SESSION 1
TRACE ELEMENT AND MINERAL ANALYSIS OF ENVIRONMENTAL AND BIOLOGICAL SAMPLES: BULK DETERMINATION, SPECIATION AND QUALITY CONTROL

STABILITY OF SERUM COPPER, SELENIUM AND ZINC

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BACKGROUND: Trace element can be determined in epidemiological studies that lasted for many years. The aim of this study was to compare the concentrations of copper, zinc and selenium in samples stored at -20°C for 3 years. METHOD: Samples[*] (one native pool of human serum and two further serum pools prepared by spiking the first with known Cu, Zn and Se concentrations) were sent to the participants of the French Trace Element External Quality Assessment Scheme after preparation and three years later. In the meantime, the samples were stored at -20°C. Twenty three laboratories sent results for the two runs for copper, 24 for zinc and 14 for selenium. Results were compared using Student t test for paired samples. RESULTS: Comparison of the two sets of results did not evidence any significant difference for the three elements and the three levels ($p > 0.10$). Mean copper concentrations were 13.9 and 13.6 µmol/l ($p = 0.31$, sample 1), 21.2 and 21.2 µmol/l ($p = 0.97$, sample 2) and 29.1 and 29.0 µmol/l ($p = 0.97$, sample 3). For zinc, mean concentrations were 9.9 and 10.1 µmol/l ($p = 0.88$, sample 1), 23.8 and 22.5 µmol/l ($p = 0.14$, sample 2) and 31.5 and 30.2 µmol/l ($p = 0.20$, sample 3). With regard to selenium mean concentration were 0.73 and 0.76 µmol/l ($p = 0.41$, sample 1), 1.57 and 1.56 µmol/l ($p = 0.88$, sample 2) and 3.21 and 3.19 µmol/l ($p = 0.93$, sample 3). These results confirm the good stability of essential trace element in frozen samples for long period of time.

COMPARISON OF DIFFERENT PROFICIENCY TESTING SCHEMES FOR Al, Cu, Se, Zn

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BACKGROUND: Trace element external quality assessment schemes monitor laboratory performance and provide a stimulus for improvement in accuracy. However, monitoring of participant performance varies according to the scheme and can lead to conflicting conclusions. The aim of this study was to compare the performance of participants in different schemes using the same samples, quality specifications and statistical methods. METHOD: Samples (one native pool of human serum and two further serum pools prepared by spiking the first with known Al, Cu, Zn and Se concentrations) were sent to all participants of the Canadian, French, Italian, New York and United Kingdom proficiency testing schemes. Results were returned to the respective scheme organizers. Robust means and robust standard deviations were calculated for each scheme and for the combined data. The robust means were taken as the assigned values. Participant Z-scores were also calculated using quality specifications previously defined by the group [1, 2]. Additional data analysis was carried out to compare reproduced by different analytical techniques. RESULTS: It was seen that, even for the same samples, the assigned values and their uncertainties vary from scheme to scheme and validate the aim of the network to develop an integrated PT scheme.

All the authors are members of the thematic network «Organisers of external quality assessment / proficiency testing schemes related to occupational and environmental medicine».

1. *Arnaud J, Weber JP, Weykamp CW, Parsons PJ, Angerer J, Mairiaux E, et al.* Quality specifications for the determination of copper, zinc, and selenium in human serum or plasma: evaluation of an approach based on biological and analytical variation. Clin Chem 2008;54:1892-9.
2. *Taylor A, Angerer J, Claeys F, Kristiansen J, Mazarrasa O, Menditto A, et al.* Comparison of procedures for evaluating laboratory performance in external quality assessment schemes for lead in blood and aluminum in serum demonstrates the need for common quality specifications. Clin Chem 2002;48:2000-7.

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[*] Samples prepared for and provided by the thematic network «Organisers of external quality assessment/proficiency testing schemes related to occupational and environmental medicine».

ULTRASTRUCTURAL DAMAGE AND HEAVY METAL ACCUMULATION IN THREE AQUATIC PLANTS

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Metal pollution in waters and soils is a major environmental and human health problem. Heavy metals are normally present at low concentrations in freshwaters, but due to the anthropogenic activities they are also the most common non biodegradable pollutant detectable at elevated concentrations in a majority of parts of the world. Aquatic plants are known to accumulate and bioconcentrate heavy metals. In this study we tested with heavy metals three aquatic plants (the monocotyledons *Lemna minor* and *Elodea canadensis*, and the moss *Leptodictyum riparium*) by *in vitro* culture. The plants were exposed to several concentrations (from 10^{-7} to 10^{-3} M) of cadmium, lead, zinc and copper salts for several days. We evaluated classical toxicity endpoints (survival percentage, relative growth rate, dry to fresh weight ratio) at first, then we assessed metal bioaccumulation in total body, tissue and cell localization, ultrastructural alterations and chlorophyll content and chlorophyll a/b ratio; these parameters could be regarded as biomarkers of heavy metal stress. *L. riparium* was the most resistant species (EC_{50} values of survival percentage were 10^{-4}M for Cu and Zn, 10^{-5} M for Pb and 0.5×10^{-5} M for Cd). Heavy metal bioaccumulation in total body was evaluated by Atomic Absorption Spectrometry; found values varied depending on the metals and their concentrations and the plant species tested. Heavy metal tissue localization was assessed by X-ray SEM microanalysis: this technique showed preferential metal localization in plant tissues of *L. minor* and *E. canadensis.* Ultrastructural observations were performed by a transmission electron microscopy (TEM): visible metal effects were shown on vacuolar and thylakoid organization in all the three aquatic plants. X-ray TEM microanalysis localized heavy metals in cell wall and cytoplasm vesicles. Chlorophyll was extracted and examined spectrophotometrically: differences were shown between plants and treatments.

BIOELEMENTOLOGY AS INTEGRATIVE APPROACH IN MEDICAL AND BIOLOGICAL INVESTIGATIONS

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The fragmentation of science, which was typical for XIX—XX centuries, induced requirement of integrative approach. Last decade, this necessity was reflected by appearance of numerous «omics» including metallomics. Since 2003, the conception of bioelements (BS) and bioelemenotogy (BE) as an integrative approach in natural science is developing in Russia (Skalny, 2003; Skalny, Rudakov, 2004 etc.). BS are obligate but not sufficient components of life, providing their biological effects in dose coordination with the genome and environment in an integral holistic system. «Primary» BS are existing in the Universe and can be involved in the construction of life. «Secondary» BS are produced by living organisms or by biotechnological processes. Permanent producing of BS is a unique and universal source of life existing. BE investigates the processes of origin, production, turnover and degradation of BS in the Universe and Biosphere. BE is the integration of geochemistry, bioinorganic, bioorganic chemistry, biophysics, molecular biology and «omics». The main analytical method in BE is speciation analysis. In Russia, the Chair of Nutrition and Bioelementology and Research Institute of Bioelementology in Orenburg State University are successfully functioning since 2003. There were two conferences with international participation (Orenburg, 2005, 2007) organized, and the journal «Bioelementologia» issued. The proposed terminology and classification will be presented.

