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Russian Society for Mass Spectrometry

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Chemistry Department**

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on Environmental Chemistry**

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Conference programme

05 December

15.00-18.00 Registration
18.00-20.00 Wellcome meeting

06 December

9.00-9.30 Registration
9.30-9.40 Openning ceremony
9.40-10.20 Yu.A. Zolotov
10.20-11.00 R.A. Zubarev, X. Xie. Isotopic resonance hypothesis of the origin of life: first experimental testing
11.00-11.30 – coffee-break

Session A. «Analytical techniques and methods, environmental monitoring and control»

11.30-11.50 J. Čáslavský, M. Vávrová, M. Bukáčková. Organophosphorus and carbamate pesticides in waste and surface water
11.50-12.20 G. Bondoux, J.M. Joumier, A. Gledhill. A new software approach for the routine accurate mass screening of pesticides in environmental samples
12.20-12.40 Gareth M Roberts, G. Horner, J. Ringer. The analysis of airborne chemical warfare agents using thermal desorption pre-concentration with GC/MS analysis employing novel chemometric software for data analysis
12.40-13.00 A.D. Pavlov, S.V. Sukhoverkhov, A.K. Tsvetnikov. Application of GC-MS to determine composition of the low molecular weight polytetrafluoroethylene
13.00-13.20 A.S. Samokhin, A.I. Revelsky, I.A. Revelsky. Absence of spectral skew, high-speed acquisition, automatic peak finding and mass spectra purification as key aspects of non-target GC/MS analysis
13.20-13.40 E. Hakalehto, O. Hänninen. Towards on site MS microbe assay in portable microbe enrichment unit with metal oxide sensors
13.40-14.00 C. Mendes, C. Jousse, I. Canet, M. Lagree, M. Traikia, M. Sancelme, M. Joly, L. Deguillaume, P. Amato, A.-M. Delort. Response of *Pseudomonas syringae* isolated from clouds to cold stress. A metabolomic study.
14.00-15.00 LUNCH
15.00-15.20 B.L. Milman, I.K. Zhurkovich. New environmental developments in reference mass spectral libraries
15.20-15.40 O. Polyakova, D. Mazur, M. Bolshov, I. Seregina, A. Lebedev. GC-MS study of Moscow snow samples in 2011 and 2012
15.40-16.00 E.S. Chernetsova, G.E. Morlock. Surface analysis by direct analysis in real time mass spectrometry employing plasma glow visualization
16.00-16.20 A.T. Lebedev, D.M. Mazur O.V. Polyakova, V.V. Artaev. The benefits of accurate mass measurements in GC/MS analysis of environmental samples
16.20-16.40 I.A. Revelsky, A.S. Samokhin, D.A. Chepelyansky, A.I. Revelsky. A new approach for comparing quality of pharmaceuticals (originals and generics) based on registration of unknown impurities using GC/MS
16.40-17.00 E.I. Savelieva, N.L. Koryagina, A.S. Radilov, N.S. Khlebnikova. Retrospective detection and identification of chemical warfare markers of in environmental and biological monitoring.
17.00-17.20 A.M. Safarov, R.M. Khatmullina, V.I. Safarova, G.F. Shajdulina, A.R. Muhamatdinova. The condition of underground waters in the petrochemical enterprises influence zone
17.20-17.40 R.D. van Zee, C.A. Gonzalez. Data and standards for greenhouse gas monitoring

07 December

Plenary lectures

9.30-10.10 M. Eberlin
10.10-10.50 A. Laskin. Chemical imaging and molecular analysis of atmospheric aerosols
11.00-11.30 coffee-break

Session B. Chemistry of water, soil and atmosphere

11.30-12.00 T. Kovalczuk, J. Zrostlíková, D. Alonso, J. Binkley. Gas chromatography coupled to ultra-high resolution multireflecting TOF MS for the analysis of persistent organic pollutants

12.00-12.20 V. Vinatier, A. Blanc, M. Vaïtilingom, M. Joly, P. Amato, L. Deguillaume, M. Sancelme, A.M. Delort. Siderophore production in cloud water

12.20-12.50 MS-Analitika

12.50-13.10 V.V. Zelenov, E.V. Aparina, D.V. Shestakov. Marine aerosol as a source of halogens in the troposphere

13.10-13.30 T. Alekseeva, P. Besse-Hoggan, M. Sancelme, B. Zolotareva, Yu. Kolyagin. Mesotriene adsorption on vertisol (Limagne plain, France): effect of soil properties

13.30-13.50 R. Kalathoor, J. Botterweck, B. Schmidt, A. Schäffer, J. Schwarzbauer. Enantioselective and stable carbon isotope analyses following microbial assisted processes in soil: bound residue formation and degradation of the herbicide metalaxyl

13.50-14.10 Y. Mamindy-Pajany, S. Sayen, E. Guillon. Investigation of nickel adsorption/desorption processes on a lime stabilized sewage sludge, a calcareous soil and sludge-amended soils

14.10-15.00 – lunch

Session C. Water and waste treatment

15.00-15.20 Bruker

15.20-15.40 D. Pujol, C. Liu, A. Olivella, F. de la Torre, H. Pereira, N. Fiol. Chemical composition of grape stalks and coffee wastes. Role of the different compounds in Cr(VI) removal

15.40-16.00 M. Pflieger, M. Franko. Degradation of fluoroquinolones used in aquaculture

16.00-16.20 L. Remenárová, M. Pipiška, M. Horník, J. Augustín. Cesium adsorption by synthesized zeolites prepared from coal fly ash

16.20-16.50 Agilent

Session D. Toxicology and ecotoxicology

16.50-17.10 G. Grbović, O. Malev, R. Sauerborn Klobučar, Ž. Cvetković, B. Cvetković, D. Dolenc, T. Tišler, A. Lebedev, O. Polyakova, P. Trebše. Stability and toxicity of selected sun protective compounds in disinfection processes

17.10-17.30 Identification and analysis of heavy metals toxicity in various plants and in their soil sources Muhammad IkramAujla, AroosaShahid and Dildar Ahmed

18.00-23.00 Conference dinner

08 December

Plenary lectures

9.30-10.10 R. Cody

10.10-10.50

11.00-11.30 – coffee-break

Session E. Biodegradation and bioremediation

11.30-11.50 B. Jovančičević, V.P. Beškoski, S. Miletić, M. Ilić, G. Gojgić-Cvijović, I. Matić, N. Marić, T.Š Knudsen, M.M. Vrvic Multistage *in situ* bioremediation of aquifer contaminated with petroleum pollutants

11.50-12.10 A.M. Zyakun Monitoring of microbial protection of plants from the phytotoxic action of anthropogenic organic compounds by using of $^{13}\text{C}/^{12}\text{C}$ ratios as an indicator

Session F. Environment and cultural heritage

12.10-12.30 E. Pons-Branchu, E. Douville, S. Ayrault, Ph. Branchu, W. Borts, M. Roy-Barman, L.Bordier, F. Thill, E. Dumont. Historical water contamination in an urban area: a geochemical study of middle age aqueduct deposits in Paris, France

12.30-12.50 J.Ranogajec, S. Vučetić, J. Kjurski, M. Radeka. Self-cleaning materials on architectural heritage: photo – induced hydrophilicity of TiO_2 coatings on historic materials

12.50-13.30 Closing Ceremony. Presentation EMEC14.

