester, Ion Chromatography (IC) for formic and acetic acid and Inductively Coupled Plasma Mass Spectrometry (ICP-MS) for Co and Mn. The results were evaluated according to the Threshold Limit Values (TLVs) of the American Conference of Governmental Industrial Hygienists (ACGIH). Results show that the environmental levels of the workplace pollutants are well below the Time Weighed Average (TWA) TLVs adopted by ACIGIH for 2002 (for three substances the TLVs were not available).

POSTER PRESENTATIONS

Session 10

IMPROVING THE ANALYTICAL PERFORMANCE OF ICP-AES FOR ULTRATRACE ANALYSIS OF ENVIRONMENTAL SAMPLES

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The determination of ultratrace elements in environmental matrices has a wide-ranging importance, including routine monitoring of pollution, investigations on chemistry of planetary systems and studies on the ecological and physiological role of essential elements. However, the analysis of environmental samples is troublesome, due to the extremely low analytical concentrations and potential interferences arising from the matrix. Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES) is a well-established technique for elemental analysis which offers several advantages, such as reduced chemical interferences, extended working range, excellent precision and multielemental capabilities. Moreover, modern instruments equipped with detectors based on Charge-Coupled Device (CCD) technology allow several emission lines to be simultaneously measured with significantly lower detection limits, especially when the axial-viewing mode is used. However, to make the instrumental performance of the technique more adequate for the analysis of environmental samples, further improvements in detection power and accuracy are needed.

The possibility of expanding the capabilities of an axially viewed ICP-AES with multichannel detection based on CCD was explored. In order to improve the detection power, ultrasonic nebulization was resorted to and its influence on the other figures of merit (plasma robustness, precision, long-term stability, memory effects, tolerance to matrix effects) were evaluated and discussed. As regards accuracy, a systematic procedure for the selection of optimal internal standards has been developed and applied to compensate for the matrix effects due to common matrices, such as inorganic acids and large amounts of Al, Ca, Fe, K and Na. Results were evaluated by the analysis of both synthetic samples and Certified Reference Materials (CRMs).

OPTIMISATION OF IRRADIATION CONDITIONS FOR SIMULTANEOUS DEUTERON-CYCLOTRON PRODUCTION OF HIGHLY-SPECIFIC ACTIVITY ^{64}Cu AND ^{66,67}Ga

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Thin- and thick-target excitation functions of ^{64,61}Cu, ^{66,67}Ga and ^{65,69m}Zn Radionuclides (RNs) have been experimentally determined by cyclotron irradiation using ^{nat}Zn(d,αxn) and ^{nat}Zn(d,2pxn) reactions in the energy range up to 19 MeV. Three stacks of thin-targets were irradiated at 19, 14 and 9 MeV deuteron energy. Each stack was composed by six ultra-high purity thin Zn foils, in addition to a series of high-purity Al catchers and Al energy degraders. In the energy range 19-10 MeV, the first Al catchers were also used as monitor foils through the Al(d,X)^{24}Na nuclear reactions, so as to verify the charge integrator accuracy by resorting to the recommended IAEA cross-section data. In the energy range below 10 MeV use was made of thin Ti foils as monitors, through the Ti(d,X)^{48}V nuclear reaction cross-sections. For ^{64}Cu (E_γ 1346 keV, 0.473 %) statistics of each measurement was not optimal; nonetheless, the decay fitting gave a very low χ^2 value of 1.66 in the worst case. All γ emissions of other RNs have counting statistics errors lower than 0.1-1 %. For each RN and each target, several tens of measurements were carried out over a period of about 18 months. A thick-target yield of 8560 ± 240 MBq C^{-1} was measured at the EOIB at 19 MeV deuteron energy, which corresponds to a saturation value of 565 ± 16 MBq μA^{-1}. An activity of ^{64}Cu of 15 GBq was produced, with a radiochemical yield of 80 %, a Zn decontamination factor of 10^6, an RN purity of 90 %, a 25.4 hr irradiation time, a 15 hr cooling time and a beam current of 100 μA.

THE INTERNATIONAL NORMATIVE FOR TOC AND CARBON DETERMINATION IN WATER SYSTEMS. CHRONOLOGICAL AND CRITICAL ANALYSIS

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The recent development of environmental technologies is the result of awareness about the respect of environment and the safety of territory as connected to the improvement of the conditions of life. Legal provisions and national and European laws almost oblige to always find new solutions to protect ecosystems. In recent years, both the public and private sectors have been more and more interested in markers of water quality and of water treatment efficiency as applied to different systems (sea, lagoons, surface water). In every countries all over the world Total Organic Carbon (TOC) is accepted as the most suitable index to monitor civil and industrial wastes. The tracking of CO_2, obtained by oxidative system is the heart of modern TOC analysers.

One of the most used methods foresees IR determination of CO_2 produced by the oxidation of the organic compounds present in water. Also other detectors can be used, but they must be characterised by mechanical resistance and stability, not interfered by other gases and not easily corroded. Moreover, they must be sensitive, affected by no drift of signal and possibly having a linear response in a wide range of concentrations. Among the IR detectors, the most popular is the Non-Dispersive Infrared (NDIR) detector both in portable and laboratory models. It allows CO_2 and other gases (CO, NO, SO_2 and NH_3) to be measured. Measurement accuracy largely depends on the oxidation system. Basically, methods can be distinguished as low (below 100 °C) and high (above 600 °C) temperature approaches with further technical and instrumental differentiation. Particularly instruments based on UV lamps operating at a double wavelength should be considered capable of exerting different oxidation behaviour.

The increasing need for pure water, essential at the industrial level (as, *e.g.*, in the production of drugs or of semiconductors) has enhanced the request of TOC analysers. The United States Pharmacopoeia (USP) recently changed abruptly the systems used to obtain ultrapure and injection water so that now TOC analysis is mandatory for water to be used in the production of pharmaceuticals. Even if not yet completely adequate, the new European guidelines approved by the CEN/ISO commission will definitely contribute to a wider diffusion of these analytical methods.

A SIMPLE METHOD FOR THE DETERMINATION OF ORGANIC AND INORGANIC MERCURY IN NATURAL WATERS

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Toxic effects of Hg are well known as well as the fact that the element exhibits markedly higher toxicity in the organic than in the inorganic form due to the increased ability of the former to cross membranes. Consequently, speciation of Hg has received increasing attention, the methods used being primarily High Performance Liquid Chromatography (HPLC) and Capillary Electrophoresis (CE). However, no laboratories of the Hungarian Environmental Inspectorates, responsible for natural water quality monitoring, possess such equipment and thus only the total Hg content can be measured by Cold Vapour Atomic Absorption Spectrometry (CV-AAS). The aim of this study, supported by the Hungarian Ministry of Environment, was to develop a simple method for the determination of both inorganic and organic Hg content in water.

The total element content is measured by reduction of Hg to the elemental state with $SnCl_2$ (CV method). A preliminary digestion step with BrCl is carried out since organic species react slowly with the reducing agent. As this reaction is slow, but not negligible, elimination of the digestion step alone does not automatically lead only to the quantification of inorganic Hg. By appropriately choosing acidity of the solutions (blank, carrier, reducing agent, sample) and minimizing the time between sample preparation and analysis, conditions under which only inorganic Hg is measured could be optimized. The content in organic Hg is calculated as the difference between the total and the inorganic amounts. Recovery for test compounds and measures to be taken against memory effects at higher concentrations were also elucidated. The method proved to be sufficiently adequate to meet present needs.

TRACE ELEMENTS CHARACTERISATION BY INAA OF THREE SEDIMENTS OF DIFFERENT ORIGIN

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Three environmental matrices proposed as Certified Reference Materials (CRMs) by the EU Standards, Measurement and Testing Programme (SMTP), formerly Bureau Communautaire de Référence (BCR), were characterised for their trace element contents. The materials are the BCR-277R Estuarine Sediment, BCR-280R Lake Sediment and BCR-320R Canal Sediment.

Several trace elements, including As, Co, Cr, Fe, Mn, Ni, Sb, Sc, Th, U and Zn, were determined by means of Instrumental Neutron Activation Analysis (INAA). The values measured in this work are compared to the certified values obtained at the end of the certification process.

A PILOT STUDY FOR THE QUANTIFICATION OF As SPECIES BY CAPILLARY ELECTROPHORESIS

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The quantification of As species is an important issue since the toxicity of its various forms varies widely. A number of separation techniques have been used to study the presence of arsenical species in different matrices, environmental and food analyses included. However, most of these methods are often difficult to perform, subject to interference and rather expensive.

Capillary Electrophoresis (CE) shows many advantages over conventional techniques due to great versatility and simple method development. In particular, compared with High Performance Liquid Chromatography (HPLC), CE offers a higher separation efficiency, requires smaller sample and relatively shorter analysis time and is characterised by lower costs and greater tolerance to complex matrices. On the other hand, this technique shows some disadvantages such as lower detection power and system performance stability. This study aimed at developing a method to obtain the separation of the main arsenical species by CE and their subsequent quantification with Diode Array Detector (DAD) UV detection at the wavelength of 192 nm. Coupling of CE with Inductively Coupled Plasma Mass Spectrometry (ICP-MS) is being explored to improve the applicability of the method to samples with medium to low As content.