REVIEW OF COPPER AND ZINC VALUES OF ARAGONESE POPULATION (SPAIN) OBTAINED BY A CREDITED LABORATORY ACCORDING TO THE NORM UNE-EN-ISO 15189

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INTRODUCTION: The values of reference used in a laboratory have to be agree with the obtained ones in the own laboratory. OBJECTIVE: Review of the copper and zinc serum levels found during the year 2008 and 2009 in a wide sample that includes all the ages of the life. MATERIALS AND METHODS: The Copper and the Zinc were analyzed respectively of 4544 and 3480 samples of whey of healthy persons by ages between 1day and 98 years. The analytical method used was the Spectrometry of atomic Absorption of flame in a novAA 300 of ANALITYKJENA. RESULTS: Copper N = 4544 cases; (0 days — 1 month, n = 41) Median = 56 ± 16.6 (SD) μg/dL, (1—6 months n = 63) Median = 89 ± 28 (SD) μg/dL, (6—12 months n = 69) Median = 107 ± 31 (SD) μg/dL, (1—6 years n = 452) Median = 125 ± 27.5 (SD) μg/dL, (6—12 years n = 307) Median = 107 ± 23.1 (SD) μg/dL, (12—25 years n = 501) Median = 91 ± 33 (SD) μg/dL, (25—50 years n = 1306) Median = 98 ± 34.2 (SD) μg/dL, (50—70 years n = 913) Median = 103 ± 25.6 (SD) μg/dL, (> 70 years n = 92) Median = 103 ± 23.8 (SD) μg/dL. Zinc N = 3480 cases; (0 days —1 month n = 3) Median = 112 ± 33.8 (SD) μg/dL, (1—6 months n = 19) Median = 91 ± 20.9 (SD) μg/dL, (6—12 months n = 43) Median = 83 ± 31 (SD) μg/dL, (1—6 years n = 270) Median = 95 ± 32.8 (SD) μg/dL, (6—12 years n = 217) Median = 92 ± 27.3 (SD) μg/dl, (12—25 years n = 401) Median = 100 ± 31.9 (SD) μg/dL, (25—50 years n = 956) Median = 94 ± 32.4 (SD) μg/dL, (50—70 years n = 771) Median = 91 ± 31.7 (SD) μg/dL, (> 70 years n = 800) Median = 90 ± 30.1 (SD) μg/dL. CONCLUSION: There is verified that the levels of copper change along the different ages of the life and the zinc is kept stable.

UNE-EN ISO 15189 ACCREDITATION: VALIDATION OF DETERMINATION OF TRACE ELEMENTS BY ATOMIC ABSORPTION SPECTROMETRY

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INTRODUCTION: We started to prepare for UNE-EN ISO 15189 Accreditation in 2006 and were certified by the national accreditation body (ENAC) in March, 2009. In this work we present the results obtained in the method validation (according to UNE-EN ISO 15189 standard) for the determination of: Cu, Zn, Pb, Se and Al by atomic absorption spectrometry (AAS). MATERIALS AND METHODS: The serum concentrations of Cu and Zn were determined by flame AAS (novAA300), and the levels of Pb in whole blood and Se and Al in serum were measured by graphite tube AAS with Zeeman background correction (ZEEnit600). Method validation makes use of a set of parameters in order to demonstrate whether the method is fit for a particular analytical purpose: calibration and linearity, Operating Range (OR), Limit of Quantification (LQ), Limit of Detection (LD), Recovery (R), repeatability, reproducibility and uncertainty (U). The acceptance criteria established were: correlation coefficient > 0.995; OR, LQ and LD according to levels of trace elements in humans; R: 80 < R (%) < 120; coefficient of variation (CV) < 10% for repeatability and reproducibility; and U < 0.2 RESULTS: Correlation coefficient: 0.9982 (Cu), 0.9997 (Zn), 0.9991 (Pb), 0.9977 (Se) and 0.9982 (Al). OR: 1.15—300 μg/dL (Cu), 1.63—300 μg/dL (Zn), 0.13—40 μg/dL (Pb), 3.24—180 μg/L (Se) and 1.38-40 μg/L (Al). LQ: 1.15 μg/dL (Cu), 1.63 μg/dL (Zn), 0.13 μg/dL (Pb), 3.24 μg/L (Se) and 1.38 μg/L (Al). LD: 0.344 μg/dL (Cu), 0.5 μg/dL (Zn), 0.04 μg/dL (Pb), 0.97 μg/L (Se) and 0.42 μg/L (Al). For the three clinical decision levels of each trace element: Recovery, 80 < R (%) < 120; and CV of repeatability and reproducibility < 10%. For all of the trace element determinations: U < 0.2. CONCLUSION: The results obtained in the method validation meet the acceptance criteria widely. Therefore we can conclude that all of the analysis methods perform adequately for the purpose throughout the range of concentrations and test materials to which they are applied.

MACRO- AND MICROELEMENTS IN TISSUES OF THE MEDICAL LEECH (HIRUDO VERBANA CARENA), GROWN AT A BIOFARM IN THE STARVATION DYNAMICS

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The main parameter of the medical leech as a remedy is the starvation period responsible for the presence of a complex of biologically active compounds in the secretion of salivary gland. Presently medical leeches are widely used for the production of remedies, nutritives, cosmetics; therefore knowledge of macro- and microelement contents in their tissue homogenates in various starvation periods is very important. We studied the levels of Cu, Zn, Mn, Fe, Ca, Mg, Cd, Pb, Ni, Co, Sr in tissues of sated and hungry medical leeches *Hirudo verbena Carena*, grown at the biofarm «Hirudo-Med.South» (Krasnodar region). Starvation periods were 3 and 5 months. The contents of macro- and microelements (μg/g) in biosubstrata were estimated on the atomic absorption spectrophotometer AAS-3. Specimens starving during 3 months had significantly higher concentrations of Zn. Mn, Mg, Pb and much lower concentrations of xenobiotics (Cd, Ni, Sr) and Fe ($p < 0.05$) compared to sated individuals. The levels of the essential Cu, Ca were similar. The specimens starving during 5 months had in their tissues much more Cu, Zn, Ca, Mg, Pb, Co and less Mn, Fe, Sr ($p < 0.05$) than the saturated individuals. Concentrations of xenobiotics Cd and Ni were similar. The observed higher and stable concentrations of essential elements against the background of lower levels of xenobiotics in the tissues of hungry specimens makes sensible the use of their homogenates in pharmacology and in cosmetic industries. The choice of the starvation period corresponding to optimal concentrations of the necessary elements is possible.

PECULIARITIES OF MICROELEMENT METABOLISM IN THE MEDICAL LEECH (HIRUDO MEDICINALIS L) TISSUES FROM NATURAL POPULATIONS

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The medical leech *(Hirudo medicinalis L.)* from the Red Data Book is an important biological resource in Russia. Anthropically caused changes are presently marked in pond ecosystems; high levels of heavy metals in the water often reduce the species diversity of hydrobionts. Cu, Zn, Cd, Pb, Ni, Fe, Mn are accumulated in bottom deposits harmfully affecting the hydrobionts, including the leech. We investigated sex mature specimens of the medical leech captured in natural ponds of the Tambov, Lugansk and Krasnodar regions. The levels of microelements (μg/g) in leech tissues and in their habitat bottom deposits were estimated by the atomic absorption spectrometry (AAS-3). The correlation analyses revealed a significant dependence of the levels of heavy metals in the leech tissues on those in the bottom deposits ($r = 0.67$—0.85; $p < 0.01$). The sequence of heavy metals concentrations in *H. verbana* tissues (Krasnodar region) was the following: Fe > Zn > Pb > Mn ≥ Cu > Ni > Cd. That in *H. medicinalis* (Lugansk region) was Fe > Zn > Mn ≥ Cu > Ni > Pb > Cd; Fe > Zn > Ni > Cu > Mn ≥ Pb > Cd (Tambov region). Thus, both species had maximum concentrations of biophyle metals (Fe and Zn) and the lowest ones of the highly toxic xenobiotic Cd. Concentrations of all microelements in the medical leech tissues varied over a wide range except the essential Zn. No correlation was revealed in Zn content between the bottom deposits and the leach tissues. The averagely inverse proportion between Mn levels in the bottom deposits and the leech tissues might evidence of the trophic entry of this microelement.