Poster presentations

Session A. Analytical techniques and methods, environmental monitoring and control

- A-1 Analysis of liquid samples without a sample preparation: 'pros' and 'contras' of different DART-MS-based approaches. E.S. Chernetsova, I.A. Revelsky, G.E. Morlock
- A-2 «Electrophoretic and chromatographic separations of bioactive compounds using hyperbranched polymer PEI-Mal as an additives in mobile and stationary phases. E.A. Bessonova, L.A. Kartsova, V.E. Potolitsyna, V.U. Koroleva, D.E. Dzema
- A-3 Quantification of estrogens in nine WWTPs of Portugal, using SPE-HPLC. M. Cardoso, V. Esteves, A.P. Fonseca
- A-4 DDT and other traditional chlorinated pollutants: continuing environmental threat in the Czech Republic. J. Čáslavský*, M. Vávrová, L. Plačková, L. Mravcová
- A-5 Determination of methylmercury muscle and skin of *Leuciscus cephalus*. Z. Králová, M. Vávrová, E. Šucman, V. Večerek
- A-6 Assessment of the level of contamination by PCB and PBDE in aquatic ecosystem of the South Moravian region. A. Jirova, Z. Kralova, M. Vavrova, M. Charvatova
- A-7 Problems of simultaneous preconcentration of platinum group metals by solid phase extraction and their determination by inductively coupled plasma mass spectrometry. J. Nevrlá, R. Komendová, L. Sommer, J. Kůta
- A-8 Fast plant oils screening for total content of F-, Cl-, Br- and S-organic compounds. A.V. Nikoshina, M.V. Fedoseeva, A.V. Golubeva, A.I. Revelsky, D.A. Chepelyansky, I.A. Revelsky
- A-9 Extraction of unbiased mass spectra in case of unresolved chromatographic peaks. A.S. Samokhin, I.A. Revelsky
- A-10 Microelement composition of some hydrobionts tissues of the Japan Sea. N.I. Steblevskaya, N.V. Polyakova
- A-11 Combination of high resolution ortho-TOF MS and the ion source with ionization of a pattern by both active particles and irradiation from glow discharge. I.V. Sulimnikov, V.S. Brusov, A.R. Pikhtev, V.V. Zelenov, V.I. Kozlovskiy
- A-12 Determination of the elemental composition of the East Arctic Seas sediments by energy dispersive X-ray fluorescence analysis. N.V. Polyakova, S.V. Sukhoverkhov, Yu.I. Krys', V.I. Sergienko
- A-13 Polybrominated diphenylethers in indoor and outdoor air and dust samples in Russian Federation. E.M. Pasynkova, A.I. Kochetkov, D.P. Samsonov, T.V. Rakhmanova, AG. Pantiukhina
- A-14 Voltammetric systems such as "electronic tongue" for express identification of the composition and the nature of wastewater. V.N. Maystrenko, A.V. Sidelnikov, D.M. Bikmeev, F.Kh. Kudasheva
- A-15 Radio-frequency time-of-flight mass-reflectron. E.V. Mamontov, A.A. Dyagilev, E.Yu. Grachev, V.V. Zhuravlev, S.A. Glushakov
- A-16 Analysis of kraft pulp wastewater by gas chromatography with mass detection. K. Bogolitsyn, M. Gusakova, A. Sloboda, I. Rodin, S. Pokryshkin
- A-17 Production of the wood fiber semi-products: features of effluents' composition. K. Bogolitsyn, M. Gusakova, N. Samsonova
- A-18 The principles of organization of the system of monitoring pollutions on industrial-urban areas. V.A. Bagryantsev, B.N. Meshcheryakov, V.N. Stepchenko, B.B. Verbitskiy, S.S. Voronich, M.A. Tikhomirova, A.Z. Razyapov
- A-19 Useful of new preconcentration techniques in CE to effectively focus of bioactive analytes in complex biological mixtures. L.A. Kartsova, E.A. Bessonova, V.E. Potolytsina, E.V. Obedkova

- A-20 Application of regular multimolecular sorbent based on Fe(III) stearate for mass spectrometric determination of residual contamination of natural waters by perfluorooctanoic acid. E.N. Chernova, O.A. Keltcieva, V.D. Gladilovich, Ya.V. Russkikh, N.G. Sukhodolov, A.A. Selutin, Z.A. Zhakovskaya, E.P. Podolskaya
- A-21 Evaluation of the anodic stripping voltammetry to study heavy metals removal by grape stalk waste in fixed-bed column. X. You, A. Florido, C. Valderrama
- A-22 Options for isolation and determination of selected pharmaceuticals from livestock excrements. K. Jarova, P. Komarkova, M. Vavrova
- A-23 LC-MS TOF analysis of erythromycin, related substances and degradation products. T.V. Andreeva, R.E. Trifonov
- A-24 Determination of volatile compounds in water, soil and sediment by Head Space-SPME-GC/MS. E.S. Brodsky, A.A. Shelepchikov, A.G. Alexandrova, V.G. Gil'nikov, E.Ya. Mir-Kadyrova, G.A. Kalinkevich
- A-25 Analytical methods for the detection of dimethyl thallium in water samples at low concentration levels. S. Sindern, L. Gronen, M. Bruchmann, S. Heister, S. Dreßen, J. Schwarzbauer
- A-26 Malachite green in suspended particulate matter and surface sediments in Germany. M. Ricking, J. Schwarzbauer, P. Apel
- A-27 Analysis of drilling fluid additives by pyrolysis- GC-MS with regard to their application as environmental marker. J. Schwarzbauer, N. al Sandouk-Linke, S. Grünelt
- A-28 Metrological aspects of the determination of the parameters COD and BOD₅ in sewages of pulp and paper industry. E. Shulgina, K. Bogolitsyn, A. Pochtovalova
- A-29 Study of the complexation process by modified carbon fibers. E.R. Valinurova, F.H. Kudasheva, L.A. Kovaleva, I.M. Khamaltdinov, I.Sh. Ahatov , A.V. Grigoryeva
- A-30 The quality status of surface water in Novi Sad municipality estimated on the presence of WFD and emerging substances. I. Spanik, J. Radonic, M. Turk Sekulic, D. Milovanovic, M. Djogo, M.V. Miloradov
- A-31 Ultratrace and isotopic analysis of uranium in environmental samples by Inductively coupled plasma mass spectrometry using high efficiency sample introduction. A.V. Saprygin, N.V. Kuzmina, A.V. Prosvirjakova, L.V. Grebenshchikova
- A-32 Characterization of environmental pollutants coming from meat industry in Vojvodina region. I.Spanik, M. Sremacki, O. Vyviurska, J. Radonic, M. Turk Sekulic, M. V. Miloradov
- A-33 The pollutant tracing in Danube river in Novi Sad. A. Pazitna, I. Spanik, O. Vyviurska, J. Radonic, M. Turk Sekulic, M.V. Miloradov
- A-34 PBDEs and POPs at the southern end of the Southern California Bight. J.V.Macías-Zamora, N. Ramírez-Álvarez
- A-35 Trace and major metal abundances in the shale and coal of various seams at Okaba coal mine, Kogi State, Nigeria. Okorie, E.O, Egila J.N
- A-36 Application of modern analytical method for assessing the environmental impacts of deicing agents on the environment. K.K. Bulatitsky, R.A. Sandu, A.N. Glushko, V.Z. Krasilshik
- A-37 Determination of composition of wax deposits as wastes of petroleum industry. N.A. Prokuda^{1,2*}, S.V. Sukhoverkhov², A.N. Markin³, N.B. Kondrikov¹
- A-38 M. Pipíška^{1*}, L. Tišáková², M. Horník¹, A. Godány^{1, 2}, J. Augustín¹. Isolation and characterization of bacteria from spent nuclear fuel pools in Slovakia.

Session B. Chemistry of water, soil and atmosphere

- B-1 Environmental levels of lead and nitrogen dioxide in urban Atlanta, Georgia, United States of America (USA): methods and preliminary results. M. E. Winsor, K. K. Amarnath, H. Kaplan, A. Combs, M. C. Martinez, R. Pickering, C. H.-Fuller, D. M. Deocampo
- B-2 The viable microorganisms of clouds. P. Amato, M. Vařtilingom, E. Attard, M. Joly, M. Sancelme, L. Deguillaume, A.-M. Delort
- B-3 Survival of microorganisms to the main stress factors encountered in clouds. M. Joly, P. Amato, M. Sancelme, M. Vařtilingom, V. Vinatier, L. Deguillaume, A.-M. Delort
- B-4 Evaluation and distribution of arsenic trioxide in seawater pollution scenario. C. Valderrama, R. Erdmann, A. Farran, J. de Pablo
- B-5 Assessment of large industrial zone effect on element redistribution in soil profile. N.A. Zhuchenko, E.V. Chipanina
- B-6 Isomers of hexachlorocyclohexane in water and sediment of the Elbe and Mulde River. M. Berger, D. Löffler, A. Martin, J. Schwarzbauer
- B-7 Humates as transportation agents of surfactants and amino acids. I.I. Germasheva, K.S. Erokhin, N.A. Glukhareva, O.E. Lebedeva
- B-8 Temperature dependent ozonation reaction of 1,1-diphenylethylene on artificial snow grains. D. Ray, J.K. Malongwe, P. Klán
- B-9 Sources and risks of organic contaminant and heavy metal burden in seafood from Jakarta Bay. L. Dsikowitzky, J. Schwarzbauer, E. Heruwati, F. Ariyani, Dwiytno
- B-10 Heavy metals in structure components of cryometamorphic soils in forest-tundra ecotone. O.V. Shakhtarova, E.M. Lapteva, G.V. Rusanova
-
- B-11 Occurrence of arsenic pollution in airborne pm in the area of gran bilbao (Northern Spain). M.P. González-Marcos, A. Blanco-Cascón, U. Iriarte-Velasco, J.I. Álvarez Uriarte and J.R. González-Velasco
- B-12 Improving Water quality by using some Bulitant removals. Abdullah S. Aljughaiman
-