INVESTIGATION OF UPTAKE PROCESSES OF MUSHROOM (*AGARICUS BISPORUS*) FROM SOIL BY ATOMIC EMISSION AND ATOMIC ABSORPTION SPECTROMETRY

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Mushrooms (*Agaricus bisporus*) were grown under controlled conditions in pots containing 20 kg of soil to which Cd, Cs, Hg, Ni, Pb and Se trace elements were added separately in the chemical form of $CdSO_4$, CsCl, $HgCl_2$, Na_2SeO_3, $Ni(NO_3)_2$ and $Pb(NO_3)_2$ in concentration ranging between 10 and 1000 mg kg^{-1} (wet mass). In order to increase the yield, in another series of investigations Mn was added to the growth medium as $MnCl_2$ at a concentration of 100 mg kg^{-1}, as Mn is known to enhance the decomposition of straw (lignocellulose) present in the growth medium.

The representative samples taken (fruit bodies, caps) were dried at 105 °C, ground and sifted through a sieve of 63 µm pore size. 250 mg of the samples were placed into Teflon vessels and dissolved in a mixture containing 5 ml of concentrated HNO_3 and 2 ml of 30 % H_2O_2 by heating at 140 °C for 3 hr. The clear solutions were made up to 25 ml with 0.1 mol l^{-1} HNO_3. Determinations of Hg were carried out by Cold Vapour Atomic Absorption Spectrometry (CV-AAS), whereas Cs was determined with a PYE Unicam 190 AAS equipment in the emission mode. The concentrations of Cd, Mn, Ni, Pb and Se in the samples were determined with an ARL 3410 Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES) spectrometer.

Preliminary results of the investigation showed that the uptake of Cs and Hg in the fruit bodies of the mushrooms investigated was significant compared with the uptake of Ni and Pb. Considerable uptake of Se was observed in the presence of yeast. Information on the potentially toxic element uptake (*e.g.*, Cd, Hg) from soil into mushrooms may be useful for the elucidation of their transport throughout the food chain.

FLOW-INJECTION PRECONCENTRATION AND ELECTROTHERMAL ATOMISATION ATOMIC ABSORPTION SPECTROMETRY DETERMINATION OF Mn IN PHARMACEUTICALS

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Catalysts, *i.e.*, oxidising and reducing agents used during chemical synthesis, might remain in pharmaceutical substances at the end of the production process. Their presence should therefore be ascertained. There are rigorous industrial limits for the maximum allowable amounts of impurities in drug substances, but the detection power and selectivity of heavy metal tests prescribed by the Pharmacopoeia in most cases do not meet these requirements. There are, *e.g.*, no limit test for Mn. Direct Electrothermal Atomisation Atomic Absorption Spectrometry (ETA-AAS) is used for determining Mn in some drug substances. Its concentration range is in the low μg l^{-1} range. On the other hand, Inductively Coupled Plasma Mass Spectrometry (ICP-MS) is also often used for the determination of the level of inorganic impurities in drug substances.

A Flow Injection (FI) chelating cellulose microcolumn preconcentration procedure was developed for Mn(II) and Mn(VII) in aqueous and 50 % aqueous ethanol and methanol solutions. The stability constants of Mn(II)-iminodiacetic acid ethyl cellulose (IDAEC) complexes were determined potentiometrically. The species distribution curves in homogeneous media were used for optimising the FI on-line preconcentration of Mn. The optimal pH range for preconcentration was 4.5-6.0. At the ten-fold enrichment factor, the limit of the detection was 0.042 μg l^{-1}. The possibility of applying the FI microcolumn preconcentration procedure depend on the complex-forming ability of the drug matrix. The results of this investigation can be used to assess the strength of interaction between Mn and the multifunctional organic molecule.

COMPARISON OF DIFFERENT SPECTROPHOTOMETRIC AND FLUORIMETRIC METHODS AND NEW BIOSENSOR OR VOLTAMMETRIC METHODS FOR MEASURING THE ANTIOXIDANT CAPACITY OF SEVERAL REAL MATRICES

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An extensive scientific literature exists concerning the measurement of the antioxidant capacity which has proved to be an extremely important index not only in the field of chemistry, but also for medicine, nutrition and drugs. A wide range of different spectrophotometric methods were proposed by various authors for the measurement of the antioxidant capacity. As each method leads to a different scale of antioxidant capacity which is valid only for the considered method, the main purpose of the present study was to compare the results obtained using spectrophotometric or fluorimetric methods with those obtained using a new recently developed biosensor, *i.e.*, a Superoxide Dismutase (SOD) enzyme and, in some cases, also with the results obtained using a cyclic voltammetric method. An additional goal was to verify whether any experimental correlation, even qualitative, existed between the scales of the antioxidant capacity obtained using some of the better known spectrophotometric or spectrofluorimetric methods described in the literature and those based on the new biosensor or the voltammetric method. The methods chosen for this comparison were based on the *N*,*N*-dimethyl-*p*-phenylendiamine (DMPD)–$FeCl_3$ and crocin spectrophotometric methods and the Oxygen Radical Absorbance Capacity (ORAC) fluorimetric method.

The comparison was performed on different samples of white and red wines and, more recently, on a dozen or so of drug products marketed specifically for their antioxidant properties, but the components and active principles of which were all of ascertained vegetal origin and provenance (dog rose, gingko, acerola, wheat germ, rutine, panax ginseng, natural vitamin E, vitamin C, betacarotene, bioflavonoids, macerated garlic). The results obviously were not compared and discussed on the basis of agreement among numerical values since each of these methods necessarily uses quite different units and numerical scales which are, at least at the present stage, nor interchangeable neither comparable. They are rather compared and discussed on the basis of possible agreement in the trend of the antioxidant capacity values obtained for the different products examined. To this end, extensive use was made of graphic representations in the form of two- and three-dimensional histograms.

CLEAN-UP OF ORGANIC EXTRACTS BY SUPERCRITICAL FLUID CHROMATOGRAPHY FOR THE DETERMINATION BY GC-MS OF TRACE ORGANICS IN REAL SAMPLES

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The determination of organic pollutants in environmental samples is generally based on the extraction of analytes from the sample and the clean-up of the extract, followed by instrumental analysis. Since the legally acceptable concentration limits of micropollutants still tend to be set lower for health and safety reasons, their identification and quantification are of increasing importance in environmental studies. The most critical steps deal with the extraction of analytes from the sample by a suitable solvent and the clean-up of the organic extract by column chromatography. The latter is aimed at reducing the presence of interfering compounds and making the instrumental response more accurate and precise.

In this study the determination of Polyaromatic Hydrocarbons (PAHs) and Polychlorobiphenyls (PCBs) in environmental samples has been considered and the most significant findings concerning the optimisation of the adsorption materials used as a stationary phase for the clean-up of various organic extracts are examined. Finally, a few applications of the optimised procedure are discussed These are based on the use of supercritical CO_2 as a mobile phase for the recovery of the analytes from the clean-up column, in particular for biological samples which are among the most difficult to be analysed.

A Py-GC-MS PROCEDURE FOR THE CHARACTERISATION OF NATURAL AND SYNTHETIC MATERIALS IN ARTWORKS

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The characterisation of natural and synthetic polymers in microsamples from artworks requires a sensible and versatile technique such as analytical pyrolysis, which has often been used for this purpose. It offers the advantage of no sample pretreatment, thus avoiding sample contamination and losses, and of the identification of both natural and synthetic materials on the same sample. Furthermore, the technique of thermally assisted reaction (pyrolysis in the presence of a particular reagent) allows polar pyrolysis products to be analysed, which otherwise would be lost.

This paper describes an analytical procedure based on pyrolysis in the presence of the silylating agent hexamethyldisilazane, on line with a Gas Chromatography Mass Spectrometry (GC-MS) system. Both natural and synthetic polymers simultaneously present in the same sample could be be thus analysed. This procedure has been applied to the diagnosis of samples collected from frescoes of the Monumental Cemetery of Pisa (Italy). These frescoes, particularly damaged during the Second World War due to a fire caused by a bombardment, are under restoration. The most significant results of the chemical investigation performed are discussed. They provide information on the proper materials and techniques to be used in the restoration work.

A STUDY OF CALCIUM OXALATE FILMS ON STONES

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The possibility of making some assumptions about the oxalate film origin on stones is strictly connected to the knowledge of the inorganic and organic composition of the considered layers, to the comparison of the morphological characteristics with those of similar investigated films and to the knowledge of the local ancient conservation uses. This study is devoted to the characterisation of calcium oxalate films collected on marble surfaces of churches of the 12th-14th centuries in Pisa and Lucca (Tuscany, Italy).

These important monuments show seriously damaged surfaces with thick black crusts due to the chemical corrosion of the calcite and to the action of atmospheric urban pollution, mainly caused by vehicular traffic. Beneath black crusts, well conserved oxalate films covering very large areas of the marble surface were detected. The films were characterised by optical microscopy, Scanning Electron Microscopy-Energy Dispersive X-Ray (SEM-EDX) Spectroscopy analysis, Fourier Transform Infrared (FTIR) Spectroscopy and Gas Chromatography-Mass Spectrometry (GC-MS) analysis. The results showed the presence of calcium oxalate in both its different mineralogical phases (whewellite and weddellite) together with gypsum, nitrate and silicates. GC-MS analysis revealed the presence of amino acid patterns, fatty acids and hydrocarbons. In particular, based on these new findings, it may be inferred that in the past a surface treatment based on the use of egg yolk and animal fats took place. The atmospheric oxidative pathway could be partially confirmed by comparison between the degradation phenomena observable on the white marble and those on the black limestone.

DETERMINATION OF TRACE ELEMENTS IN SEAWATER SAMPLES BY COUPLING ION CHROMATOGRAPHY WITH ELECTROTHERMAL ATOMISATION ATOMIC ABSORPTION SPECTROMETRY

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The study of environmental processes is often related to the quantification of trace compounds by sensitive and reliable analytical methodologies. Electrothermal Atomisation Atomic Absorption Spectrometry (ETA-AAS) is a very useful instrumental technique for trace element determination since it allows the analytes to be concentrated directly in the furnace, thus minimizing both chemical and physical sample pretreatment, especially if coupled with very efficient continuous high volume sample introduction devices. In the analysis of high salt content samples, such as seawater, these devices have to be connected to a sample purification system for salt removal which is generally based on liquid-liquid extraction or column chromatographic separation.