METAL CONTENT IN FRUIT BODIES OF WOOD-INHABITING FUNGI COLLECTED IN SITES WITH DIFFERENT LEVEL OF ENVIRONMENTAL POLLUTION IN THE CZECH REPUBLIC

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Fruit bodies of several common wood-inhabiting fungi *(Fomes fomentarius, Fomitopsis pinicola, Piptoporus betulinus, Stereum hirsutum, Schizophyllum commune and Hirneola auricula-iudae)* were collected in the National Park Krkonoše, National Park Šumava and in the region of the capital Prague. The aim was to compare selected metal content (Al, Be, Cd, Cu, Fe, Mn, Pb, Zn) in fruit bodies collected in both polluted and unpolluted areas. Measurements were done in 1997-9 and then repeated in 2007—2009. Fungal samples were homogenized and after microwave digestion metal content was measured by Atomic absorption spectroscopy. In general, samples from clean areas contained higher concentrations of Zn than those from polluted sites. Levels of metals ranged from units of ppm (Pb, Cd) to tenths (Al, Cu, Mn). Concentrations of biogenic Mn and Zn were higher than others. Distribution of metals within fruit bodies was not uniform with Mn peak in the core *(Fomes fomitopsis)* supporting its key role in wood decay via ligninolytic complex (Mn-dependent peroxidases) in white-rot fungi. Contrary to Mn, higher amounts of Al and Fe were found in the cortex, supporting the metal uptake from both dry and wet atmospheric deposition. Microphotographs of soil particles on the surface of fruit bodies obtained by scanning electron microscopy are shown as well. Significant amounts of Cd were found in hymenium that may indicate their accumulation in spores. In general, more than 50 samples were collected in each area each period. No significant changes were found in the capital of Prague, but slight increase of Pb, Cu and Cd content was found in both National Parks in past ten years resulting probably from continuous industrialization of the landscape.

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INDICATOR ABILITY OF BIOSUBSTANCES IN MONITORING OF OCCUPATIONAL EXPOSURE TO TOXIC METALS

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Modern industry inevitably generates risk for peoples' health due to occupational and environmental contact with toxic substances. To improve monitoring system, watching influence of toxic metals on human health in industrial plants served by Federal Medical-Biological Agency of Russia, we compared indicator features of different biological substances. Four types of biological samples (whole blood, plasma, urine, hair) from 263 workers of «Khimprom» chemical plant (Novocheboksarsk, Russia) were subjected to multielement analysis by ICP-AES/ICP-MS method. In each biological substance 19 to 25 chemical elements, including main toxic metals (Cd, Hg, Pb, Sn etc.) were determined. The obtained results were calculated with regard to workers' individual data on occupational exposure to chemical elements. Hair was found to be most sensitive to load of toxic trace metals: Pb, Mn, Cr, Be, Ni, while occupational contact with macro elements (Na, P), trace metalloids (Si, B) and some other metals (Zn) did not express itself in hair element profile. Whole blood relatively weakly indicated moderate occupational load of metals except Pb and Mn, but effectively reflected deficiencies of essential elements: I, Cr, and shifts in K/Na ratio, which are likely to be secondary effects of harmful occupational factors. Blood plasma reflected only the contact with Be, P; urine — only with Ni. It was also found that in both whole blood and plasma the changes for absolute majority of elements (with the only exception of Mg and Zn) were similar. Thus, monitoring of occupational exposure to toxic metals is expedient to be carried out using hair analysis, while general estimation of occupational harmful influence on mineral metabolism requires simultaneous investigation of two biosubstances: hair and whole blood, or hair and blood plasma, with whole blood being more preferrable. Analysis of urine is appropriate for monitoring of particular chemical elements, e.g. nickel.

TXRF STUDY OF ELEMENTAL COMPOSITION OF *AMANITA MUSCARIA* MUSHROOMS

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Over the last several decades, total reflection X-ray fluorescence (TXRF) analysis was proven to be an easy and versatile method for the determination of trace elements. TXRF can be applied to different sample types, like solids in form of micro fragments, powders, suspensions, thin films or liquids. The required sample amount is in the low μg or μl range, respectively. In TXRF the samples are prepared as thin film or layer, thus matrix effects are negligible. Quantification is possible by means of the known concentration of an internal standard element. However, because of the large size and high operative costs, the historical application of this method was restricted to large research and development laboratories. With the recent introduction of low-power benchtop instruments, this analytical method is now utilized in small laboratories for phytoforensic research and routine applications. This has opened new doors in the rapidly growing field of agricultural and food chemistry. This presentation will present a brief outline of the instrumental design and theory of TXRF followed by case studies demonstrating how the technique is utilized in every day laboratory analysis in comparison with other methods like AAS (atomic absorption spectroscopy). Recent research into detoxification of *Amanita muscaria* mushrooms has focused on the removal of organic toxins. In this presentation, we focus on the importance of the analysis of inorganic compounds found in mushrooms. Mushrooms contain very high water levels. When dried, the inorganic elements are concentrated many times over. We demonstrate the use of various sample preparation methods for TXRF analysis of dried mushrooms. This study provides evidence suggesting that the mushroom sequesters critical trace elements such as vanadium. Besides vanadium, selenium, copper, chromium and other elements will be studied.

INFLUENCE OF BORON APPLICATION ON YIELD AND FATTY ACID COMPOSITION IN SOYBEAN VARIETIES

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This study was conducted to determine the effects of different boron (B) dosages on four soybean (*Glycine max* (L.) Merr.) varieties. The experiments within the pots in a controlled glasshouse were laid out in a three factor completely randomized design, with 4 replications where 0, 2 and 12 mg/kg B treatments were evaluated. Three kg's of boron-deficient soil, with a basic B content of 0.2 mg B per kg soil, was used. B contents of the dried samples were determined by ICP-AES (Varian — Vista Model Axial Simultaneous). Additionally, dry weight, total oil, biomass, seed yield (g/pot), seed protein contents (AACC 46—30 method; Combustion Nitrogen Analyzer, Leco TruSpec CN) as well as fatty acid composition of the seeds were determined. Protein contents of the seeds increased, whereas dry weights decreased with B application Türksoy variety seed oils had the highest ratios of stearic and oleic acids and the lowest ratios of linoleic and α-linoleic acids The highest total oil content together with low ratios of saturated fatty acids were determined in Deficiency variety oils There were 13% and 20% decreases in total oil of the seeds when B treatment was 2 and 12 mg/kg, respectively; except Deficiency variety which the seeds had 8% higher oil content than the control seeds after B application at toxic level. Palmitic, linoleic, stearic (except ME3399 variety) and oleic acid (except Türksoy variety) ratios increased with B treatment. while generally linoleic acid levels decreased After B application at toxic levels, ME3399 variety seed oils showed higher α-linoleic acid levels when compared to control samples.