Session C. Water and waste treatment

- C-1 Assessment of synthetic musk compounds in waste waters. M. Vávrová, J. Čáslavský, L. Zouhar, M. Štefka, P. Komárková
- C-2 Cr(VI) removal by exhausted coffee from binary mixtures (Cr(VI)-Cu(II)). C. Liu, J. Poch, F. de la Torre, N. Fiol, I. Villaescusa
- C-3 Application of the interpolymer complexation method for wastewater treatment. O.S. Brovko, I.A. Palamarchuk
- C-4 Ecological and economic evaluation of metallurgical dust emitted from the Kola MMC. A.G. Kasikov, S.V. Drogobuzhskaya, A.M. Petrova, N.S. Areshina
- C-5 Recovery of selenium-containing wastes and middling products of the gas-cleaning system in copper-nickel production. N.S. Areshina, A.G. Kasikov, S.V. Drogobuzhskaya
- C-6 Recycling of spent sulfuric acid of sulfuric acid alkylation isoalkanes with alkenes obtain commercial products. A.G. Mustafin, A.D. Badikova, T.V. Sharipov, F.H. Kudasheva
- C-7 Physicochemical characterisation of surfactant modified activated carbon. U. Iriarte-Velasco, E. Arrizabalaga, M.P. González-Marcos, J.I. Álvarez Uriarte, J.R. González-Velasco
- C-8 Electrochemical disinfection of water by using stand-alone photovoltaic power system. S. Hostin, M. Gabčová

Session D. Toxicology and ecotoxicology

- D-1 Determination of concentrations of estrone and estradiol in *Rana/Pelophylax perezi* males, by RIA. M. Cardoso, V. Esteves, A. P. Fonseca
- D-2 Ecotoxicological evaluation of selected foam extinguishing agents. H. Zlámálová Gargošová, M. Vávrová
- D-3 Study of bioaccumulation of selected pharmaceuticals in terrestrial organisms. P. Lacina, P. Dvořáková, H. Zlámálová Gargošová, J. Oborná, J. Nevrlá, P. Škarková, M. Vávrová
- D-4 V.R. Kastratovic, Ž.K. Jaćimović², D.D. Đurović, R.M. Zejnilović, S.D. Krivokapic. The distribution of chromium in the organs of aquatic macrophytes.

Session E. Biodegradation and bioremediation

- E-1 Monitoring degradation of biocompatible copolymers using high performance liquid chromatography and gel permeation chromatography. J. Oborná, M. Vávrová, L. Mravcová, L. Michlovská
- E-2 Searching of ways for synthesis of biodegradable polymers based on polyethylene. R.Z. Musin, F.R. Garieva, J.P. Mashkova, A.H. Karimova
- E-3 Fate of the herbicide sulcotrione in a black vertisol. E. Dumas, T. Alekseeva, M. Sancelme, P. Besse-Hoggan, C. Forano
- E-4 Cr(VI) sorption onto biomaterials – ion exchange and isotopic study of sorption mechanisms. H. Šillerová, M. Komárek, V. Chrástný

Session F. Environment and cultural heritage

- F-1 Absorption spectra as the indicator of black ink aging during the sheet-fed offset press. J. S. Kiurski, D. Ž. Obadović, I. B. Oros, M. J. Cvetinov
- F-2 Ž. Jaćimović, M. Kosović, N. Latinović, V. Leovac, Z. Tomić. The influence of some pyrazole derivatives and its newly synthesised transitional metal complexes on the inhibition of *Phomopsis viticola* Sacc. (Sacc.) under laboratory conditions.

Session G. Green chemistry and best available technologies

- G-1 Analysis of tar formed by gasification of biomass. M. Vávrová, V. Chytil, L. Mravcová, M. Lisý, M. Baláš, J. Čáslavský
- G-2 Low temperature preparation of a platinum catalyst. Kozjek Škofic
- G-3 Hydrogenation of phenylacetylene catalyzed by carbon coated metal nanoparticles: possibility of inherent catalytic activity of carbon shell. A.V. Erokhin, E.S. Lokteva, A.Ye. Yermakov, M.A. Uimin, D.W. Boukhvalov
- G-4 Analysis of chemical composition brown algae of the White sea. K.G. Bogolitsyn, P.A. Kaplitsyn
- G-5 Binding of asymmetrical dimethylhydrazine by sphagnum peat: influence of certain factors upon the process. K.G. Bogolitsyn, A.Yu. Kozhevnikov, M.P. Semushina
- G-6 Selective production of chloroaniline, N-ethylaniline or quinoline derivatives from chloronitrobenzene on Ni, Ni-Au, Ni-Pd and Ni-Zn catalysts. N.E. Kavalerskaya, E.S. Lokteva, E.V. Golubina
- G-7 Comparative analysis of composition of birch polypore and its nano-disperse form. D.R. Sharafutdinova, L. Sh. Nigmatullina, O.B. Bazanova, G.N. Konygin, D.S. Rybin, Strelkov N.S.
- G-8 Geopolymerization of fly ash as possible technology for stabilization of electric arc furnace dust. D. Djurović^{1*}, I. Nikolić², M. Tadić²

Isotopic Resonance Hypothesis of the Origin of Life: First Experimental Testing

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Stable isotopes, especially of the elements C, H, N and O, may not be just passive participants in life emergence and development, but can play active role in these processes. This is a new paradigm that, if proven, can change our understanding of how the world around us functions.

The basis of this paradigm is the isotopic resonance hypothesis that emerged from the detailed consideration of peptide molecular masses. Molecular mass can be characterized by two classical parameters, the monoisotopic mass and the average isotopic mass. Projection of polypeptides onto a plane created by two dimensions derived from these two parameters affords an easy visualization of mass spectrometry data [1]. In 2008, we have found that peptide masses mapped on a 2D mass plane form a peculiar global feature, a ‘band gap’ stretching across the ‘peptide galaxy’, with a narrow line in the centre [2]. The *a priori* probability of such a feature to emerge by chance is less than 0.01. Peptides contributing to the ‘line’ have elemental compositions following the rule:

$$\{S=0; H = 2C - N\} \quad (1).$$

The reason for the line emergence is a peculiar “resonance” between the isotopic abundances and monoisotopic masses of the biological elements C, H, N and O. Nine out of 20 amino acid residues satisfy rule (1). These residues (G, A, V, L, I, N, Q, S and T) are believed to be among the first emerging amino acids [3]. The presence of the isotopic resonance reduces the complexity of polypeptide molecules and may have increased their rate of production/destruction or interconversion, which in turn may have influenced the choice of these residues for terrestrial life. There is also evidence derived from the literature analysis [4] that the isotopic resonance may influence the rate of growth in living organisms.

Here we present first results of a series of experiments designed to test the isotopic resonance hypothesis. In particular, the *E. Coli* growth rate in a mixture of ¹⁴N- and ¹⁵N-containing minimal media is consistent with its predictions, with $p < 0.001$. The implications of this finding for life and environment on Earth will be discussed.

1. K.A. Artemenko, A.R. Zubarev, T.Yu. Samgina, A.T. Lebedev, M.M. Savitski, R.A. Zubarev // *Anal. Chem.* **81**, 3738–3745 (2009).