This study describes an analytical instrumentation for the determination of trace metals in seawater samples in the range of pg g^{-1} by ETA-AAS. In particular, the system is based on the on-line coupling of an ion chromatographic system, for the separation of the analytes, with an ETA-AAS equipped with a new device for the continuous injection of large volumes of sample in the furnace at a flow of up to 2 ml min^{-1}. The optimised experimental conditions and the results relevant to the application of the proposed procedure to the determination of Cd and Pb at pg g^{-1} levels in a Certified Reference Material (CRM) of seawater are presented.

INVESTIGATION OF CYPERMETHRIN-CYCLODEXTRIN COMPLEXES BY DIFFERENT ANALYTICAL METHODS (UV-SPECTROPHOTOMETRY AND THERMAL ANALYSIS)

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Natural extracts of the herb *Chrysanthemum roseum* have been used as insecticide for almost 400 years. The active substances of the above herb are called pyrethrins. The synthetic pyrethroids (which are simple chemical analogues of the pyrethrins) were developed in the 1970's. The major advantages of these derivatives are in their increased stability and selective biological activity. The low toxicity for mammals and the fast degradation make them very useful insecticides in the household and agricultural application. The pyrethroids are nearly insoluble in water and have low light stability. Their application is therefore limited. In most cases inclusion complex formation with cyclodextrins improves stability, wettability and dissolution rate of poorly soluble substances. This investigation was focused on the interaction of cypermethrin, one of the most effective synthetic pyrethroid, with Cyclodextrins (CDs). Preparation and investigation of the cypermethrin-CD inclusion complexes were carried out with different complexation methods. The solubility and light stability were also studied.

Four complexation methods were tested, namely, coprecipitation, suspension, kneading and "melting in solution" at the cypermethrin/b-CD stoichometric ratio of 1:2. The complexes were examined by UV spectrophotometry and thermal analysis, *i.e.*, Differential Scanning Calorimetry (DSC), Thermogravimetry (TG) and Derivative Thermogravimetry (DTG). The melting technique was found to be the most effective complexation method. By investigating the solubility of cypermethrin in aqueous solutions of different CDs it was established that the highest solubility of cypermethrin occurred in the case of methylated cyclodextrins. The equilibrium constants were calculated from solubility isotherms and on the basis of these results the DIMEB complex was found to be the more stable. The effect of UV irradiation at 254 nm on the decomposition of cypermethrin and the complex as well was investigated by UV spectrophotometry using 50 % aqueous ethanolic solutions. It revealed that the rate of decomposition of cypermethrin was retarded in the presence of methylated bCDs.

MODELS OF PESTICIDES INSIDE CAVITIES OF MOLECULAR DIMENSIONS.

ROLE OF THE CAVITY SIZE

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Dicarboximide-type pesticides, namely vinclozoline [3-(3,5-dichlorophenyl)-5-methyl-5-vinyl-1,3-oxazolidine-2,4-dione], iprodione [3-(3,5-dichlorophenyl)-N-(1-methyl-ethyl)-2,4-dioxo-1-imidazolidinecarboxamide] and procymidone [3-(3,5-dichlorophenyl)-1,5-dimethyl-3-azabicyclo[3.1.0]hexane-2,4-dione] are widely used as preventive, curative and persistent fungicides particularly effective against *Botrytis*, *Monilia* and *Sclerotinia* on field crops, in vineyards and in greenhouses. They are used for treatment of tree fruits, strawberries, hops and various types of vegetables. All these compounds contain the dichlorophenyl group attached to a nitrogen atom of the dicarboximide moiety of the heterocycle ring. Trace amounts of these pesticides can be determined in foods by methods based on their alkaline degradation to 3,5-dichloroaniline. The reduction mechanism of free and cyclodextrin cavity bound fungicides was already characterised.

Three types of Cyclodextrin (CD) molecules (α-, β- and γ-CD) with different cavity sizes were investigated. Voltammetric measurements could demonstrate interactions of all three fungicides with CD. The free form of fungicide yields two irreversible reduction waves, the first around 2.2 V and the second at more negative potentials. Addition of CD increases the currents of both processes and leads to a considerably different pattern of anodic reoxidation products. A very sharp and distinct peak on the subsequent scan in the cathodic direction corresponds to the reduction of an adsorbed host-guest complex of one of the products, most likely chloride anion. Enhanced dechlorination was confirmed also by Gas Chromatography – Mass Spectrometry (GC-MS) detection of the reduction products of the complexes. The reduction of free fungicides involves opening of heterocyclic ring as a main process, whereas the cleavage of one or two chlorine atoms from a dichlorophenyl moiety predominates in the presence of CDs. Quantitative GC-MS analysis of the degradation products in the presence of β-cyclodextrin suggests that the relative strength of the host-guest type of interactions changes in the order vinclozoline - procimidone - iprodione. It could be thus ascertained that cavity dimensions play an important role in the overall reduction process. A study of the possible modes of interaction between vinclozoline and all three CDs was carried out. Electronic structure and stabilization energy calculations were performed using a semiempirical Austin model (AM1) method within the Spartan programme package. One of the major conclusions of these calculations is that inclusion of vinclozoline with its heterocyclic ring into the cavity occur in such a way that the stabilisation of the supramolecular structure is achieved by interactions of two carbonyl groups of vinclozoline with hydrogen atoms of secondary hydroxyl groups at the rim of the cavity. Substantial change of LUMO (electron accepting orbital) upon inclusion of vinclozoline into the cyclodextrin cavity is consistent with the interpretation of the reduction mechanism changes.

DETERMINATION OF HERBICIDE CONTENT OF NATURAL FRESHWATER BIOFILMS BY A GAS CHROMATOGRAPH-MASS SPECTROMETER SYSTEM

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Since several herbicides are widely used in agriculture, their fate and effects on the environment are of primary importance. Their ability to be biomagnified makes them dangerous to the aquatic environment. In the early stage of the process, the dissolved herbicides can be bound to biofilms (periphyton communities), formed on natural or artificial substrates in the photolytic surface layer of water bodies. This study focused on the influence of substrates and season on the herbicide presence in natural biofilms. Biofilms were grown seasonally in the Lake Velence (Hungary). Different substrates were tested and compared, *i.e.*, three natural materials (andesite, granite, reed) and an artificial one (polycarbonate).

Samples were prepared by combining liquid- and solid-phase extraction. Gas Chromatography Mass Spectrometry (GC-MS) determinations were carried out and triazines and chloracetanilide herbicides could be detected in the biofilms. At the same time in the lake freshwater samples the herbicide concentration rarely exceeded the Limits of Detection (LoDs). In the six-week-old biofilm samples the presence of herbicides depended on the season as well as on the substrate quality.

RADICAL INTERMEDIATES IN ELECTRON TRANSFER REACTIONS OF A DYPHENYL-ETHER HERBICIDE BIFENOX

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Chlorinated diphenyl ethers are commonly used herbicides for weed control especially in rice production. The phytotoxic activity of diphenyl ethers is achieved by preventing chlorophyll synthesis in plants. However, the inhibition of protoporphyrinogen oxidase, blocking the chlorophyl production, is efficient also in heme formation and human hemoglobin synthesis. Hence, these compounds can cause porphyrin accumulation diseases such as *Porphyria*. Recently it was reported that the relatively high occurrence of gall bladder cancer in risk areas could be attributed to contamination of water sources by residues of such herbicides. Nitrodiphenyl ethers with a substitutent in the ortho position on one of the benzene rings exert herbicidic activity only after illumination. It was proposed that the inhibitory effect may be connected with production of reactive free radicals upon photoactivation.

An electrotrochemical study was undertaken to identify the intermediates formed after an uptake of electrons at the electrode interface. Contrary to photochemical production of radicals, the electrochemical generation under potentiostatic control allows well-defined electron transfer to occur to a specific redox active group. The compound selected for this study was bifenox, *i.e.*, methyl 5-(2,4-dichlorophenoxy)-2-nitrobenzoate. Its structure suggests that electron transfer will most likely lead to primary multielectron reduction of the nitro group. The redox cleavage of the C-Cl bond in aromatic chloro compounds is known, however, to proceed at considerably more negative potentials. Furthermore, the benzoate esters are reduced under aprotic conditions to the corresponding anion radical. These ester anion radicals are unstable and cleave to benzoate anion and the alkyl radical, which can react even with the starting ester. Hence, the reduction process of bifenox can in principle involve anything from one to eleven electrons and resulting intermediates can produce chloro-, methyl- and nitroradicals. Reduction in acetonitrile yields two reduction steps at –1.0 and –1.5 V, involving one and three electrons, respectively. The three-electron reduction produces short living intermediates detectable at the scan rate of 30 V s^{-1} or higher. These intermediates are seen as anodic/cathodic peaks in the range –0.5 to –0.8 V. The reduction mechanism and effects of the molecular environment are discussed.

PHOTODEGRADATION STUDY FOR ASSESSING THE ENVIRONMENTAL FATE OF SOME TRIAZINE-, UREA- AND THIOCARBAMATE-TYPE HERBICIDE

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The photodegradation features of 13 nitrogen-containing herbicides, namely atrazine, cyanazine, terbuthylazine, terbutryn (triazines), diuron, fenuron, chloroxuron, methabenzthiazuron (ureas) and buthylate, cycloate, EPTC, molinate, vernolate (thiolcarbamates) were investigated. The compounds were completely decomposed by a high pressure Hg vapour lamp and the degradation process was followed by subsequent gas chromatographic measurements. The structure of the degradation products was ascertained by Gas Chromatography – Mass Spectrometry (GC-MS) measurements.