DETERMINATION OF TRACE ELEMENTS IN BIOLOGICAL FLUIDS

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From the point of view of elemental status human body is considered to be complicated dynamic polyelemental system. There is optimal concentration range of each element in human body for performing essential biological functions. Organism media trace element level is adequately reflected by analysis of such biological fluids as whole blood, blood plasma and serum and urine. All Biological fluids are complicated analytical objects not only due to their difficult matrix composition, but also extremely low levels of the majority of the trace elements. Strict requirements for methods of trace element determination in biological fluids are obvious. Nevertheless, practically there is no wide range of choice concerning trace element analysis of biological fluids, as the scope of appropriate methods is limited by mostly inductively coupled plasma mass spectrometry (ICP-MS) and graphite furnace atomic absorption spectrometry (GFAAS), more seldom neutron activation analysis (NAA) and voltammetry (VA) are used for such a purpose. Determination of trace elements of considerable content (with level about milligrams per litre) allows using such techniques as X-ray fluorescence, inductively coupled plasma atomic emission spectrometry and flame atomic absorption spectrometry, those techniques often demands prior concentration procedure. GFAAS is conventional technique for the trace element analysis. Despite the satisfactory detection limits, possibility to determine a wide range of elements, relative accessibility of devices this method due to its relative low efficiency is gradually yielding to ICP-MS. Complicated composition of biological fluids creates the variety of problems for analytics, concerning interfering matrix influences. Sample digestion, sample dilution, using of Stabilized temperature platform concept (Zeeman background correction, furnaces with L'vov's platforms, modifiers) promotes minimization of interferences in GFAAS. The majority of GFAAS biological fluids investigations concerns the determination of such elements as Pb, Se, Cd, As, Hg. In our studies the range of elements is slightly extended. Direct methodologies of GFAAS determination of Mn, Cr, Ti and Hg in whole blood and Al in blood plasma have been already certified. At present time we are making our efforts to design and certify the methodologies of direct analysis of Tl and Be in blood using GFAAS. Polyelemental character, the velocity of the analysis and contemporary analytical level of metrological values provides high efficiency of ICP-MS technique for estimation the interactions and inter-influences of the elements in human body. The method is selective; however there is a variety of interferences during complicated objects analysis, mostly of spectral nature. Some of those interferences can be coped mathematically or by using alternative isotopes. Still the elimination of polyatomic ions spectral interferences is individual problem for each object, conditions of analysis and usable device. Usage of high resolution mass spectrometry with inductively coupled plasma is the most effective way of copying polyatomic ions interferences. Dynamic reaction cells of different design are used for minimization of such interferences in conventional quadrupole mass spectrometers. There are two different common approaches to trace element analysis of biological fluids: analysis after sample digestion and without it. Direct analysis of biological objects allows eluding the appearing of systematic errors during mineralization step; moreover it considerably simplifies and accelerates the analysis. Despite the presence of effective techniques and approaches to trace element analysis of biological fluids, the data obtained by independent authors often differs critically. That is probably related to the absence of certified methodologies of quantitative trace element analysis with the established error parameters.

NEW METHODS OF DETECTION OF METABOLIC MARKERS THAT INDICATE ABNORMALITIES OF METALLO-LIGAND HOMEOSTASIS

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Imbalance of elements and change in metal-ligand homeostasis is one of the toxic effects on the system on molecular level. Metabonomics is one of the new analytic technologies that facilitate the detection of various metabolic changes in biological fluids during intoxication. Markers of direct toxic effects of cadmium and mercury are well known. New methods are required to detect indirect toxic effect resulting from imbalance of elements and change in metal-ligand homeostasis. These methods should also detect specific metabolic markers and any change in concentration of metals in metal-binding proteins such as cadmium-metallothionein complex (CdMT) and ferritin. In our research we used metabonomic technologies: «tandem» method of detecting quantitative metabolic changes in biological fluids on line HPLC-NMR-MS, PFIA, ICP-MS, GRS (gamma-resonance spectrometry), histochemical methods. We have conducted comparative quantitative analysis of change of specific metabolites in urine in ethyl-mercury poisoning. We have observed significant increase of levels of succinate, lactate, acetate and ethanol in urine during the experiment. Increased concentration of ethanol is a result of decreased activity of alcoholdehydrogenase. The following metabolic products determine degree (severity) of mercury intoxication: valine; taurine; glucose and trimethylamine oxide (TMAO). TMAO is a general biological marker of the «toxic kidney». In our experiments in vivo on line we noticed that changes in homeostasis were associated with increased amount of metallothionein, formation of CdMT with increased levels of cadmium in this compound. Change in ferritin concentration is another biomarker of intoxication. This is thought to be a result of impairment of storage and metabolism of iron. Our experiment showed no change in concentration of ferritin. However we were able to observe changes in GRS spectrum of ferritin which signifies change in electronic state of iron atoms. These changes were dependant on the levels of mercury in urine samples. Most probably these changes in Iron atoms arose from the presence of mercury and cadmium ions in the globules of ferritin rather than from the change in ligand content or the charge of Iron atoms. The advantage of GRS is to allow simultaneous detection of atom structure and mobility. Functional activity of protein (ferritin is this instance) is determined by mobility of its fractions which is caused by conformational transformations. PFIA is a new technology for detection Ions of Metals. It measures (quantitatively and semiquantitatively) Ions of metals in real time and takes just a few minutes. Its limitations are Hg(II) — 2 ng/ml, Cd(II) — 7 ng/ml. We applied this method to detect abnormally high level of mercury cadmium and zinc in the urine of mice while the concentration of iron stayed normal (in comparison with controls). Metabolic intracellular changes precede structural abnormalities. New method of staining of histological samples (USA 2004) allows judging if certain oxyphilic, basophilic and particularly amphoteric components are present in particular intracellular structures. It also enables to bring together and compare results of physic-chemical and morphological experiments.

THE EFFECT OF ENVIRONMENTAL POLLUTION WITH MICROELEMENTS ON NATURAL SMALL MAMMAL POPULATIONS IN THE URALS

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Investigation of the effect of technogenic pollution on an organism is an important aim of medico-ecological monitoring. Due to its geographic position and historic reasons the Ural region has long ago become a risk zone of pollution with heavy metals and radioactive elements. Bioaccumulation of heavy metals: Fe, Mn, Cu, Zn, Cd, Pb in the tissues of ecologically contrasting species *(Clethrionomys glareolus, Apodemus uralensis, Sorex araneus)* from natural populations inhabiting background and technogenic areas is species specific and dependent on the effect and its duration. A research on the levels of Cu, Zn, Cd, Pb in the «soil-plant-animal» system has shown that correlations of metals change as they pass the food chain while their accumulation in sections depends both on the plant and animal species and their physiological condition. It is experimentally shown that a high level of homeostatic regulation limits the accumulation of heavy metals in tissues and effectively removes Cu and Zn from an organism but poorly eliminates Cd. Against the background of the deficiency of essential microelements (Fe, Mn, Cu, Zn, Ca) there is a correlation between the higher total Cd levels in livers and spleens in *Clethrionomys glareolus, Apodemus uralensis* and the growing intensity of catabolic processes. This results in a lower fetal body mass at birth ($r = -0.75$; $r = -0.8$; $p < 0.05$), and in the upset of the early adaptation processes of animals in anthropically altered ecosystems permanently affected by technogenic pollution. The analysis of the obtained data has proved that an in creased level of a complex of toxicants in the environment has combined effect of xenobiotics (Cd, Pb) on organism and is a factor responsible for heavy metabolic and functional disturbances, population health and number.