2. R.A. Zubarev, K.A. Artemenko, A.R. Zubarev, C. Mayrhofer, H. Yang, E.Y..M. // *Eur. J. Biol.* **5**, 190–196 (2010).

3. E.N. Trifonov // *J. Biomol. Struct. Dynamics*, **22**, 1–11 (2004).

4. R.A. Zubarev // *Genomics, Proteomics & Bioinformatics*, **9**, 15–20 (2011).

Chemical imaging and molecular analysis of atmospheric aerosols

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Fundamental understanding of the complex chemistry of atmospheric aerosols, its environmental impacts is a challenging task because no single method of analytical chemistry is capable of providing the full range of analytical chemistry information. Electron microscopy and micro-spectroscopy approaches can visualize individual particles and their internal structures; however, they largely exclude molecular-level information, and are limited to elemental and chemical bonding characterization. Contemporary methods of high resolution mass spectrometry can provide detailed information on the molecular content of organic aerosol, but these methods use bulk particle samples and provide no knowledge of the individual particle composition. Therefore, application of complementary analytical methods of chemical analysis is necessary for comprehensive characterization of aerosol properties ranging from bulk molecular composition of aerosol organic constituents to microscopy level details of individual particles. Combined assessment of the results provided by complementary analytical chemistry techniques offers unique insights to understand the composition and environmental chemistry of aerosols. This presentation will give an overview of our recent field and laboratory studies of atmospheric aerosols with an overall goal to understand fundamental relationship between composition of airborne particles and their environmental impacts.

A new approach for comparing quality of pharmaceuticals (originals and generics) based on registration of unknown impurities using GC/MS

I.A. Revelsky*, A.S. Samokhin, D.A. Chepelyansky, A.I. Revelsky

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Quality control of pharmaceutical products (containing the same active compound and manufactured by different companies) is very important task. It is well known that pharmaceuticals containing equal quantities of the active compound can have different side effects. It means that these effects are caused by impurities being present. The number of such impurities, their nature and content usually are not known. Common approach to quality control is based on the quantitation of small set of known (target) impurities.

We propose a new approach for comparing quality of pharmaceuticals. It is based on selective isolation of volatile and semi-volatile organic impurities from respective matrix of pharmaceutical product and GC/MS(EI) analysis of solvent-free entire concentrate. Use of capillary GC provides high efficient separation of components of complex mixtures. Identification of compounds is based on use of EI mass-spectra libraries. Usefulness of proposed approach will be demonstrated using different original pharmaceuticals and respective generics.

Acknowledgements

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The analysis of airborne chemical warfare agents using thermal desorption pre-concentration with GC/MS analysis employing novel chemometric software for data analysis

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The acute toxicity of chemical warfare agents (CWA) requires an air sampling and detection system which can identify trace levels of these compounds potentially in complex matrices. This is a requirement at both military installations where on-line near real time (NRT) analysis is typically required and more recently for civilian defence for pre-emptive monitoring at key locations.

Thermal desorption (TD) is an essential component of the analytical GC/GCMS system, providing sample pre-concentration for maximum compound sensitivity. TD technology will be described for both off-line pumped tube sampling and on-line analysis for near real time (NRT) data acquisition. Air monitoring within a mobile analytical laboratory will be discussed as an example of a real world sample employing a Markes International TD system (UNITY 2). Multiple levels of tube automation will be reviewed extending to grab sampling using automated canister technology.

For on-line NRT analysis a next generation high flow TD system is described containing two internal focusing cold traps working in tandem, i.e. one taking the air sample, the other injecting into the MS system. This overlap provides total air sampling continuously (i.e. 24-7) with no sampling blind spots. Markes TD technology cools the focussing cold trap/s electro thermally (i.e. no cryogen) using individual Peltier coolers. This enables sub ambient temperatures to be attained and when combined with high sample flow rates maximises CWA retention in the sorbent bed of each trap. Injection into the GC or GCMS for speciation and detection is achieved using either a splitless or split technique, the former working synergistically with the high flow sampling to provide the highest sensitivity.

Several CWA examples will be shown including the analysis and identification of GB in a complex gasoline matrix, HD (Mustard) in diesel, Lewisite1 and 11 and finally underivatized VX.

For CWA compound identification, a new GCMS based data mining software was employed. The software uses a chemometric approach to data analysis and incorporates a baseline noise suppression algorithm and spectral deconvolution. A user can select to identify either pre-determined (i.e. target) compounds from specific libraries imported from NIST, or the software can be configured to detect all compounds within the sample both target and unknowns.

A new software approach for the routine accurate mass screening of pesticides in environmental samples

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Summary

A new scientific information system has been developed to facilitate the routine use of LC/Tof for the environmental screening of pesticides and other contaminants by non MS experts. The sophisticated data filtering criteria are designed to minimise the number of false negative and false positive results. Application to real environmental samples is presented.

Abstract

With progresses in instrumentation, leading to major gains in sensitivity and linearity, it's now possible to use high resolution MS analysers, like TOF instruments, for food safety and environmental analysis. Regarding food safety, the SANCO Directive defines a screening detection limits as corresponding to a maximum false negative rate of 5 % and recommends a maximum false positive rate of 5 %. Although addressing the food safety methods, the SANCO guidelines are universally recognised as references in other application fields, including environment.

TOF-MS provides accurate mass full spectrum information, at an acquisition speed compatible with Ultra Performance LC. Recently a new scientific information system, which acquires and processes these complex UPLC-MS^E datasets for accurate and efficient pesticide identification and quantification, was introduced. This new system streamlines the workflow and utilises all the available data to ensure that all non-compliant samples are detected whilst minimising false positive results.

The LC/MS method was developed on an ACQUITY I-Class UPLC / XEVO G2-S Qtof from Waters operated in positive electrospray mode. Instrument control, MS data acquisition and processing were through the recently introduced software, UNIFI. All data were acquired in MS^E mode. In this mode, the collision cell switches very quickly from low collision energy for obtaining the molecular weight information of the compounds, to high collision energy, for the fragmentation information. This provides full unbiased, accurate mass information on both precursors and products in a single injection.

Data were searched against a subset of 479 LC-amenable pesticides extracted from the Scientific Library within UNIFI. Molecular formulae, fragment ions and retention times were included for identification and confirmation. The list of the compounds found in the sample based on the exact mass information was rationalized automatically by using the isotopic pattern, fragments and retention time. Further investigation for compounds that were not present in the library was undertaken using structural elucidation tools including elemental composition, isotopic pattern matching and halogen filtering.

**Gas chromatography coupled
to ultra-high resolution multireflecting TOF MS
for the analysis of persistent organic pollutants**

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Persistent Organic Pollutants (POPs) are halogenated organic compounds used for decades as different preparations - pesticides, flame retardants, and for the manufacture of a variety of commercial goods. This group includes, but is not limited to, polychlorinated dibenzop-dioxins (PCDDs), dibenzofurans (PCDFs), polychlorinated biphenyls (PCBs), and polybrominated diphenyl ethers (PBDEs). Unfortunately, these compounds bioaccumulate, and their unfavorable health and environmental effects have led to their regulation in many countries. Analysis of POPs in environmental or biological samples is challenging due to a wide range of concentrations in because of reduction in signal sensitivity and inadequate chromatographic baselines induced by major components in complex². In addition, analysis can be further complicated by POP decomposition products, metabolites or miscellaneous halogenated materials present in samples. Many of these interfering compounds produce similar mass spectral data and can be present in higher concentrations than targeted compounds. The development of instrumental techniques that can provide a high-speed but comprehensive analysis of environmental samples per time unit would significantly improve analysis of POPs.

In this study, PCBs and PCDDs were targeted in the analysis of sediment and fish tissue samples; however, several untargeted classes of POPs were discovered and characterized. Multireflecting TOF MS with Folded Flight Path™ (FFP™) technology provided the required resolving power (50,000 FWHM) for accurate mass measurements (< 1 ppm) and ROBUST molecular formula determinations.

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Organophosphorus and carbamate pesticides in waste and surface water

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Pesticides are frequently used mainly in agriculture for regulation of harmful organisms. In the Czech Republic, almost 400 approved compounds are contemporary used for this purpose [1]. Unfortunately, almost all chemicals show various adverse side effects to a greater or lesser extent. Occurrence and levels of these compounds are therefore carefully followed mainly in foodstuffs, but also in the environment.

This study was oriented on the occurrence of selected pesticides from the group of organophosphates (chlorpyrifos, diazinon, parathion, dimethoate, phosmet) and carbamates (carbofuran, aldicarb, methiocarb, pirimicarb, propamocarb) in the waste and surface water from the area of Brno city. Samples were collected at the inflow and outflow of the waste water cleaning plant (WWTP) Brno-Modřice (from April 18 to May 1, 2012) and from the receiving river Svatka approx. 1 km upstream and 500 m downstream the outlet from the WWTP (April 22, 2012). Target analytes were isolated by optimized method based on Solid Phase Extraction, gas chromatography with mass spectrometric detection (GC/MS) and comprehensive orthogonal two-dimensional gas chromatography with mass spectrometric detection (GCxGC-TOF MS) were used as final analytical methods.