All of the compounds studied had measurable photochemical activity, although the actual and average degradation rates varied significantly. The most significant processes of photodegradation of triazines are the partial or complete loss of side-chains, or rather the substitution of the heteroatom-containing side chain to a hydroxyl group. Loss and oxidation of the alkyl chains are the dominant processes also during the degradation of ureas. Moreover, secondary processes are the substitution of the halogen atom with a hydroxyl group and the hydroxylation of the aromatic ring. In the case of thiolcarbamates, the most frequent processes are the α- and β-oxidation of alkyl groups linked to the nitrogen atom. In most cases, N-formyl and N-dealkylated products could be identified in the degradation mixture.

STUDY OF ACETOCHLOR AND ATRAZINE INTERACTION WITH NATURAL FRESHWATER BIOFILMS IN LABORATORY EXPERIMENTS

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Biofilms (microbial communities formed in waters on submerged solid phase surfaces) have an important function of pollutant sorption in the aquatic environment. The Extracellular Polymeric Substances (EPS) produced by the microcolony (consisting of polysaccharides, proteins, lipids and nucleic acids) concentrate nutrients as well as inorganic and organic toxic compounds. Members of the biofilm communities can also consume, *e.g.*, chlorinated aromatics as carbon sources during starvation. Experiments were performed to investigate the accumulation and degradation of acetochlor and atrazine herbicides by natural biofilms in seminatural environment. The biofilms were colonised in the Lake Velence (Hungary). They were grown on artificial substrates of polycarbonate film strips, which were vertically submerged into the water (20-30 cm beneath the water surface) in plexiglass racks. After four weeks of colonisation the biofilms were transported to the laboratory and kept in thermostated aquaria for two more weeks. The aquaria were filled with herbicide-spiked lake water (containing 12.5 ng g^{-1} acetochlor and 12.5 ng g^{-1} atrazine). Degradation of these herbicides was investigated with and without biofilms. In the latter case their accumulation was also checked.

The sample preparation method and the quantitative determination by Gas Chromatography Mass Spectrometry (GC-MS) were controlled and optimised for both herbicides. Changes in acetochlor and atrazine concentrations over time and occurrence of their decomposition products in the aquarium water as well as in the biofilms were detected. The microbiological effects were followed by taxonomic investigations. On the basis of these experimental results it could be concluded that no photodegradation actually takes place, but rather other biological decomposition processes play a significant role under these experimental conditions. In the case of the two herbicides tested, a different trend of concentration decrease in the water phase caused by the presence of the biofilm was observed. Furthermore, accumulation of atrazine and acetochlor in biofilms was observed at concentration levels of 77 ng g^{-1} and 335 ng g^{-1}, respectively. On the other hand, the measured accumulation ratio in each case amounted only to less than 1 % of the total added herbicide amount.

DRY AND WET ATMOSPHERIC DEPOSITION OF PAHs ONTO THE LAKE BALATON

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Lake Balaton is the largest lake in Central Europe with a surface area of 600 km^2 and an average depth of 3.25 m. Its monitoring for pollutants is fundamental to the solution of environmental protection problems. Determination of different polluting Polyaromatic Hydrocarbons (PAHs) in aerosol, precipitation and sediment samples collected at the Lake Balaton was carried out. The aim of collecting precipitate and aerosol samples in the same site at the same time was to determine the distribution of elements in wet and dry depositions. Samples were collected in three sampling sites around the lake from April 2002 to April 2003. Wet-only samplers for the precipitation and membrane pumps with 47 mm Whatman GF/F glass-fiber filters were used for the collection of particles for 45-65 m^3 air volume. For fractionation by particle size, aerosols were sampled by a Berner-type eight-stage cascade impactor. The concentration of PAHs in different samples was determined by a High Performance Liquid Chromatography Fluorescence Labeling (HPLC-FL) method. Separation was done by a 5 µm particle size LiChrospher C18 PAH, 250 mm x 4 mm column.

The transport processes of the most carcinogenic and teratogenic PAHs (15 EPA priority compounds) in the Lake Balaton is discussed. The measured distributions of the PAHs have been analysed by advanced statistical and soft-computing techniques to detect significant correlations and extract potentially useful information that can be used for the identification of a chemical mass balance model. The distribution of PAHs has been found similar at each sampling site, thus indicating that the sources are the same, *i.e.*, mostly traffic in the summer (tourist season) and domestic heating in the winter. A Chemical Mass Balance (CMB) model based in part on Fuzzy-algorithm is suggested.

DEVELOPMENT OF A MONITORING NETWORK ON THE LAKE BALATON

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A monitoring network was developed to obtain information on the present level of harmful pollutants in the Lake Balaton, as well as in its catchment area and harbors. Determination of different inorganic pollutants (toxic metals) in aerosol, precipitation, water and sediment samples was carried out. Aerosol was sampled by a Berner-type impactor with particle size fractionation and on membrane filters. It has been found that the concentration of elements in the dry depositions depended very much upon the particle size distribution of samples. For fractionation by chemical bonding, a three-stage sequential leaching procedure was applied. Particular attention was paid to distinguish between environmentally mobile and environmentally immobile fractions because these represent the two modes by which the metals are bound to the aerosol. The environmentally mobile elements are the most susceptible ones to be released into lakes or rivers. Sediment samples were collected from the top 10 cm layer of the bottom of lakes. The sample was dried at room temperature, then stones and plant fragments were removed by passing the dried sample through a 2-mm sieve. The sieved sample was powdered and finally passed through a 63 μm sieve. A four-step sequential leaching procedure was applied for the determination of the distribution of elements.

The concentration of major and trace elements was measured by Atomic Absorption Spectrometry (AAS) and Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES) with an RSD of less than 5 % from solutions. Standards were prepared from ultrapure chemicals. Analytical blanks were performed on filters from the same batch, on centrifuge tubes and on PTFE beakers. Results of the sum of four fractions of bottom sediments of the Lake Balaton, rivers on its catchment's area and harbors were compared to Sediment Quality Values (SQVs) and Sediment Background Values (SBVs). Data show that the average concentration of elements was usually less than that of SQVs and other background data for soils and geochemical values.

NEW DERIVATIVE ENZYMATIC-SPECTROPHOTOMETRIC METHOD FOR CHOLINE-CONTAINING PHOSPHOLIPID DETERMINATION IN SEVERAL BIOLOGICAL FLUIDS

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The determination of phospholipids, important constituents of biological cell membranes, can be performed by chromatographic methods, which are however laborious, time-consuming and not easily automated. Furthermore, separation-extraction processes of the sample and derivatisation of the analyte are generally required. Alternatively, the phospholipid concentration can be obtained by total phosphorus analysis using the molybdate-vanadate or the Bartlett's method. Also these methods require preliminary sample treatment using $HClO_4$ or a $HClO_4$-H_2O_2 mixture at about 180 °C. In more recent years, a selective and direct enzymatic-spectrophotometric method was adopted, which is based on two consecutive reactions catalysed, respectively, by phospholipase D and choline oxidase enzymes and on the subsequent reaction between H_2O_2, obtained in the latter enzymatic reaction, with phenol and 4-aminophenazone in the presence of peroxidase with the formation of a red dye. Measurements are performed at 500 nm. However, this method may present some drawbacks if the sample is pigmented or turbid. It was precisely to overcome these difficulties that a new method based on the above two enzymatic reactions was proposed. It exploits the first and/or second derivative in enzymatic-spectrophotometric analysis to directly determine the phospholipid (lecithin) content in human serum, amniotic fluids and bile samples, thus minimising sample pretreatment.

The results of the such determinations showed that serum samples can be analysed without any pretreatment. In the case of amniotic liquids, on the other hand, it was often necessary to resort to a sample volume larger than that one usually needed by the method owing to the very low phospholipid concentrations usually found in this type of sample. In the case of bile, on the other hand, a preliminary dilution of the sample was required using the same buffer as for the enzymatic test. Even when only very small volumes of bile were sampled, the solution concentration in phosphatidyl choline was such as to produce absorbance values exceeding by far the upper limit of the method linear range. The advantages of the derivative method were observed primarily in the analysis of bile samples containing traces of blood. In this case, the aim was to minimise chromatic interference by slightly varying the wavelength at which the first and second derivative peaks and troughs were read. It was also deemed advisable to apply the internal standard method. The results obtained show that also in these cases the first derivative method may still be applied even if the peak reading wavelength is slightly shifted. When this was done the recovery tests confirmed the reliability of the first derivative method.

THERMOVALORIZATION IN THE INTEGRATED MANAGEMENT OF WASTE

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In the year 2002 approximately 30 million tons of Solid Urban Waste (SUW) were produced in Italy, but no more than 5.5 million were collected separately. Data analysis showed that, despite the progress made with separated waste collection and with the process of quality recovery, dumps are still the most common means of disposal. As regards thermovalorization, even if the number of active thermal plants and the amount of thermo-valorized waste have increased by more than 10 % from 1999 to 2000, the total processed waste appears to be too little compared to the amount of waste produced and it is still below the average value in the EU countries. This presentation aims at describing three different scenarios for the affordable quantity of thermally valorizable waste till the year 2005.