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10 YEARS OF INTERCOMPARISON EXERCISES IN IAEA SYSTEM

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The implementation of accepted quality assurance practices to analytical chemistry is recognized as a prerequisite to producing data that fall within acceptable limits. Whether the target analyte is a trace metal or an organic constituent of environment, quality assurance and quality control are necessary to analytical data validation. For more then 30 years, the Marine Environmental Studies Laboratory of International Atomic Energy Agency (MESL IAEA) has conducted intercomparison exercises as worldwide laboratory performance study. And for more than 10 years Laboratory of Applied Hydrochemistry and Analytical Chemistry of State Oceanographic Institute is apermanent participant of such exercises in trace metal determination in environmental samples. For the assessment of each lab performance, an individual Z-score was calculated for all metals. The percentage of Z-score ($|Z| < 3$) was used to assign the laboratory performance to a group level graded from 1 to 4 as follows: group 1 — labs with $|Z| < 3$ for $\geq 90\%$ of the data; group 2 — labs with $|Z| < 3$ for 75% to $< 90\%$ of the data; group 3 — labs with $|Z| < 3$ for 50% to $< 75\%$; group 4 — labs with $|Z| < 3$ for $< 50\%$. During this period the lab attained the next results. Measuring of 5 elements (Cd, Cr, Cu, Ni, Pb) in IAEA-405 (marine sediments) — group 2; measuring of 8 elements (Al, As, Cd, Cr, Cu, Mn, Ni, Pb) in IAEA-407 (biota) — the same group 2; measuring of 12 elements (Al, As, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, V, Zn) in IAEA-433 (marine sediments), IAEA-436 (biota), IAEA-356 (marine sediments), IAEA-158 (marine sediments) — group 1.Description of pre-treatment techniques: wet mineralization (aqua regia and hydrofluoric acid for sediment samples; nitric acid for biota samples), closed vessels, microwave oven. For trace metals measuring spectrometer «Spectr AA-800» (Varian) was used. Instrumental parameters: AAS, graphite furnace, Zeeman background correction.

RELATION OF SELENIUM CONCENTRATION BETWEEN PAIRED CEREBROSPINAL FLUID AND SERUM SAMPLES AND FIRST SELENIUM SPECIATION RESULTS

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The beneficial health effects of Se demanded the development of rapid and accurate methods for analysis. For total Se analysis a flow injection method with ICP-DRC-MS as a selenium-selective detector was optimized and validated. The method characterization parameters were: LOD: 26 ng/L, LOQ: 86 ng/L, linearity: 0.05 — >10 μg/L, $r^2 = 0.9999$, serial or day-to-day precision at 2 μg/L: 4.48% or 5.6%. Accuracy was determined by a) recovery experiments (spiked CSF); b) comparison of FI-ICP-MS measurement with graphite furnace atomic absorption (GFAAS) measurements of diluted serum samples; c) Se determination in urine and serum control materials. Recovery (a) was 101.4%, measurement comparison with GFAAS (b) showed 98.8%, and accuracy was 96.8% or 105.6% for the serum or urine control material. Analysis time per sample was short and typically below 2 minutes for the complete quadruplicate Se-determination. This method was used to determine Se in 35 paired serum and CSF samples, resulting in a serum-Se concentration range of 42 —130 μg/L and in a CSF-Se concentration range of 1.63—6.66 μg/L. The median for Se in 35 individual CSF samples was 3.28 μg/L, the mean (± SD) was 3.67 (1.35) μg/L, whilst for individual serum samples the median was 81 μg/L and the mean (± SD) was 85 (26) μg/L. Relating the paired Se concentrations of CSF and serum samples it turned out that Se-CSF (behind blood brain barrier (BBB)) is independent on Se-serum concentration (before BBB). The transport of Se across BBB depends on a strictly controlled transporter and not on diffusion along a concentration gradient. Preliminary studies on Se-speciation in CSF and serum used hyphenated techniques: SEC coupled to ICP-DRC-MS and IEC-ICP-DRC-MS. This technical setup provided good characterization and even identification of Se-species. Predominantly Se-proteins but nearly no LMM-Se-compounds were found in CSF. Some of these proteins were identified and were related to proteic Se-species in serum.

ELEMENTAL COMPOSITION OF MEDICINAL PLANT DRUGS SOLD OVER-THE-COUNTER IN SAO PAULO CITY, BRAZIL

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Medicinal plants have been used to treat diseases for thousands of years. In Brazil, the use of medicinal plants is very popular due to the assumption that herbs which are of natural origin are safe and without side effects and they are sold over-the-counter. Medicines derived from medicinal plants are, in general, cheaper than those from synthetic products and used for self-medication. Consequently, it becomes important to ensure the quality of the plant material and detect presence of contaminants. Trace elements present in these plants can also constitute part of active constituents. In this study neutron activation analysis (NAA) was applied to evaluate the element composition of drugs from the plants (Ginseng, Ginkgo biloba, Centella asiatica, Mulberry and Aloe vera) from different origins. Samples bought in natural product drugstores and pharmacies in capsule or tablet forms were ground to a homogeneous powder. Aliquots of these samples were irradiated along with synthetic element standards in the IEA-R1 nuclear research reactor. Short and long irradiations were carried out for determination of As, Br, Ca, Co, Cr, Cs, Fe, K, Mn, Na, Rb, Sc, Se, Zn and lanthanides. The induced gamma activities were measured using an HPGe detector coupled to a gamma ray spectrometer and the element concentrations were calculated by the comparative method. Comparisons made between the results indicated difference in their element contents depending on the origin of the sample, as well as, the age of the leaves. Correlations between the effect of the medicinal plants and their element content were found for Ca, K and Zn. Toxic elements such as Hg, Cd, Cu, Sb were not detected. Arsenic was detected in some samples but at very low concentrations at the ng/g levels. Biological certified reference materials were also analyzed for quality control of the analytical results.