The highest levels in raw waste water in the range of low $\mu\text{g.L}^{-1}$ were found for methiocarb. Propamocarb, dimethoate and phosmet level were below the limits of detection or they were detected exceptionally, other target compounds occur at the levels of hundreds ng.L^{-1} . The cleaning technology was found to be inefficient for methiocarb and pirimicarb, for other target compounds the removal efficiency was low (17 – 60 %), the highest value was found for chlorpyrifos (70 %). The comparison of target compounds levels in the samples collected upstream and downstream of the discharge point confirmed that the WWTP is important point source of pesticide contamination.

Acknowledgment

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Data and standards for greenhouse gas monitoring

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The commercial availability of a new generation of spectroscopic sensors has greatly reduced the barrier to routine field measurement of greenhouse gases and other atmospheric species. At the same time, a number of satellite missions are planned to measure greenhouse concentrations from space, using passive and laser-based spectroscopic techniques. These instruments have incredible precision (e.g. 0.05 $\mu\text{mol/mol}$, 95% confidence interval). However, the absolute accuracy of these measurements can be compromised if the spectroscopic constants used to calculate the analyte concentration from the spectroscopic measurement are poorly known; similarly, the precision of the measurement can be compromised if the uncertainty in the standards used in calibration are larger than the uncertainty of the instrument. The need for spectroscopic reference data and reference materials with low uncertainties is further increased by the demands for field measurements with extremely low uncertainties. For example, the World Metrological Organization has a data quality objective for measurements of methane of ± 1 nmol/mol, nominally $\pm 0.1\%$ of the present tropospheric concentration [1]. In another example, the Orbiting Carbon Observatory to be launched by the U.S. National Aeronautics and Space Administration in 2014 has an objective of measuring regional carbon dioxide concentrations with an uncertainty of ± 1 $\mu\text{mol/mol}$, nominally 0.25% of the present tropospheric concentration [2].

To meet these needs, the National Institute of Standards and Technology has a program to generate spectroscopic reference data and produce reference materials, linked to the International System of Unit (SI) and with uncertainties that will enable realization of field and satellite measurements with uncertainties significantly less than 1 %. The spectroscopic measurements are made using a unique cavity ring-down instrument. Key features of this instrument are its link to frequency standards, which allows for the measured signals to be modeled from first principles, and its link to thermodynamic standards, which allows for the number density of the gas under study to be accurately known. Spectroscopic line intensities measured using this instrument have uncertainties $\approx 0.3\%$. To generate reference materials, five new primary standard mixture suites, replicating dry air and containing several greenhouse gases (CO_2 , CH_4 , N_2O , CO , SF_6), have been gravimetrically prepared. These primary standards, in turn, have been used to certify the chemical composition real air samples collected at Baring Head, New Zealand and Niwot Ridge, Colorado USA as Standard Reference Materials[®], which will be sold to the public. The uncertainties associated with the concentration of the greenhouse gases in these reference materials meet or exceed the World Metrological Organization data quality objectives. Together, these standards and data should enable a new generation of greenhouse gas concentration measurements, with firm links to the SI.

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The condition of underground waters in the petrochemical enterprises influence zone

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Underground waters are the important component of the natural environment. They possess special "sensitivity" to anyone technogenic influences. In this connection underground hydrosphere as the most dynamical component of underground horizons, can play a role of the geological environment ecological condition indicator.

The research of underground waters condition has been executed in the area of Bashkortostan Republic Belaya river left coast, where petrochemical branch industrial objects are located. For a long time on this site of Belaya river, during the summer period, the intensive output of mineral oil in superficial waters is repeatedly observed. Underground waters pollution could occur owing to receipt of the polluted technological waters in them, seeping through couches of aeration zones, and also at hit of liquid mineral oil, forming congestions in underground horizons as a result of emergency outflow and passages.

The underground waters condition has been characterized by results of the water samples research selected from observant chinks. The maintenance of dissolved and cut mineral oils in water samples is defined by infra-red-spectroscopy method; identification of organic components, specific for petrochemical manufacture is led by gas chromatography mass spectrometry.

The received data have shown, that mineral oil concentration in underground waters was astable. In the investigated water samples there were revealed oil hydrocarbons, among which were found out alkanes, isoalkanes, cycloalkanes, aromatic hydrocarbons, sulfur and other organic connections. On a background of most frequently involved mineral oil concentrations (from $<0,05$ up to $1 \text{ mg} / \text{dm}^3$) in water of separate chinks concentration of mineral oil reached $6,8 \text{ mg} / \text{dm}^3$. In water samples there were found out components, specific for oil refining products, in particular, additives for gasolines. In some chinks on a water surface the presence of a hydrocarbonic layer has been fixed.

In chinks, located in limits and outside of the enterprises payable area, underground congestions of mineral oil and their migration have been revealed. The received results show the remote consequences of repeated hit of various mineral oils to underground horizons for many years. Lenses of mineral oil can be located and stay at underground horizons, or quickly move in sand-gravel layers at decrease of subsoil waters level.

Monitoring of the Moskvoretsky basin for heavy metal content

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The problem of environment protection is one of the most vital problems for humanity. Scientific and technical progress while improving life quality, at the same time causes a number of environmental problems associated with natural water pollution with toxic substances, particularly with heavy metals. Thus the increase of iron concentration in the environmental medium, especially in water, and its subsequent ingress to human organism, according to the International Agency for Research on Cancer, can cause DNA mutation and tumor growth. Excessive concentration of manganese in the human organism, first of all, has the impact on the functioning of the central nervous system. It is displayed in increased fatigability, sleepiness, deterioration of memory functions. Manganese is a polytropic poison that envenoms lungs, cardiovascular system, causes allergic and mutagenic effect. Therefore, the content of iron and manganese in water is strictly rated, and development of new, express and cost-effective methods of quantitative determination of these metals is important and practically significant.

The purpose of this study is to develop a new method for determination of content of iron and manganese in natural waters based on the studies of regularity in seasonal and temporal variations of such parameters as sediment concentration and colority, and determination of correlation of these parameters with the content of iron and manganese in water.

To solve the assigned tasks there were studied the locations of possible contamination sources. Also there was carried out systematic analysis of water quality for the last ten years in the Moskvoretsky basin at the reach of the Moskva river from the village Karinskoye to the township Rublyovo. Thus, by studying the patterns of seasonal and annual changes in the parameters of sediment concentration and colority, there was developed a new method for determining the concentration of iron and manganese in aqueous media. Based on the developed method there was proposed the technique for indirect determination of iron content according to the results of the analysis of sediment concentration and manganese content based on the results of the colority analysis using the correlation equations deducted during the study. The proposed method of environmental monitoring is a simple, fast and reliable method for indirect daily determination of iron and manganese content in the water of supply sources. This method increases the reliability of the whole system of natural water quality control, quicker identifying the source of possible contamination with heavy metals. This express-method allows to reduce the consumption of expensive reagents, reduces the cost of skilled labor, requires minimum testing time, and in case of implementation, will bring positive economic effect.

Retrospective detection and identification of chemical warfare markers of in environmental and biological monitoring

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The analytical chemistry of chemical warfare agents (CWA) still remains an urgent issue in view of the large amounts of land- and sea-dumped chemical weapons and threat of chemical terrorism. At the same time, with the progress of chemical demilitarization, increasing significance is being attached to the determination of CWA degradation products (CWA markers) in different media. In investigations of situations associated with the alleged possible use of and exposure to CWA, the first stage should involve detection and identification of CWA markers and the second, estimation of the quantities of the identified markers in the matrices in focus. The methodical basis of the first stage is screening, and the methodical basis of the second stage is formed by procedures for quantitative analysis adapted for specific matrices and compounds. The principal problem of toxicological screening is interpretation of the GC-MS chromatograms of complex mixtures including both target and background matrix components. Primary identification of components of complex mixtures, even in the case of their poor chromatographic separation, can be performed using the US NIST Automated Mass Spectral Deconvolution and Identification System (AMDIS) with on-on-line Analytical Database of the Organization for the Prohibition of Chemical Weapons (OPCW) containing mass spectra and retention indices of scheduled chemicals controlled under the Chemical Weapons Convention. However, in the monitoring of objects allegedly contacted with CWA, the range of target analytes is generally not exhausted by scheduled chemicals. Therefore, the on-line screening software package is also provided by small-scale databases containing reference information for analytes expected in the monitored objects. Screening of biological objects has become possible only recently with the accumulation of knowledge of the metabolism and pharmacokinetics of CWA, as well as development of new analytical technologies for bio-sample analysis. On the one hand, the determination of CWA markers in samples of the biological origin is an integral part of risk assessment of human health hazards in various objects. On the other hand, the determination of CWA degradation products in environmental and toxicological analysis has developed in two independent fields of research. Development of unified approaches to the environmental and biological monitoring of CWA markers is an urgent scientific and methodical task in the chemistry of highly toxic chemicals.