The incineration of SUW is examined on the basis of technological, environmental and economic factors in different types of plants (with and without energy and heat recovery), due account being given to the quantity and quality of emissions and the possible recovery of CO_2. The best solution for the future, economically and environmentally, might be the transformation of waste in synthesis gas that can be used as energy and heat sources in a conventional power plant. From current knowledge it is easy to infer that today thermodestruction with energy recovery and the combined energy-heat cycle could be an option with great benefits for the environment and could be even competitive when compared to other options for replacing present polluting sources of energy.

TRACE AND MINOR ELEMENTS IN WATERS FROM EXPLORATORY WELLS IN A MUNICIPAL SOLID WASTE LANDFILL

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One of the main problems concerning landfill sites is the need to reduce environmental and sanitary risks coming from potential contamination of ground and surface waters by leachate. The formation of the latter is generally related to running and construction features of the plant, internal factors (waste moisture, water production and consumption during waste biodegradation) and external factors (meteorology and hydrology of the examined site). In addition, the leachate quality depends on the composition of stored solid waste.

The fit-for-purpose monitoring of a landfill, which is essential to understand and anticipate its behavior, is based on two different aspects, namely: *i)* structure inspection consisting in the regular check of waterproofing coatings. Their potential deterioration is generally due to shear strain and tensile stress of bearing surfaces acting on the bottom of the basin. The lithological properties of the side walls is another element that can explain this process; *ii)* quality check of the aquifer in the area surrounding the landfill consisting in the periodical analysis of aqueous samples collected by means of a series of monitoring wells. In this work the results obtained during two monitoring projects of three wells in a landfill of Southern Italy are discussed. The following elements were determined: Cd, Cr, Cu, Fe, Hg, Ni, Pb and Zn. Data obtained are also grouped on the basis of the composition of the landfill leachate.

CHEMICAL AND ECOTOXICOLOGICAL APPROACH TO EVALUATE METAL CONTAMINATION IN MAR PICCOLO (TARANTO)

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Mar Piccolo is situated near the city of Taranto. It is a coastal lake similar to a lagoon, consisting of two basins which have a depth average of 9-13 m. It is an important area of environmental studies because of its geographic configuration. Moreover, it hosts a military navy base and is affected by some human activities, such as the outlet of several sewers. The objective of this study was to evaluate, by means of chemical and ecotoxicological tests, the contamination risk due to the presence of metals and organic xenobiotic compounds.

In particular, attention was focused on the total and bioavailable Cd, Cu, Fe, Mn, Ni, Pb and Zn contents and on total and anthropogenic organic carbon. The ecotoxicological studies, based on Microtox® testing, were carried out in solid phase (sediments) and allowed the acute toxicity of matrices to be determined. Mathematical relationships between the ecotoxicological response (EC_{50}) and the chemical parameters (total and bioavailable metal concentrations and total and xenobiotic organic carbon contents) were investigated in order to identify the chemical pollutants primarily affecting the health of ecosystems.

MONITORING OF HEAVY METALS DERIVING FROM URBAN ACTIVITIES IN THE MACCHIAGRANDE OASIS (ROME)

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Macchiagrande's oasis is located near the Leonardo da Vinci-Fiumicino airport (Rome) and is close to an agricultural centre. Since 1987 this area has been included in those managed by the WWF Italia. A chemical monitoring programme was set up in order to evaluate the possible impact of the airport activities on the environment. In particular, the determination of the total metal concentration (Cd, Cu, Mn, Ni, Pb and Zn) for a certain number of superficial soils covering the whole surface of the oasis was carried out. At the same time, also some chemical-physical parameters such as pH, redox potential, cation exchange capacity and total organic carbon were measured.

Metal concentrations were generally low but for a restricted zone which showed a high Pb content. Hence, sampling was repeated at various depths in this area to try to identify the Pb source. Apart from the total Pb content, also chemical speciation of this metal was attempted both in superficial samples and in soil cores. In addition to this, the determination of Pb was performed both on plants and on dust deposited on leaves. As regards Pb speciation, the highest Pb portion turned out to be the mobile fraction, thus pointing to the fact that the Pb source was probably the runaway adjacent to the investigated area.

THE ISS CONTRIBUTION TO AN IAEA PROFICIENCY TEST FOR TRACE ELEMENTS IN FISH TISSUE

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The use of Certified Reference Materials (CRMs) to assess the accuracy of chemical measurements in different fields such as chemistry, biochemistry, food analysis and environmental protection is nowadays mandatory. In this context, the International Atomic Energy Agency (IAEA) launched a campaign to certify a new CRM based on a matrix of fish tissue for the chemical elements Al, As, Cd, Co, Cr, Cu, Fe, Hg (total and methyl-Hg), Li, Mn, Ni, Pb, Sb, Se, Sn, Sr, V and Zn. The Istituto Superiore di Sanità (ISS) participated in this project and the elements As, Cd, Cr, Cu, Fe, Hg (total), Ni, Pb, Se, Sn and Zn were determined.

Six aliquots of *ca.* 0.5 g each of the candidate CRM were weighed and subjected to acid-assisted digestion in a Microwave (MW) oven. Arsenic, Fe, Ni and Zn were quantified by Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES) (a) and Sector Field Inductively Coupled Plasma Mass Spectrometry (SF-ICP-MS) (b), Cu and Se by ICP-AES and Quadrupole Inductively Coupled Plasma Mass Spectrometry (Q-ICP-MS) (c), Cd, Cr, Pb and Sn by SF-ICP-MS and Hg by Cold Vapour Atomic Absorption Spectrometry (CV-AAS) (d). To estimate the performance of the 105 laboratories participating in this proficiency test, the organisers applied the *z*-score approach. The *z*-score values for the ISS were as follows: As, - 0.13 (a) and 0.04 (b); Cd, - 0.04; Cr, - 0.90; Cu, - 0.10 (a) and 0.00 (c); Fe, 0.25 (a) and 0.14 (b); Hg, 0.22 (d); Ni, - 1.03 (a) and - 1.01 (b); Pb, - 0.40; Se, 0.11 (a) and - 0.54 (c); Sn, 3.30 and Zn, - 0.15 (a) and - 0.23 (b).

All experimental data, with the exception of Sn, were therefore acceptable and could be included in the calculation of the certified values. The concentration value for Sn was eventually given only as an informative value. In any case, it should be noted that, the value obtained for this metal (137 ± 12 μg kg^{-1}) is very close to that reported by the organisers (100 ± 50 μg kg^{-1}, with a 95 % confidence interval of 60.0 - 130 μg kg^{-1}).

CHARACTERISATION OF ENVIRONMENTAL MATRICES BY SPECTROSCOPIC TECHNIQUES: RESULTS OF AN INTERLABORATORY TEST

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To be rapid and accurate, the determination of trace elements in environmental matrices requires the use of adequate methods that are able to combine highly sensitive instrumental analytical techniques with efficient digestion treatments. This is the case of techniques like Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) and Inductively Coupled Plasma Mass Spectrometry (ICP-MS) that can, in fact, produce much analytical information in a short time, often significantly shorter than that necessary to pretreat the samples. Moreover, the digestion procedure must assure a complete decomposition of the matrix in order to release all the analytes in the solution in a chemical form compatible with the analytical method.

The Microwave (MW) digestion has proved to be particularly suitable to achieve high levels of precision and accuracy in the determination of heavy metals in environmental samples, such as soils, sediments, plants and sludges. As a consequence, the number of official methods for the analysis of environmental matrices based on acid-assisted MW digestion is continuously increasing. Among others, last year two new methods were approved by the European Community, namely the EN 13656:2002 (*Characterisation of waste – Microwave assisted digestion with HF, HNO_3 and HCl acid mixture for subsequent determination of elements*) and the EN 13657:2002 (*Characterisation of waste –Digestion for subsequent determination of aqua regia soluble portion of elements*) methods, derived from the prEN CEN/TC292/WG 3 N310 and prEN CEN/TC292/WG 3 N100 projects.

This presentation illustrates the results obtained during the participation of the authors in interlaboratory tests organised in order to evaluate, optimise and validate the procedures proposed for the dissolution of the sample by MW digestion and the subsequent ICP-MS, ICP-AES and Cold Vapour – Atomic Absorption Spectrometry (CV-AAS) determinations. Several reference materials were used for the validation process, namely, Fly Ash Powder (CW6), Ash Powder (CW4), Ink Waste Powder (CW12), Sewage Sludge Powder (SL11), Sewage Sludge Powder (CRM BCR 146R) and Incineration Ash Powder (CRM BCR 176). The results obtained in the authors' laboratory were compared, in terms of trueness and precision, with the consensus values.

PESTICIDE METABOLITES AS CONTAMINANTS OF GROUNDWATER RESOURCES: ASSESSMENT OF THE LEACHING POTENTIAL OF ENDOSULFAN SULFATE, 2,6-DICHLOROBENZOIC ACID, 3,4-DICHLOROANILINE, 2,4-DICHLOROPHENOL AND 4-CHLORO-2-METHYLPHENOL

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Once in the environment, pesticides may be transformed into a large number of degradation products, commonly defined as metabolites. Many studies report the presence of pesticide metabolites in groundwater, although they are rarely included in monitoring programmes also for the difficulty of identifying those of primary importance. Due consideration being given to this, an approach was developed by which over 60 metabolites could be selected, relevant to various categories of pesticides widely used. This approach consists of: *i)* individuation of metabolites from parent compounds extensively used in agriculture; *ii)* evaluation of existing data on the environmental, toxicological and ecotoxicological properties of metabolites so as to preselect those to which priority should be attached; *iii)* assessment of the leaching potential of metabolites with known or unknown environmental properties by applying the Groundwater Ubiquity Score (GUS) index after measuring their K_{oc}, *i.e.*, the partition coefficient between soil organic carbon and water (which expresses the mobility of non-ionic compounds in soil) and soil DT_{50} (*i.e.*, the half-life of the soil concentration of a compound which expresses its persistence with quick, standardised laboratory tests); *iv)* validation of the behaviour of the "potential leachers" (GUS $\geq$ 2.8) by means of soil leaching column experiments; and *v)* research into selected groundwater bodies lying underneath agricultural areas where the relevant parent compounds are used.