QUALITY ASSURANCE OF TRACE ELEMENT ANALYSIS IN HUMAN MATRICES

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BACKGROUND: According to the German Guideline for Quality Assurance in Medical Laboratories (RiliBäK), external quality assurance schemes must be regularly performed to ensure the quality of the laboratory results. Since 1995 external quality assurance schemes are offered for trace elements. An evaluation of these schemes over a 6-year period shows,that the pass rates of the participant laboratories have significantly improved, especially with regard to trace elements such as Al in serum/plasma or Hg in urine. For several trace elements such as Cu, Zn, and Fe in serum/plasma good pass rates were observed over the whole period. MATERIALS AND METHODS: Matrix controls (urine, plasma/serum) from RECIPE, spiked with Al, As, Pb, Cr, Cd, Co, Cu, Mn, Ni, Hg, Se, Zn, and F, were used and two different levels of concentration were measured. RESULTS: The pass rates for Al, As, Pb, Cr, F, Cd, Co, Mn, Ni, and Hg in urine generally improved. Good pass rates (> 70%) also were observed for Zn, Se and Cu in urine. Similarly to the analysis from urine, enhanced pass rates were obtained for Al, As, Cr, Fe, Cd, Co, Mn, Ni, Se, and Zn in serum/plasma. Positive tendencies also were observed for As, Co, and Ni (increase > 30%). For Cu, high pass rates were commonly obtained (> 90%). DISCUSSION: The interlaboratory test results were determined by statistical calculation of the median, arithmetic mean and standard deviation of the remaining values. The target value ranges were defined by a variation coefficient of 12% and a confidence interval δ ± 3s. The evaluation of the external quality assurance schemes showed a general improvement of the pass rates. A reason is to be seen in the permanently enhanced requirements for diagnostic laboratories with regard to internal and external quality assurance. A further reason lies in the quality of reference materials. The special designed controls from RECIPE provide high quality with regard to packaging, homogeneity, long time stability, batch consistence, and stability after reconstitution.

ORGANIC TRACE ELEMENTS IN LAYING HENS' DIET

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In recent decades the use of trace elements in organic form has become a widespread practice in the field of animal nutrition, supported by the numerous positive results (Pierce et al., 2009). Different trials demonstrated that trace elements in organic form are inert from a chemical viewpoint, i.e. they do not interact with other nutrients and show a more rapid absorption in vitro, thus suggesting that they may be used in animal diets in smaller quantities compared to inorganic forms (Ji et al., 2006). Hundred forty four Warren laying hens were divided into six groups of 24 birds: D — control diet: premix containing sulphate trace elements; C25, C50 and C75 — diets containing metal amino acid chelated Fe, Cu, Zn and Mn in amount equal respectively to 25%, 50% or 75% of that one of control premix; D75—C25 — diet containing 75% of four minerals like as in the control premix and 25% of chelated trace elements; D25—C25 — diet containing 25% of minerals like as in the D premix and chelated trace elements in amount equal to C25 diet. In the yolk and albumen of eggs laid during a three-day period at 0, 45 and 90 days from the beginning of the treatment, Zn, Fe, Mn and Cu were determined by air-acetylene-flame atomic absorption spectrometry. Differences were detected only halfway through the trial in the Mn content of yolk and in the Cu content of albumen with statistically lower values in group C50, whereas the highest content was found in groups D and C75. By the end of the trial the differences had disappeared. demonstrating that with smaller doses of chelated trace elements, the content of these minerals similarly remains constant and comparable to that found in eggs laid by hens whose diets include higher quantities of inorganic trace elements It may be added, moreover, that using chelated trace elements in different combinations and for longer periods of time may have a positive effect on the various parameters, in view of the satisfactory results reported by other authors.

SILVER IN MEDICAL LEECH *(HIRUDO MEDICINALIS)*

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Dental diseases are accompanied by violation/disturbance of macro- and microelements equilibrium in the tissues of the body. The equilibrium may be restored by involving ionic forms of essential elements with chemotherapeutic drugs or natural medicine which is the medical leech *(Hirudo medicinalis)*. Despite of the long history of medical use of leeches their elemental composition is virtually unexplored. The particular interest in investigation of the leach elementome is to study the poll of silver which has an anti-inflammatory and bactericidal action. The report presents the results of the elementome aspect connected with determination of the silver content in the leach organisms which are used in dentistry. We discuss the features of the biosamples preparation for the analysis and also the chemical mechanisms of the ionic and elemental forms of *Hirudo medicinalis* native silver. Researches with the use of ICP — MS, ELAN DRC II demonstrated that the average leech silver content is 2.88 (1.06 — 7.50) µg/g (N = 12). It significantly exceeds the silver content in human skin 0.035 ± 0.015 µg/g (dry weight) or blood plasma 0.011 µg/ml of people working at silver manufactures (silver galvanoplastic, allocation of silver from ores and alloys). The detected amounts of silver are comparable to its content in human blood plasma (5 kg) in case of poisoning by silver (1 g), accompanied by signs of argyria. The results suggest the participation of silver ions in the biogenic processes at dental procedures with the use of *Hirudo medicinalis.*

DETECTION OF THE ESSENTIAL AND TOXIC ELEMENTS IN CHILD BIOLOGICAL SUBSTRATES BY ICP-MS TECHNIQUE

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The peculiarities of the application of ICP-MS technique for determination of the wide range of elements in different biological samples were investigated. Although the technique enables simultaneous determination of the major and trace concentrations, strong matrix interference dictates thorough investigations of matrix effect when ICP-MC is used for analysis of specific probes. The Agilent 7500 c instrument was used in these experiments. The methodology of the ICP-MS analysis of (1) urine and blood samples of the babies of several days to 2 months age and (2) hairs of the kids below 10 years age were investigated. In case (1) main problems were caused by the small volume of the probes and problems with adequate reproducible sampling. Different sampling techniques and levels of blank experiments with different instruments were checked. The daily urine is typically used for analysis. The problem of adequate sampling of a baby's urine in the conditions of a hospital dictated the use of a more simple sampling technique. It was found, that analysis of a sample collected in the morning provides the results, which are diagnostically undistinguishable from the analysis of a whole daily urine volume. The purity of the primary solutions used for the dialysis of the sick babies and the variations of the elements composition of dialysate solution after pumping the solutions through the babies during the medical procedure were investigated. The increase of the concentrations of some elements after the dialysis was detected. Namely, Cu concentration increased in some cases up to 20 times, while Zn and Sr concentrations increased 2 times and 1.6 times, respectively. The results of the measurements helped to correct the procedure of the patience's treatment. Optimal strategy of hair and blood sample mineralization was checked. The acid digestion of the samples was found as insufficient because of high blank level. The best results were obtained using mw- digestion in closed Teflon vessels. The limited volume of the blood samples of babies dictated the use of the vessels of 6 mL volume. Following analytes were determined: Na, Ca, Pb, Cr, Cd, Mn, Zn, Cu, Co, As, Ag, Se, Sb, La, Ce, Au, U in hair and Li, Be, B, Al, Ni, Sr, Mo, Ba, Tl, Bi, Cr, Cd, Mn, Zn, Cu in blood and urine samples. It was found that Cl-ion does not bias the results of As, Se and Cr determination in hair. In urine samples the concentration of Cr is much lower, which dictated the use of DRC for elimination of ClO^{53+} и ArC^{52+} interferences. In the investigated samples sulphur caused the most pronounced interference. 500 mg/L of S decreased the analytical signals of the masses from Li to Ba up to 30%. The technique of internal standard did not help in this case. The best results were obtained using the method of additions. The developed analytical procedure was verified by the analysis of the Reference Standard Materials.