Application of GC-MS to determine composition of the low molecular weight polytetrafluoroethylene

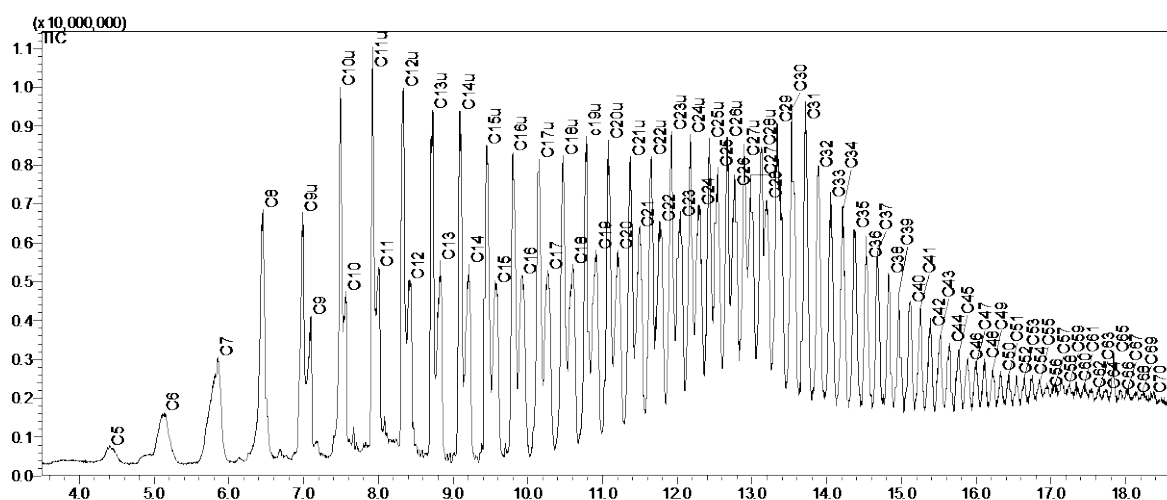
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The investigation of low molecular weight polytetrafluoroethylene (PTFE) with chromatographic methods is very difficult for its almost complete insolubility in all solvents. Only slowly evaporating it into pyrolyzer or multifunction injector Optic-3 you can inject the sample of PTFE in the chromatography column.

The composition of the different samples of PTFE was studied by the GC-MS method with the pyrolyzer and injector Optic-3. Fluoropolymers with the number of carbon atoms from 5 to 70 were identified on the chromatograms (Fig.1). There is a good separation of the saturated ("alkane") and unsaturated ("alkenes") PTFE peaks of fluoropolymers with the number of carbon atoms from 9 to 28 in the column like Ultra ALLOY-5. The first column goes "alkene" polytetrafluoroethylene, followed "alkane". "Alkane" and "alkene" peaks are badly divided for the fluorocarbons with the number of carbon atoms from 5 to 8 and from 29-70.



The electron impact mass spectra of the PTFE are similar in fragmentation to those of the hydrocarbons. There are two ion series of the saturated and unsaturated fluorocarbons in these mass spectra, like alkane and alkene series in the hydrocarbon mass spectra. It was found that most intense ion for the saturated fluoropolymers is the ion with m/z 69 and for unsaturated is the ion with m/z 131. "Alkane" series to include ions with m/z 69, 119, 169, 219 and etc. increasing on the mass of CF_2 equal 50. "Alkene" row begins with m/z 131 and then with the increase m/z 50.

It was found that the molecular weight distribution of fluoropolymers in the samples of PTFE depends on the conditions of their production.

Absence of spectral skew, high-speed acquisition, automatic peak finding and mass spectra purification as key aspects of non-target GC/MS analysis

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Today target GC/MS (or LC/MS) analysis is one of the most popular approaches used in environmental chemistry. Presence of a priori information about analytes simplifies significantly analysis of complex samples. For example, in this case multiple reaction monitoring can be used to eliminate chemical background and increase sensitivity (however information about all non-target analytes will be totally lost).

Detection and identification of non-target analytes is much more complex task (in comparison with confirmation and quantitation of target compounds). It can be explained by absence of a priori information about retention times, unique m/z values, the number and concentration of components, possible interferences and etc. The most quick and easy approach which can be used for tentative identification of totally unknown compounds is library search against electron ionization mass spectral databases. Success of library search depends greatly on quality of purified mass spectra. Use of time-of-flight mass spectrometers allows high-speed registration of unbiased mass spectra across chromatographic peak. The more points are registered per chromatographic peak, the easier it is found difference between peak shapes corresponding to different components. Moreover absence of spectral skew enhances opportunities of automatic data processing algorithms.

Advantages and disadvantages of quadrupole, ion trap and time-of-flight mass spectrometers will be discussed (in the context of non-target GC/MS analysis). Possibilities of automatic data processing will be demonstrated on the example of analysis of several environmental samples.

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New environmental developments in reference mass spectral libraries

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Chemical compounds have been commonly identified by searching reference mass spectral libraries. New libraries and new enhancements in current ones are requisite for identification of emerging pollutants and more reliable recognition of common ones when new methods/techniques are developed. In our research, three kinds of innovations have been implemented:

1. New libraries/sublibraries of tandem mass spectra (MS^2) for some group of environmental contaminants.
2. New type library of MS^2 spectra.
3. Replenishment of the MS^1 spectral library for identification of supermolecular objects, i.e. qualitative analysis II.

First, new libraries of tandem mass spectra of (a) pesticides and (b) microcystins were developed. All the spectra were extracted from the literature and Internet. The first data set was built from 1723 $MS^{>1}$ spectra of 490 pesticides. Testing of the library showed that the percentage of 1st rank correct identifications (true positive rate, TPR) was 80-94 %. There were 75 spectra of 28 compounds entered in the second library. Here TPR reached the value of 73-83 %. It is concluded that MS^2 spectral libraries generated from the numerous literature/Internet sources and used in H(U)PLC-ESI- MS^n technique, are not less efficient for the goal of identification of unknown compounds than very common EI- MS^1 libraries (TPR \leq 79 %).

Second, considering that MALDI mass spectrometry is a principal analytical technique for different analyte groups, the new type reference library was proposed, with mass spectra obtained by means of the recently commercialized technique of MALDI LIFT-TOF/TOF. Such product-ion spectra are suitable for prompt and reliable characterization/identification of fullerene derivatives in environmental analysis. In the presentation, LIFT-TOF/TOF spectra of fullerenes are briefly considered and discussed.

Third, the new development refers to the database replenishment of reference MALDI spectra of bacteria. Those are essentially protein fingerprints characteristic for different species and genera. Spectra of some microorganisms, e.g. cholera vibrio, may be not available in the commercial mass spectral database. Their reference MALDI spectra were specially acquired for strains isolated from environmental water and cultivated in vitro.

Developments of databases considered in the presentation have enlarged the scope of environmental applications of mass spectrometry.

GC-MS study of Moscow snow samples in 2011 and 2012

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Moscow is one of the biggest cities in the world with population over 10 million people. It's also a big industrial center. Thousands of different chemical substances are emitted to the atmosphere daily, because of work of industrial factories, transport, 20 Thermoelectric plants (TEP), construction works etc. Official state ecological laboratories are regularly monitoring only inorganic gases (CO, CO₂, NO_x, SO_x), dust, vanadium pentoxide, benzene, toluene, ethylbenzene, xylenes, phenol, formaldehyde, benz(a)pyrene. And nevertheless there is no list of priority pollutants in Moscow. Therefore, basing on the analysis of snow we tried to estimate the pollution of atmosphere in winter and to make up a list of priority pollutants for Moscow.