This study reports the results of K_{oc} and soil DT_{50} experiments used for the definition of the leaching potential through the GUS index of five metabolites, namely, endosulfan sulphate (ES) from endosulfan, 2,6-dichlorobenzoic acid (DBA) from dichlorobenil, 3,4-dichloroaniline (DCA) from propanil, 2,4-dichlorophenol (DCP) from 2,4-D and 4-chloro-2-methylphenol (CMP) from MCPA. The K_{oc} values found for all these compounds were always lower than 300, indicating high mobility in soil, in particular in the cases of DBA and ES (K_{oc} < 18). Soil DT_{50} values of DBA and ES were around 24 days, whereas the other metabolites showed very short half-lives (< 3 days). DBA and ES had the highest leaching potential (GUS > 3.8), whereas CMP, DCA and DCP had very low GUS values (-0.88, 0.32 and 0.20, respectively). In short, the intrinsic characteristics of 2,6-

dichlorobenzoic acid and endosulfan sulphate are typical of leachers, but their significance as groundwater contaminants should be further surveyed through leaching in soil columns treated with their parent compounds.

FRESHWATERS IN URBAN AREAS: QUALITY AND MANAGEMENT

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The deep link between humans and water courses has been historically of primary importance for the development and progress of civilization. In the past, many great peoples owed their exceptional evolution to the close relationship established with big rivers which yielded undeniable benefits in many activities, such as agriculture, transports, defense, climate regulation and public health. At present, this relationship is of great relevance as large urban agglomerations are still placed along the course of big rivers. Yet, the continuous advance of technology and the growth of anthropic pressure is giving rise, almost everywhere, to a progressive decay of the quality of river waters. At the same time, the importance of rivers has been often ignored and almost turned into open air dumps. The good maintenance of river environments needs a deep knowledge not only of the quality of their waters, but also of the strict relationship with wide urban centers. In this context, a protected area placed inside the city of Rome (Regional Park of Appia Antica) has been investigated. It represents a perfect tool to test the reactions of a green area to a massive anthropic impact.

The ecology of freshwaters that are in the Park (Almone river and other little brooks) has been studied through the analysis of biological, chemical and hydrological parameters. In the early stage of the study adverse conditions were found for almost all the considered freshwaters with the only exception of Marrana della Caffarella that showed an ecosystem under better conditions, even if very fragile. Similar results were found in the second year of work in which new areas recently added to the Park were also studied. On the basis of these findings some indications may be drawn for the management of these urban surface waters so as to undertake the quali-quantitative restoration of the water resources and the recovery and conservation of the habitat. The data obtained in this investigation represent a first valuable tool to evaluate the impact of existing and future facilities and public works placed directly or in the neighborhood of the Park.

EVALUATION OF THE BIOLOGICAL QUALITY OF FRESHWATERS AND STUDIES ON THE ECOLOGICAL ROLE OF PROTECTED AREAS

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Protected areas play an important ecological role in the territory due to their function as a biological corridor and tank of faunal recolonisation, thus favouring the preservation of biodiversity. When these areas are placed in a drainage basin or have a drainage basin inside them, they carry out the aforesaid functions also in favour of freshwaters, acting furthermore as an important buffer strip. This is essential for the reduction of nitrates and phosphates that are washed away in the water bodies by rainwater or hypogean waters. The freshwaters amplify and integrate the functions of the protected areas carrying out the fundamental role of connecting them and increasing the functionality of the whole drainage basin.

A study was launched to assess the biological quality of several rivers and streams that run in the protected areas of the Latium region (central Italy) for which in particular the structure and the naturalistic value of the benthic community and the potential role as a biogenetic tank were investigated. The biological quality of 32 freshwaters, placed in 19 protected areas, was estimated by the Extended Biotic Index (EBI). This biotic index is based on the analysis of the benthic macroinvertebrate community collected in a river and allows a river section to be classified in one of five Quality Classes (QCs) from I (unpolluted environment) to V (strongly polluted environment). The results obtained so far show no clear general relationship between the size (or type) of the protected areas and the biological quality of the freshwaters present inside them. Protected areas can effectively contribute to preserve or to improve the biological quality of the freshwaters that run inside them, provided that the anthropic impact is represented only by agricultural activities or moderate urbanisation. On the other hand, in situations of massive urbanisation or strong industrialisation, the presence of protected areas does not seem to have immediate positive effects on the biology.

A PILOT STUDY ON THE CONTENTS OF SELECTED POLLUTANTS IN FISH FROM THE TIBER RIVER (ROME)

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The environmental integrated assessment of territorial areas allows their actual status to be described with specific regard to pollution and ecosystem quality. This information is to be considered as the starting point for appropriate planning of interventions and territory management to reduce potential risk factors for ecosystems and human health. The integrated approach takes into account the complete water cycle, the catchment basin as a whole and the characteristics of aquatic ecosystems in an ecological perspective so as to identify new strategies for river catchment basins. Sustainable management can thus be planned to take care of human (social and economic) needs along with the preservation of natural systems for future use. This approach has been applied in a recent project aimed at the study of the catchment basin of the Tiber river (Latium, Italy). The project is based on specific fields of activities, namely: *i)* evaluation of benthic macro invertebrates communities (Extended Biotic Index, EBI) and macrophyta which represent, through qualitative and quantitative analysis, an indirect, yet reliable and low-cost method to estimate water quality; *ii)* application of the Independent Forum on Forests (IFF) Index (*i.e.*, functionality river index), a new method which allows the global environmental state of river to be evaluated with special consideration of its functionality from an ecosystemic point of view, as a result of a synergic integration of several biotic and abiotic factors in aquatic and terrestrial ecosystems; *iii)* exploitation of fish communities as indicators of the ecological quality of aquatic ecosystem through fauna characterisation (composition and abundance, presence/absence of species specifically sensitive to typical modifications); *iv)* determination of dangerous substances that are introduced in the environment and their effects on the ecosystem (water, sediment, fish).

In this framework, a pilot study was undertaken which aimed at the quantification of selected toxic trace elements in fish caught in different tracts of the Tiber river (urban area of Rome and different rural areas upstream and downstream). The analysed species were *Leuciscus cephalus* (*Ciprinidae*) and *Anguilla anguilla* (*Anguillidae*). Four potentially toxic trace elements, namely As, Cd, Hg and Pb, were detected in freeze-dried and homogenized muscular tissues of the fish. Determinations were carried out by means of Sector Field Inductively Coupled Plasma Mass Spectrometry (SF-ICP-MS). Preliminary data (ranges of concentration in µg g^{-1}: As, 0.7-3.6; Cd, 0.0002-0.001; Hg, 0.1-0.3; Pb, 0.02-0.09) reveal no significant differences among the sets of results relevant to the various sampling stations. The total content of each element seems to be related with a general condition of low-level pollution of the area under study.

MICROBIOLOGICAL QUALITY OF ITALIAN SEA SAND

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Sea sand productivity is generally linked to the nourishment input as well as to the bacterial, protozoan and metazoan communities. Previous studies carried out to estimate the potential sanitary risk of the exposure to beaches have provided no epidemiological evidence. Other investigations suggested that potentially pathogenic microbial species, even though showing no disease transmission, seem to be correlated to the seasonal changes, with a higher incidence in summer. The main source of pathogens on the beaches seems to be represented by pets excrements. Nevertheless, the risk resulting by potentially pathogenic bacteria highly decrease because of their poor survival in the humid sand substrate, but could be considerable in the case of long-term exposure. Possible person to person infections, particularly in crowded beaches, are not supported by remarkable evidence and the risk to be infected through sand contac seems to be minimal due to the short survival of the pathogens and the way of exposure.

Sand samples were collected and analysed during the "Goletta Verde" survey of the Italian coastline in summer 1999. Beaches from the 15 Italian regions were monitored. The number of sampling points per region ranged between 2 and 15. Seawater samples were also collected and analysed at the same sampling sites to determine the presence of one of the microbiological parameters defined in the Italian Presidential Decree 470/82 for bathing waters. The samples of sea sand were analysed for *Staphyloccus* and for different genera of mycetes. Data of sea sands and water were processed by the SPSS Statistical Package. Raw data, log data and geometric mean values were subjected to statistical tests (correlation, linear and non linear relationships, PCA and ANOVA). Data analysis has evidenced a widespread and homogeneous distribution of the micotic taxa in the Italian beaches. The levels of microbial contamination of sea sands are generally higher than those observed in the waters due to bioaccumulation. The diseases which could be transmitted by skin contact are related to the relative infecting dose and the most widespread illnesses could be related to several species of fungi and bacteria. Despite of the fact that few studies have been performed to determine the Guideline Values of Word Health Organisation, preventive measures and health risk assessment should be considered.

ANALYSIS OF 60 PCB CONGENERS IN DRINKING WATER SAMPLES AT THE 10-50 pg l^{-1} LEVEL

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A method was developed to determine 60 Polychlorobiphenyl (PCB) congeners in water in order to evaluate the quality of drinking water from public wells in the area of Brescia. In this zone PCBs were produced until 1984 and the ensuing contamination affected air, agricultural water and surrounding lands and hence also agricultural products, animals and fish. Contamination of the environment is still present in several sites and consequently it is advisable to check drinking water purity.