CONCENTRATION LAVEL OF HEAVY METALLS WHITHIN MARINE AEROSOLS OF WESTERN ARCTIC SEAS, SOUTHERN ATLANTIC AND ARCTIC OCEAN

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Issues of laboratory of applied hydrochemistry and analytical chemistry (SOI) are connected to marine aerosol chemistry. We are measuring concentration of heavy metals (HM) within marine aerosols since 2002. Ocean's surface supplies lower atmosphere with 109 ton aerosol matter per year and becomes high-capacity source of world's aerosols due to its size and continuity of aerosol-generation (O'Dowd C.D. et. al, 2007; Buseck P.R. et al., 1999). Marine aerosols here are the agent of seas self-cleaning system. Marine aerosols, formed from sea surface, contain plenty of pollutants in fair quantity, including heavy metals. This fact is extremely important for the coastal cities and recreation areas; chemical composition of marine aerosols is becoming a significant ecological factor of environment. The seas belong to vary climatic zones have different levels of HM concentration in marine aerosols; in some cases the difference reaches two order. Seas of western arctic, southern Atlantic and Arctic Ocean have lower HM concentration, in comparison with the southern seas. For instance: Ni and Cr for 3 degrees, Pb and Mn is lower for 2 degrees; Zn — for a degree. Concentrations in these regions can be considered as natural background. Black, Caspian, Azov and Mediterranean seas defines with high concentration of HM in marine aerosols. In some cases it can have harmful effect on shoresmen's health. Concentration of Al, Cr, Ni, Zn within marine aerosols can reach, in some cases, 1000—2000 ng/m^3. This can be coursed by anthropogenic factors such as wastes, navigations, ecological accidents.

QUALITY ASSESSMENT OF MEASUREMENT

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Assessing the quality of measurements is of interest to organizers of external quality assessment schemes (EQAS, or proficiency testing schemes), laboratory analysts and managers, users of laboratory results and quality metrologists. Metrologists influence the choice of statistical tests applied to test data, terminology and conduct of testing programmes, as illustrated by the drafting of ISO 17043. Scheme organizers run test programmes, suggest or define standards of acceptable and non-acceptable performance, and interact with participants and oversight authorities. Laboratory personnel are responsible for the quality management system (method validation, IQC, audits etc.) and to choose whether to accept the standards set by scheme organizers or to adopt their own. Users receive and act upon the laboratory results. Rarely, users will enquire about the quality of results and some may express opinions as to the quality (standards) appropriate to their work. Schemes within the same analytical sector may often be in competition which can cause confusion among participants. The Network of EQAS in occupational and environmental laboratory medicine established collaborative projects designed to enhance assessment of measurement quality and to improve the reliability of laboratory results. Inclusion of the same samples in different EQAS (for trace elements in clinical samples) has demonstrated; variations in assessment of performance which can give conflicting outcomes for individual participants; participants of some schemes perform better than those of other schemes; some methods in use are inappropriate. To address the issue of variations in assessing the quality of measurements, and in response to comments from some participants,standards derived from biological variation, rather than on the analytical performance of participants have been developed. Evaluation of test materials with respect to homogeneity and stability, and work on methods to give the assigned value to test materials, has also been undertaken. Following from these projects, further collaboration is planned which will provide better quality assessment of measurement to scheme participants and their users.

NEXT GENERATION ICP-MS nexION 300 FOR ELEMENTAL, ISOTOPE AND SPECIATION ANALYSIS IN CLINICAL AND BIOLOGICAL RESEARCHES

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ICP-MS method (Inductively Coupled Plasma Mass Spectrometry) is recognized as a most universal method for elemental and speciation quantitative analysis for clinical/biological applications. For a wide range of elements in clinical samples (typically very small volume) ICP-MS is the only applicable method. Isotope ratio analysis gives a possibility of using stable isotope as a marker instead of radioactive isotope. This is a proper approach for standard samples certification. Calibration linearity, wide concentration dynamic range, relatively low matrix effects, no need in matrix based standard and in speciation standard samples, new advances in interference correction open new possibilities to ICP-MS analysis. Near 30 years PerkinElmer SCIEX is a leader in ICP-MS innovations. Dynamic Reaction Cell in ELAN DRC (1999) defined next 10 years of ICP-MS development. In ELAN DRC II new Axial Field Technology (2002) for DRC makes ICP-MS analysis of difficult samples (like clinical and biological) simpler. A good review of interference removing techniques, of their advantages and disadvantages can be found in: *Tanner S., Baranov V., Bandura D. 2002. Reaction cell and collision cell for ICP-MS: a tutorial review // Spectrochimica Acta. Part B. Vol.57, pp.1361—1452.* If summarize publications for the last 10 years it possible to make a list of typically measured elements in human body by Standard ICP-MS systems, by DRC systems and by Collision Cell systems: Pb, Se, Al, Be, Tl, As, Cd, Hg, Zn, V, Fe, Cr, Co, Ni, Mn, Mo, Li, K, Na, Rb, Cs, Pt, Pd, Rh, Au, Ag, Br, I, P, Ca, Mg, Sr, Ba, B, Sn, Sb, Te, Bi, Ti, Zr, Ta, W, Ga, Ge, In, Sc, La, Ce, Th, U, Pu. The Universal Cell Technology (UCT™) in the new 7th generation ICP-MS NexION 300 just presented at Pittcon'2010 gives a possibility to use advantages of each mode of operation in a single instrument: Standard, Collision (KED) and Reaction (DRC). More to this, the NexION 300 incorporates new 3-cone plasma interface and new Quadrupole Ion Deflector — those new subsystems greatly increase sensitivity, reduce matrix effects and completely remove cell contamination (no need for cell maintenance and replacement which are typical for competing ICP-MS systems). Using NexION 300 ICP-MS, new generation Chromera® II software and new HPLC platform Flexar™ from PerkinElmer LAS makes elemental speciation separation and detection most accurate and simple. «By adding the LC, GC or IC separation capability to the NexION 300, the instrument is able to answer «what forms» of a species are present in a sample and not just «how much». This allows to pinpoint the exact toxicity, bioavailability, metabolism and environmental mobility of elements...» — those words from NexION brochure are not just words. NexION 300 ICP-MS: three modes of operation, two interference removing techniques in one revolutionary instrument. It permits to do analytical things the way you want.

BLOOD MERCURY LEVELS AND SOURCES OF EXPOSURE. EMA STUDY 2009

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BACKGROUND: There is an increasing concern about the potential adverse effects of perinatal exposure to methylmercury on brain development and on the risk of cardiovascular disease in adults. The aim of the present study was to determine the blood mercury levels of volunteer employees of the Hospital Clinico San Carlos in Madrid, Spain, and assess their relationship with fish intake.MATERIAL AND METHODS: A cross sectional study was conducted on volunteer employees of the Hospital Clinico San Carlos. A total of 395 subjects (313 women and 64 men) were enrolled in this study. A fish intake frequency questionnaire (EMA® Questionnaire) was administered after signing the informed consent. The blood mercury concentration was determined by cold vapour atomic absorption spectrometry in a Perkin-Elmer flow injection mercury system, FIMS-400. The statistical package SPSS 15.0 was used for data analysis. RESULTS: Mercury (µg/L): median (IQR): 7.9 (5.2—11.5). Maximum value: 53.80 µg/L. Approximately 71% of participants have concentrations higher than the limit of 5.8 µg/L established by the US Environmental Protection Agency. It has been observed that 30% have a weekly intake expressed as µgHg/kg bw/week higher than the JECFA PTWI (1.6) and 79.1% higher than the NRC RfD (0.7). A positive correlation has been observed between micrograms of mercury intake through fish and blood mercury levels ($r = 0.702$, $p < 0.001$). We have not observed statistically significant differences in blood mercury concentrations by gender ($p = 0.250$) or menopause ($p = 0.142$). CONCLUSIONS: Blood mercury levels positively correlated with fish consumption, particularly swordfish and tuna. It would be desirable to advise vulnerable groups, women who might become pregnant, pregnant and breast-feeding women and young children to limit the consumption of certain species of predatory fish. Further research is required to assess the effects of these blood mercury levels on the risk of cardiovascular disease in Spain.