Snow was chosen as an excellent preserving matrix allowing keeping the majority of chemical compounds including not very stable ones. Besides it allows estimating long term atmospheric pollution in winter time and carrying out easy sample preparation. Sixteen snow samples were collected along the perimeter of the Moscow belt road in March 2011 and 2012. The samples were analyzed using GS-MS and ICP-MS as analytical tools to identify the qualitative and quantitative composition of organic and inorganic ecotoxins. Sample preparation was carried out according to US EPA 8270 method. The results have shown more than 500 individual compounds in each sample, of which about 25 semi volatile priority pollutants (US EPA list), 75 saturated hydrocarbons, 19 polychlorinated biphenyls, 24 phthalates, 16 PAHs, 48 alkylated aromatic hydrocarbons, 30 organochlorines, 12 phenols, and other different sulphur and nitrogen substances. As far as this research is a continuation of our work in 2011, besides compounds that were identified in both years (2011, 2012), some of them we referred as compounds of special interest (benzonitrile, chloriodomethane, dichloronitromethane, bromobenzene, 2-fluoro-methylbenzoate, 2-fluoro-9-fluorenone, 2-phenylbenzothiazol, 2-bromo-5-methylpyridine, hexahydrotriazine, benzothiazole, 1,1,2,2-tetrachloroethane). Considering the metal pollution the highest concentrations were for aluminium, copper, vanadium and zinc.

All the samples were also studied with 12T FT ICR instrument (Bruker) in positive ion ESI mode. The data were evaluated using Bruker software and homemade program. Van Krevelen diagrams were reconstructed. For all the samples CHOS containing molecules dominated over other compounds.

As a result a list of candidates for the priority list pollutants in Moscow air was proposed. It contains petroleum hydrocarbons, benz[a]pyrene, dibutylphthalate, polychlorinated biphenyls, 1,1,2,2-tetrachloroethane, copper, zinc, vanadium, aluminium.

Surface analysis by direct analysis in real time mass spectrometry employing plasma glow visualization

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Precise monitoring of the gas stream from the Direct Analysis in Real Time (DART) ionization source during analysis, based on the use of the colored light from the metastable gas plasma glow, is suggested for the first time. When pure helium was used for DART ionization, a violet light spot on the target surface was seen in the darkness. If 10% of neon was added to helium, the light turned red and became much brighter. However, the usefulness of a helium-neon mixture for DART mass spectrometry (DART-MS) was limited due to a more complex mass spectra composition and mostly accompanied by a reduced detectability of analytes, if compared to helium DART-MS.

Using plasma glow visualization, it is possible to track metastable gas distributions during surface scanning and to document them by video recording. Such visualization is highly convenient for choosing the optimal coordinates for DART-MS analysis and will support scanning and imaging MS of surfaces. The efficiency of analyte desorption from a porous silica gel layer and its ionization was estimated as low. The detectability was reduced if compared to comparable amounts on glass tips or slides due to deep analyte penetration and/or metastable gas scattering after its collision with the surface analyzed. The spatial resolution was significantly reduced using a modified DART cap, but impacted by the decrease in sensitivity. Also the significant influence of the Vapur vacuum pumping speed on the mass spectra composition was demonstrated.

Further optimization of the DART-MS setup is required, which will be eased by employing the developed approach for plasma glow visualization, providing precise monitoring of the metastable gas distribution on surfaces and their scattering.

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The benefits of accurate mass measurements in GC/MS analysis of environmental samples

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The most widespread standard analytical procedures for the quantification of priority pollutants are based on the low resolution mass spectrometry methods. However, accurate mass measurements allowing establishing the elemental composition of analytes make the overall analysis much more reliable. High resolution mass spectrometry becomes almost compulsory for LC/MS, when just a molecular ion or few fragment ions (MS/MS) are taken into account. Nevertheless accurate mass measurements greatly benefit target analysis, significantly reducing the probability of false positives and improving detection limits due to better S/N ratio; non target analysis with the use of spectral libraries; and manual structural elucidation in GC/MS studies, providing elemental composition for all the ions in mass spectra. In a snow sample (very simple matrix) the presence at least 12 ions with the same integer mass 252 (primary ion for the detection of benz[a]pyrene), but different exact mass was confirmed. Taking into account the possibility that several isomeric compounds produce each of the ions with exact mass (elemental composition) one can expect about a hundred of interfering ingredients in the sample. Without HRMS the chances to get false positive result may be rather high. Probability of false positives increases with the increase of the matrix complexity as the chances of the presence of a compound with close to the target analyte retention time and containing an ion with the same nominal mass in its electron ionization spectrum becomes higher.

More than 20% of the overall number of tentative identifications based on the score provided by NIST11 library search based on the low resolution mass spectra (Pegasus IVD instrument, LECO) was corrected using accurate mass data during analysis of environmental pollutants in the snow samples collected in Moscow. HRMS approach was carried out with Pegasus GC-HRT instrument (LECO, USA). Correct hits were in the hit list created by NIST11 library in many cases, however far from the top at positions which usually are not taken into account. Manual interpretation also benefits greatly when operating with accurate masses. Several compounds were identified using the fragmentation rules for the organic compounds in electron ionization conditions and accurate mass measurements. Recording of full mass spectrum allows revealing an unlimited number of compounds in the sample. Besides that the data remain available and retrospective analysis is always possible without the need to reinject the sample.

Analysis of liquid samples without a sample preparation: 'pros' and 'contras' of different DART-MS-based approaches

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Direct Analysis in Real Time mass spectrometry (DART-MS) allows eliminating or reducing the sample preparation prior to MS analysis. In first DART sources the gas flow was directed horizontally and the sample introduction was not automated, which caused poor reproducibility of DART data [1]. In a novel DART source varying the angle of gas towards the analyzed sample has been introduced, providing the access to surfaces [2,3]. The DART-based ID-CUBE source is a cost-saving solution for analyzing liquids [4]. In this study, the general capabilities of DART-MS for analysis of liquids were investigated using three different DART-MS-based approaches, including analysis of:

- Liquids on glass sticks in a horizontal flow of gas from DART source;
- Liquids as dried spots on glass surfaces utilizing the angle for DART-MS;
- Liquids as dried spots on a metal grid.

Direct analysis of liquids, applied on tips of glass sticks, lacks detectability due to small amounts of liquid retained on tips (< 1 µL). Analysis of dried residues on a glass surface allows the simple preliminary concentration by applying a sample several times onto a glass carrier and letting it dry. Due to such preliminary concentration it is possible to increase the amount of analyte to be analyzed by two or even more orders of magnitude. Besides, storage and transportation of liquid samples in the state of dried residues is beneficial for many application fields. However, when the detection by DART-MS from flat surfaces is performed, the part of analyte ions is not reaching the mass analyzer due to losses in the environment after reflecting from surface. By the application of liquid samples on a metal grid and their further analysis by DART-MS with a horizontal gas flow the advantages of both approaches are combined without limitations regarding the sample volume. This allows concentrating the analytes from liquid samples on a grid in a simple and convenient way and analyzing them using an optimal DART configuration. Such enhancement of DART-MS capabilities in trace analysis is important for its prospects as a method of choice for an ultrafast environmental analysis and other fields of chemical analysis.

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Application of modern analytical method for assessing the environmental impacts of deicing agents on the environment

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In struggle the winter slipperiness on road facilities widely spread chemical method based on use of deicing reagents (DR) for the melting of snow and ice. These agents are either individual chemical compounds (NaCl; CaCl₂; MgCl₂, etc) or multicomponent mixtures based on them. Adding objects of DR leads to the inevitable contamination of the environment to the basic components and impurities contained in the DR.

In this connection required of analytical methods to control DR, providing high sensitivity of detection of limited impurities.

Currently for multicomponent analysis of various objects in "IREA" of atomic spectrometry techniques are used - atomic emission spectrometry (AES) and mass spectrometry (MS), using inductively coupled plasma as the source of excitation or ionization. With its high performance in sensitivity, accuracy, reproducibility, both methods have a number of limitations related to the effect of matrix composition on of the test results. In AES it is due to the superposition of interfering spectral lines on the analytical lines of elements determined, and in MS - the influence of polyatomic ions with the matrix element on the analytical peaks.