The limits of quantification for the various congeners vary from 10-20 pg l^{-1}, for the lower chlorinated congeners, to 50 pg l^{-1}, for the highly chlorinated ones. To reach these limits it is fundamental to minimise both the procedural and the blank sample contribution. This goal was achieved by checking all the solvents used throughout the procedure and for washing the glassware. The water used for the blank was pre-extracted. The approaches resorted to for compensating and flaging the incidence of the blank for each analytical result is also presented.

BIOMONITORING OF POLAR AREAS BY MEANS OF THE ANTARCTIC ENVIRONMENTAL SPECIMEN BANK (BCAA)

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The Antarctic Environmental Specimen Bank (BCAA in the Italian acronym) is an integral part of the Italian Project *Chemistry of Micropollutants* of the Italian Antarctic Research Programme (PNRA in the Italian acronym). The BCAA started in 1994 and since then it is housed at the Department of Chemistry and Industrial Chemistry of the University of Genoa. One of the aims of this facility is the biomonitoring of the coastal marine ecosystems at Terra Nova Bay (Ross Sea, Antarctica), where the Italian Base is located. This project was, in fact, developed to study the distribution and diffusion of Cd, Hg and Pb using benthic organisms as bioindicators to establish temporal variations in the bioavailability of heavy metals in this coastal marine environment.

To this end, abiotic and biotic samples were collected in the Terra Nova Bay during different expeditions (from 1988 to 2002). Those samples include nine species of benthonic marine organisms (*Adamussium colbecki, Laternula elliptica, Odontaster validus, Sterechinus neumayeri, Trematomus bernacchii, Iridaea cordata, Phyllophora antarctica, Parborlasia corrugate* and sea cucumber), marine sediment, particulate matter embedded in pack-ice, snow, water column, microlayer and aerosol. Sediment samples were separated in two different granulometric fractions, *i.e.*, less than 2000 μm and below 63 μm, and the concentrations of metals bound to carbonates and organic labile fraction were determined in solutions obtained by a sequential extraction procedure. Accuracy of the procedure was tested using Certified Reference Materials (CRMs) similar as much as possible to the environmental matrices analysed. A correlation between Cd and Pb concentrations in benthonic organisms and marine sediment was found. Finally, an increasing trend in Hg concentration was noted for organisms in the marine coastal food web, *i.e.*, from algae through benthic primary consumers, detritivorous, filtering and omnivorous benthic invertebrates up to benthic fish.

CHARACTERISATION OF THE MULTIELEMENTAL CANDIDATE CERTIFIED REFERENCE MATERIAL *ADAMUSSIUM COLBECKI*

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The preparation of the multielemental candidate Certified Reference Material (CRM) IRMM 813 *Adamussium colbecki*, an Antarctic bivalve mollusk, was carried out jointly by the Istituto Superiore di Sanità (ISS), Rome, Italy and the Institute for Reference Materials and Measurements (IRMM), Geel, Belgium. This project aimed at the ascertainment of the feasibility of the certification of the concentration of selected trace elements in this material and was undertaken in the framework of the Italian National Programme for Research in Antarctica. The mollusk was collected in the vicinity of the Italian research station (Terra Nova Bay). The raw mass (*ca.* 40 kg) was treated following a detailed protocol for freeze-drying, grinding, sieving homogenising and bottling and a total number of 532 vials were prepared, each containing *ca.* 3 g of powder. On a number of representative samples of the candidate CRM, the water content, the particle size distribution and the microscopic structure of the particles were ascertained.

As regards the homogeneity of the material, twenty representative samples were randomly selected to verify the inter- and intra-vial homogeneity. To this end, the content of As, Cd, Cr, Cu, Fe, Mn and Zn was determined by means of Inductively Coupled Plasma Mass Atomic Emission Spectrometry (ICP-AES) and Sector Field Inductively Coupled Plasma Mass Spectrometry (SF-ICP-MS). No significant differences were found among the various vials (RSD generally lower than 3 %, but in the some cases around 8 %). The observed variations remain in the order of the fluctuations expected for the overall analytical procedure adopted. The actual certification of the candidate CRM will take place under the coordination of the IRMM.

CADMIUM AND Pb IN BLOOD OF ITALIAN SUBJECTS: PRELIMINARY REPORT OF CURRENT TRENDS

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Cadmium and Pb are environmental pollutants, known to cause adverse health effects in humans even after long-term exposure to low concentrations. Human exposure is generally assessed by monitoring the concentrations of these metals in blood. Various factors, such as age, sex, smoking habit, occupation, alcohol consumption and diet, have been shown to influence the concentrations of Cd and Pb in blood. The use of leaded gasoline and inhalation of Cd from cigarette smoking were reported to be the main sources of exposure for the general population in Europe.

Following the phase-out of leaded gasoline in the European Union, a decrease in Pb blood levels of the general population has been observed in several European countries. Within the framework of the project *Human Exposure to Xenobiotics with Potential Endocrine Activities: Evaluation of Reproductive and Developmental Risks*, the concentrations of Cd and Pb in blood samples from a group of Italian subjects were measured by means of analytical procedures based on Atomic Absorption Spectrometry (AAS), validated according to the EURACHEM guidelines. The preliminary results of this study are discussed.

POST-MARKETING EVALUATION OF CITRATE LEVELS IN HUMAN ALBUMIN SOLUTIONS: VALIDATION OF THE ANALYTICAL METHOD AND RESULTS OF SURVEYS

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Parenteral exposure to Al, a non-essential, toxic metal, may occur upon injection of pharmaceutical products, including Human Serum Albumin (HSA) solutions. Beside Al contamination during industrial processing of HSA, the first glass container can be an ongoing source of Al within the period of shelf life. In the recent past, batches of HSA were recalled because of non-compliance with the requirement of European Pharmacopoeia (Eph) (limit of 200 µg l^{-1} for Al in HSA if intended for administration to patients undergoing dialysis or to premature infants).

During a survey carried out in this occasion it could be shown that citrate level influences the increase of Al concentration in HSA. Consequently, the Italian Authority has set a limit for citrate content in HSA and a programme was started for evaluating the HSA preparations marketed in Italy. As no official method is available for the determination of citrate in HSA, method validation was necessary in order to comply with the criteria set forth in the European Directorate for the Quality Assurance Documents – 2001 of the Quality of Medicine (EDQM) document which is in agreement with the International Standard ISO 17025. The results of the validation study and the findings of post-marketing surveys already carried out are reported and discussed.

POST-MARKETING SURVEILLANCE OF HUMAN ALBUMIN SOLUTIONS: VALIDATION OF THE ANALYTICAL METHOD AND RESULTS OF SURVEYS

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Parenteral exposure to Al, a non-essential, toxic metal, may occur upon injection of pharmaceutical products, including Human Serum Albumin (HSA) solutions. As Al accumulation in tissues may lead to the development of diseases in groups at risk, the European Pharmacopoeia (EPh) has established a limit of 200 µg l^{-1} for Al in HSA if intended for administration to patients undergoing dialysis or to premature infants. Aluminium contamination of HSA may occur during industrial processing, but also the first glass container can be an ongoing source of Al during the product shelf life. For this reason, measurements of the Al content have been included in post-marketing surveys of HSA (European Directive 93/39/EEC). According to the EPh, determinations should be performed by means of Electrothermal Atomisation Atomic Absorption Spectrometry (ETA-AAS). Calibration materials were prepared by spiking HSA with known amounts of Al (range 0 – 300 µg l^{-1}) and a solution of $Mg(NO_3)_2$ $6H_2O$ (3 g l^{-1}) and Triton X-100 (0.2 %, v/v) was used as the matrix modifier. Both samples and calibration materials were diluted 1:8 with ultrapure water.

According to the standard ISO/DIS 17025, the validation of analytical methods is required as a prerequisite for the reliability of the data and is a necessary part of a laboratory quality system. The validation of the above method was achieved on the basis of the EURACHEM Guide *The Fitness for Purpose of Analytical Methods* (1995). In particular, the following characteristics of the method were evaluated: limit of quantification, limit of detection, linearity range, sensitivity, repeatability and intermediate precision, trueness in terms of recovery of spiked amounts and analysis of the EPh reference material H0900000 *Human Albumin for Aluminium Validation BRP*. The results of the validation study and the findings of post-marketing surveys already carried out are reported and discussed.

BREATH ANALYSIS

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Over the last few years the application of breath analysis for the routine monitoring of metabolic disorders connected to specific disease is becoming more and more attractive due to its non-invasive nature. Several applications have already been reported in the literature, such as volatile S compounds in hepatic diseases, ethane, pentane and isoprene as potential markers of lipid peroxidation and various Volatile Organic Compounds (VOCs) as environmental pollutant. Moreover, 2,5-dimethyl furan is supposed to have a high discriminatory power in Gas Chromatography Mass Spectrometry (GC-MS) profiles to differentiate between smokers and non-smokers.

Breath samples are generally collected using a Tedlar® bag of suitable volume and transferred onto a freshly conditioned thermodesorption tube filled with various absorbents according to the chemical characteristics of the compounds of interest. A cooled injection system is used for the cryofocusing of the desorbed volatiles and a GC-MS system is resorted to for the separation and identification of the various classes of organic compounds. A Solid Phase Micro-Extraction (SPME) fiber has also been used, although it is characterised by worse Limits of Detection (LoDs). A critical overview of the analytical devices and procedures used for breath analysis is presented. The results of the identification of chemicals in human breath are also discussed.