BLOOD MERCURY ANALYSIS: COLD VAPOUR VS. DIRECT METHOD

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BACKGROUND: In recent years concern has grown with respect to the content of methylmercury in fish and the possible adverse health effects. Therefore, the measurement of blood mercury is currently of great interest; thus it is desirable to have methods that permit the analysis of a great number of samples in an accurate manner. The objective of the study is to compare the measurement of blood mercury using cold vapour atomic absorption spectrometry and the direct method based on EPA method 7473. METHODS: A double-blind study was carried out on blood samples taken from 45 volunteers. Mercury was measured by cold vapour atomic absorption spectrometry in a Perkin Elmer flow injection mercury system FIMS 400 after the acid digestion of the blood samples by heating them up to 60° for 12 hours. Subsequently, blood mercury was measured again in a direct manner without carrying out the digestions in a DMA-80 Milestone based on the EPA 7473: thermal decomposition, catalytic reduction, amalgamation, desorption and atomic absorption spectrometry. The statistical package SPSS 15.0 was used for data analysis. RESULTS: We obtained an intraclass correlation coefficient of 0.988 CI 95%: 0.978—0.994; $p < 0.001$. In the Bland Altman plot the mean of the differences was — 0.3 and the limits of the 95% agreement interval were: 3.2 to —3.8. CONCLUSIONS: The obtaining of an intraclass correlation coefficient close to 1 indicates that all of the observed variability can be explained by the differences between subjects and not between methods or the different observers. Upon evaluation of concordance by Bland Altman plot, almost all the measurements concord (difference equal or close to 0) and are included in the 95% confidence interval of the mean of the differences. Nor did we observe discordance with higher levels of mercury, given that the differences are homogeneous across the horizontal axis. This analysis indicates a high level of concordance between the measurements of the two methods.

NANOPARTICLES IN NATURAL WATERS

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Processes of mineral destruction and aerosol generation, chemical and biological processes, industrial pollution are most important in formation of nanoparticles in natural waters. There are four chemical groups of natural nanoparticles: aluminosilicates and silicates, biogenic, inorganic and carbonic nanoparticles. Most of trace elements in natural waters are occluded or adsorbed on nanoparticles (including aluminosilicates) that play an important role in trace elements delivery. Determination the concentration gradient of trace elements in natural waters after nanoparticles destruction and without it is the main object of this paper. Materials and methods: three trademarks of mineral water: Novoterskaya Tselebnaya, Narzan and Essentuki No17. Nanoparticles were detected using dynamic light scattering with Zetasizer Nano ZS (Malvern) and measure about 200 nm in Essentuki No17 and 10 nm in Novoterskaya and Narzan. For determining the concentration of occluded trace elements the graphite Zeeman AAS was applied. Concentration of Ni, Mn and Cr determined with atomic absorption spectrometer «Spectr AA-800» (Varian); microwave oven MDS2000 for mineralization was applied. Following sample preparations were used: (1) interaction with aqua regis; (2) interaction with aqua regis and microwave mineralization; (3) interaction with aqua regis and hydrofluoric acid and microwave mineralization. Determining the concentration of Ni, Cr and Mn after mineralization in hard conditions (microwave mineralization) show increasing concentration of trace elements in 10 times with interaction with aqua regis and in 20—30 times with interaction with aqua regis and hydrofluoric acid. Destruction of aluminosilicates and elements release cause this increasing of concentration.

SPATIAL VARIATION IN ENZYME ACTIVITY AND TRACE ELEMENTS IN WOOD DECOMPOSED BY *FOMES FOMENTARIUS*

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Wood colonized by saprotrophic basidiomycetes represents a unique ecosystem strongly affected by fungal metabolism. Typically, this environment is characteristic by low pH and the presence of extracellular enzymes of lignocellulose decomposition which depolymerise the wood cell wall components and thus create an environment with accessible small molecular mass compounds to be utilized by wood-associated microorganisms. Some biogenic metals play also an important role in delignification of wood (Mn, Fe, Cu), either by participation in enzymatic reactions (Mn-peroxidase) or by production of free radicals (Fenton systems). The aim of this work was (1) to quantify the activity and spatial distribution of extracellular enzymes (laccase, Mn-peroxidase, endoglucanase, cellobiohydrolase, β-glucosidase, endoxylanase, β-xylosidase and N-acetylglucosaminidase) in fruiting body of white-rot basidiomycete *Fomes fomentarius* and adjacent colonized wood and (2) to compare them with an amount of metals. Enzyme activities were measured by fluorometric assays and content of metals by Atomic Absorption Spectroscopy. A colonized birch log (*Betula pendula*) was collected in hardwood forest in the Czech Republic. Spatial distribution analysis revealed higher activity of cellobiohydrolase, β-glucosidase and endoxylanase in fungal fruiting bodies and higher activity of laccase and Mn-peroxidase in more distant wood parts. Ligninolytic enzymes were found mainly in colonized wood while the activities in fruiting bodies were low. Concentrations of Mn were higher than concentrations of other elements, especially in fruiting body core. The results support the hypothesis that Mn rather than Fe, Cu or other metals participates in the delignification mechanisms *in vivo*.

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INTERFERENCE OF GADOLINIUM ON THE MEASUREMENT OF SELENIUM IN HUMAN SERUM BY ICP-QMS

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BACKGROUND: Selenium is an important essential trace element. It is a component of several enzymes, it affords protection against reactive oxygen species and it may prevent the development of some cancers. Deficiency of Se occurs if there is inadequate intake. Selenium is also toxic if there is excessive exposure. Deficiency or toxicity is diagnosed by measuring the Se concentration in serum or whole blood. INVESTIGATION: A serum sample analysed by ICP-QMS with a collision cell gave a Se concentration of 16.8 μmol/L (reference range 0.89—1.65 μmol/L). This extraordinarily high concentration would normally be seen only after a massive exposure. It was suspected that an interference was affecting the ICP-QMS measurement and the sample was reanalysed by Zeeman ETAAS, with a result of 0.65 μmol/L. In looking for a possible explanation it was noted that $^{156}Gd^{2+}$ would superimpose on $^{78}Se^{+}$, the isotope used for the selenium measurement. The sample was re-examined and found to contain very large amounts of Gd and it was later confirmed that the patient had had a magnetic resonance imaging (MRI) scan using a contrast agent containing Gd, on the same day as the sample was taken for the Se measurement. To demonstrate the degree of interference from Gd^{2+} ions, a serum sample, spiked to contain 0, 0.2, 0.5, 1.0, and 5.0 mg/L Gd gave Se concentrations of 1.05, 1.67, 2.13, 3.35 and 6.54, respectively. It has previously been reported that following an intra-venous injection of 2 mg Gd per kg body weight to volunteers, peak plasma levels were 1570 mg/L, falling to 15.7 mg/L after 12 h. CONCLUSION: We observed that Gd-contrast agents for MRI cause a positive interference on the measurement of Se by ICP-QMS. Interference was found with Gd concentrations as low as 0.2 mg/L and can mask Se deficiency. Further examples have since been seen in this and other laboratories.