A PILOT STUDY ON THE ROLE OF Cd AND Pb IN THE ETIOLOGY OF RENAL TUMOURS

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Over the period 1955-1994 the number of cases of renal tumors as well as of deaths caused by this pathology have dramatically increased in Italy by a factor of 18 and 5, respectively. This trend became striking at the end of the 1970's, probably as a consequence of the increase in environmental pollution which is considered to be the prime cause of at the least 80 % of neoplastic diseases. In this context a study was undertaken with the purpose of ascertaining the concentrations of two polluting metals, namely Cd and Pb, in the parenchyma of kidneys affected by tumors in an attempt to elucidate whether a correlation existed with those in the kidney of phoetuses, newborns and individuals deceased for non-tumoral diseases. Cadmium and Pb compete, in fact, with Zn in many enxymes participating in the replication and restoration process of DNA. Its replacement by Cd and Pb may induce genetic alterations which play a crucial role in the development of tumors.

The two metals were quantified in healthy and tumoral renal tissues of 20 subjects. After acid-assisted Microwave (MW) digestion of the samples, determinations were carried out by means of Sector Field Inductively Coupled Plasma Mass Spectrometry (SF-ICP-MS). Results show that Cd and Pb are present at high concentrations in the healthy parenchyma of tumoral kidneys, by far exceeding those detected in the kidneys of foetuses and individuals died of other pathologies. On the other hand, in tumoral tissues the concentration of Cd is very low and that of Pb substantially high. The average values for the two metals (in $\mu g\ g^{-1}$, dry tissue) are, respectively, as follows: Cd (tumor), 1.96 ± 2.65; Cd (healthy tissue), 73.82 ± 36.42; Pb (tumor), 0.32 ±0.42; Pb (healthy tissue), 0.36 ± 0.08. As metallothioneins are mostly present in the cells of proximal tubules and Cd is taken up by these substances, its accumulation in these tissues may well lead to a genetic damage eventually resulting in cancer. Last, but not least, the simultaneous presence of the two metals might also result in a synergic action with an ensuing higher risk of tumoral disease.

DETERMINATION OF Sr AND ITS RELATION TO OTHER ALKALINE EARTH ELEMENTS IN HUMAN BRAIN SAMPLES

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Strontium might be an essential element for human beings and play an important role in bone metabolism. Increased knowledge on Sr concentrations in different biological samples might help understanding better its influence on the human body. The aim of the present work was to determine the Sr content of human brain samples of control and Alzheimer's disease-affected patients as well as to compare such data with the concentration of two contaminanting alkaline earth elements (Ca, Mg).

Microwave (MW)-assisted and high-pressure Parr bomb digestions were used for sample dissolution. The Sr content of the digested samples was measured both by Electrothermal Atomisation Atomic Absorption Spectrometry (ETA-AAS) and Inductively Coupled Plasma Mass Spectrometry (ICP-MS). Although the sensitivity of ETA-AAS is adequate to determine this element at the ng ml^{-1} level, several conditions had to be optimised, namely pyrolysis programme, chemical modifiers [$La(NO_3)_3$, KNO_3] and background correction (λ = 460.7 nm). Calcium and Mg were measured by Inductively Coupled Plasm Atomic Emission Spectrometry (ICP-AES). Accuracy of measurements was tested by the Certified Reference Material (CRM) NBS SRM 1577 Bovine Liver. Instrumental settings were checked throughout the measurements process by means of the CRM NIST-SRM 1643c Trace Elements in Drinking Water.

MINOR AND TRACE ELEMENT CONTENTS IN PITUITARY GLAND OF NORMAL HUMANS: AN EVALUATION OF ANALYTICAL DATA

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In the study of trace elements in the different human brain areas, a critical evaluation of the values available in the literature is of great importance in attempting to establish reliable baseline levels, *i.e.*, Reference Values (RVs) for toxicological assessment studies. This presentation reviews the published values of minor and trace elements in the pituitary gland (hypophysis). Eighteen published papers are taken into account, fifteen of which refer to the entire gland, whereas in three of them only the adenohypophysis is considered.

It turns out that essential elements such as Cu, Fe, Se and Zn were more frequently determined, whereas As, Br, Ca, Co, Cr, Cs, K, Mg, Mn, Ni and Rb were seldom investigated. Mercury was determined by several authors because of the concern caused by Hg release from dental amalgam fillings. Most values were obtained by Neutron Activation Analysis (NAA), which appears to have played a pioneer role in this field. Literature data on trace element levels in pituitary gland are at present insufficient to establish RVs; rather, they can be considered only as indicative values. Future investigations based on large populations of control subjects with standardisation of the preanalytical factors and the use of fit-for-purpose Certified Reference Materials (CRMs) should therefore be envisaged.

TWENTY YEARS OF THE METOS PROJECT: AN ITALIAN NATIONAL EXTERNAL QUALITY ASSESSMENT SCHEME FOR TRACE ELEMENTS IN BIOLOGICAL FLUIDS

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The METOS Project, started in 1983 and still running, is an External Quality Assessment (EQA) Scheme for laboratories performing specialised analyses in occupational and environmental laboratory medicine. Besides the organisation of EQA exercises, initiatives for further education of the participants and the harmonisation of EQA procedures at an European level are carried out.

Participation in EQAS allows laboratories to demonstrate their competence as required by international standards for laboratory accreditation. The organisation of the scheme includes the preparation of control materials, their distribution to the participants as required to avoid identification of the samples, the statistical analysis of the results and the evaluation of laboratories' performance according to international guidelines and criteria set by the organisers. An overview of the scheme operation and the current performance of participants is discussed.

VALIDATION OF AN ASSAY FOR THE QUANTIFICATION OF THE vWF ANTIGEN (vWF:Ag) IN PLASMA DERIVATIVES

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Article 114 of Directive 2001/83/EC requires the evaluation of individual manufacturer's batches of plasma derivatives by an Official Medicines Control Laboratory (OMCL) within the EU before the batch is placed on the market. This procedure is known as Official Control Authority Batch Release (OCABR). At present the OMCL Network for batch release involves 17 Member States in the European Union with the main aim to support mutual recognition of certificates issued (and tests performed). In order to guarantee a harmonised approach among members of the OMCL Network, the European Directorate for the Quality of Medicine (EDQM) develops and issues common guidelines and procedures upon request of the Commission of the European Communities.

The OCABR guideline outlines the administrative procedure which should be carried out by OMCLs for the critical evaluation of the manufacturer's protocol and the tests to be performed on the products (sampled from each batch) submitted by the manufacturer. For the Factor VIII (FVIII) concentrates for the treatment of Von Willebrand Disease, OMCLs should perform the following tests: solubility and appearance, potency of FVIII and quantification/activity of von Willebrand Factor (vWF). The OCARB guideline requires test for vWF to be performed using the same method chosen by the manufacturer, among those recommended (quantification of the vWF antigen, vWF:Ag test). However these methods have not yet been satisfactorily validated. Method validation, including validation of statistical model (parallel-line or slope ratio), is necessary in order to comply with the EDQM document *Quality assurance documents – 2001* which is in agreement with the International Standard ISO 17025. Therefore, since one of the manufacturers submitting samples to the Italian OMCL declared to use the method based on vWF:Ag test, the Italian OMCL has implemented and in-house validated the same analytical procedure. The results of the validation study are reported and discussed.

A SURVEY OF WORKLOAD, FACILITIES AND AWARENESS OF UNCERTAINTY OF MEASUREMENT AMONG ITALIAN LABORATORIES PERFORMING ANALYSES IN OCCUPATIONAL AND ENVIRONMENTAL MEDICINE

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Within the framework of the European Thematic Network of the European organisers of External Quality Assessment/Proficiency Testing Schemes (EQAS/PTSs) related to occupational and environmental medicine, a questionnaire was administered to participants in national EQASs to collect information on the participants' workload, needs for new EQASs and laboratories' compliance with the requirement of the standard ISO/DIS 17025 for the estimate of uncertainty of measurement.

In Italy, 64 laboratories out of 79 (81 %) replied. The trace elements most commonly determined were Al in serum (43.8 % of laboratories), Cr in urine (60.9 % of laboratories) and Pb in blood (89.1 % of laboratories). Methylhippuric acid, hippuric acid and mandelic acid in urine were the organic substances more frequently determined (60.9 %, 50.0 % and 48.4 % of laboratories, respectively). Generally, participants expressed interest for new EQASs, even at the European level, to assist them in demonstrating the quality of their results, especially for those analyses for which no Certified Reference Materials (CRMs) are available. In 2001, only 5 of the 64 participants (7.8 %) estimated the uncertainty of at least some of their measurements, but in 2003 30.9 % of the participants stated to have done so, at least for some of their measurements.

THE TECHNOLOGICAL AND ECONOMICAL MANAGEMENT OF THE ENVIRONMENT VARIABLES IN THE PHARMACEUTICAL-CHEMICAL INDUSTRIES

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The technological progress involves increasing industrial risk, especially as regards the pharmaceutical-chemical sector. Pharmaceutical-chemical industries and other industrial activities introduce a risk coefficient variable within space and time. The variable time modifies the parameters in relation to the life cycle of the process and the life cycle of a chemical plant. In order to establish control systems of the process for environmental safety and health monitoring aspects, data from the Hazard and Operational Study (HAZOP) are resorted to.

The variable space influences the coefficient of chemical risk in the area of the production cycle that involves all the areas of the Management of Integrated Production (including the waste of the production recycling). For prevention purposes many companies have adopted the Integrated Management System (IMS). The IMS also considers environment, health and safety inside and outside industrial areas, in compliance with the criteria set forth by the standards UNI, ISO, 14000 and OHSAS 18001. This study is concerned with the application of the IMS in the chemical-pharmaceutical industry. This approach represents a major cultural change. It will be necessary thus to develop the economical strategy indispensable to assist industries in the implementation of the appropriate environmental and technological programme.

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