This requires adapting those methods for analyzing such samples as the DR. In the development of analytical methods for the determination of limited DR environmental contaminants (Hg, As, Co, Cd, Ni, Cr, Se, Zn, Ni, Cu, Pb, Mo) in "IREA" realized complex of studies influence of major components (Na, Ca, Mg) concentration on the intensity of the analytical peaks. On this basis the optimal conditions for measurement, methods of accounting matrix and spectral effects, scheme calibration have been chosen.

It is shown that both methods of analysis allow realize simultaneous multi-element determination of limited trace elements. The detection limits for various elements lay in the range 0.01 - 0.001 mg / kg (mg/dm³) in solid or liquid samples. Analysis of results for content of impurities in the DR purchased for capital megapolis shows that these impurities are almost not create additional environmental burden on the environment. The environmental influence afford key components DR - NaCl, CaCl₂, etc.

Electrophoretic and chromatographic separations of bioactive compounds using hyperbranched polymer PEI-Mal as an additives in mobile and stationary phases

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In recent years there has been an increased interest in new class of polymers: dendritic macromolecules and hyperbranched polymers. These unusual properties have made the dendritic polymers the focus of intensive research of their application in chromatographic and electrophoretic methods to identify diagnostic markers of various diseases in body fluids and toxic substances in the environment.

Also these materials have shown promising results in a few of test separations in CE and HPLC.

In our study we have investigated the potential of using of new hyperbranched polymers (hbp) polyethylenimins, functionalized with maltose (PEI-Mal), with different molecular weights (5 and 25 kDa) and degree of modification with maltose, as a components of the mobile or stationary phases in electrophoretic and chromatographic separation of bioactive substances (steroids, vitamins, proteins). Electrophoretic and chromatographic methods may, moreover, be convenient methods of studying the interaction of dendrimers with bio-active analytes of different nature.

We have obtained that these polymers can modify the separation selectivity of small (vitamins) and large (peptides, proteins) molecules, mask the silanol groups at a low pH, eliminate analyte-wall interactions, as a consequence of forming the dynamic coating. The last fact is very important in the separation of positively charged compounds, such as basic proteins.

PEI-Mals have been shown to be potential pseudo-stationary phases for electrokinetic chromatography. They have been also successfully employed as dynamically and covalently bonded capillary coating in the determination of proteins. In this case it was realized a capillary electrochromatography. It has provided higher efficiency (600000 t.p./m) and improve in the selectivity and reproducibility. Using PEI-Mals as a bonded stationary phase have shown that the sensitivity of proteins can be significantly improved due to presence of *on-line* concentration of the sample zone in acidic buffer. The best results were achieved with coupling of sample stacking with electrokinetic injection (FESI) and LVSS.

We have also investigated HBPs PEI-Mal affect on retention parameters of water- and oil-soluble vitamins in thin-layer chromatography (HPTLC), as an additives to the mobile phase and as a coating material, compared to traditional surfactants (cationic CTAB) and cyclodextrines.

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Quantification of estrogens in nine WWTPs of Portugal, using SPE-HPLC

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Determination of natural and synthetic estrogens in Waste Water Treatment Plants (WWTP) is fundamental for risk assessment regarding the endocrine disrupting effects in the aquatic environment. A methodology of analysis based on HPLC procedure with UV detection and a C18 [1-3] column has been developed for the simultaneous determination of estrogens in water samples in less than 9 minutes. The estrogens analysed were estrone, 17 β -estradiol, 17 α -ethinylestradiol and estriol. A pre-concentration of the analytes in water samples, was achieved using a SPE procedure with polymeric Strata-X cartridges. The use of SPE-HPLC method allows limits of detection of 0.089 $\mu\text{g L}^{-1}$ for estrone, 0.25 $\mu\text{g L}^{-1}$ for estradiol, 0.45 $\mu\text{g L}^{-1}$ for estriol and 0.11 $\mu\text{g L}^{-1}$ for ethinylestradiol. Samples collected from nine WWTPs inputs and outputs located at the Portugal Central Region, were analyzed and the concentrations obtained were in the range of 0.15-0.72 $\mu\text{g L}^{-1}$ for estrone, 0.10-0.51 $\mu\text{g L}^{-1}$ for estradiol, and 0.11-0.23 $\mu\text{g L}^{-1}$ for ethinylestradiol.

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The quality status of surface water in Novi Sad municipality estimated on the presence of WFD and emerging substances

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Novi Sad, Serbia's second largest city is the capital of the northern Serbian province of Vojvodina and the administrative centre of the South Bačka District with an urban population of 286,157, while its municipal population is 372,999. The city is located in the southern part of the Pannonian Plain on the banks of the Danube, while facing the northern slopes of Fruška Gora mountain. Novi Sad's drinking water is derived from the Danube River either directly or by using several groundwater aquifers. In the first case, the drinking water abstraction point is located only several hundred meters downstream of the municipality waste disposal point. Besides the potential influence of the quality of the Danube River water on groundwaters, both water sources are endangered by different forms of land-use in the backland, such as agricultural lands, drainage canal systems and industrial sites. Perhaps the most significant potential pollution sources on Ratno ostrvo are the Novi Sad Oil Refinery and the TE-TO heating & power plant, located only several hundred metres from the nearest water supply wells. Also, general agricultural production in the backland can not be neglected since it is widespread, especially in the backland zone where an alternative groundwater source of regional significance is planned. On the right river bank, the "Petrovardinska ada" source is directly endangered by illegal settlement (with septic tanks) and dump sites, unauthorised traffic and an old industrial complex in the vicinity. Unfortunately, the City of Novi Sad has joint collector for both industrial and municipal wastewater, directly discharged into Danube. Therefore, it is extremely useful to recognize the source of wastewater by the specific chemical and biological pollutants. The aim of this work was determine presence and concentration of environmental pollutants that are included in Water Framework Directive, Drinking Water Directive and Norman list of emerging pollutants.

Danube surface water has been sampled 100m downstream of each waste water discharge in order to assess the impact of wastewater streams on ecotoxicological status of the river. The sampling site located upstream of the city of Novi Sad, before all discharge points has been selected in order to assess the ecotoxicological status of the river Danube prior to any local urban impact. A totally, 86 organic and inorganic compounds have been selected for target analysis. Depending on the type of contaminant, GC-MS, HPLC-DAD, AAS or electrochemical analyser were used to determine concentration of selected pollutants. Among 69 organic compounds selected for target analysis, 29 were found in concentrations above limit of detection (LOD), while fluorene, phenanthrene, anthracene, fluoranthene, four of 8 EPA PCBs congeners (153, 138, 180 and 194), Di-(ethylhexyl)-phthalate, dibutyl phthalate, diethyl phthalate, bezothiazol, organochlorine pesticides (p,p'-DDD, p,p'-DDE, p,p'-DDT, Endosulfan alpha, Endosulfan beta), pentachlorobenzene, trifluralin, hexachlorocyclohexane gamma, hexachlorocyclohexane delta and hexachlorobenzene were found in concentrations higher than environmental quality limits.

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DDT and other traditional chlorinated pollutants: continuing environmental threat in the Czech Republic

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Organochlorine compounds have been produced in large scale and widely used in many applications. Due to their negative influence on various environmental compartments, which was often discovered after long time of their usage, they are often subjects of various environmental studies. Our study focused attention to DDT and its metabolites and to polychlorinated biphenyls, which could be classified as “traditional” persistent organic pollutants. DDT use was abandoned in the Czech Republic in 1974 (with exception for DDT on stocks, which could be used until complete consumption) [1]. Polychlorinated biphenyls have been produced in former Czechoslovakia from 1959 to 1984 with maximum values within the period of 1977 – 1983 [2].

The river Jevišovka and its close neighbourhood were selected as model locality. This small river springs in the south-eastern part of the Czech-Moravian Highlands in the altitude of 556.71 m and flows mainly in the south-eastern direction. After 81.72 km it flows into the Dyje River in the altitude of 175.46 m with an average flow of $1.35 \text{ m}^3 \cdot \text{s}^{-1}$. The river flows partly through protected area (Jevišovka Natural Park), partly through agricultural area, without any important industrial production. Sediment samples were taken along the river flow in nine places. Soil samples were taken from the agricultural fields close to the sediment sampling place. Pressurized solvent extraction was used for the extraction of target compound. The extracts were purified by the column chromatography on silica and analysed by gas chromatography on two parallel capillary columns of different polarity with electron capture detection. PCBs were found in low concentrations; but relatively high levels of DDT and its metabolites reaching the value of $500 \text{ ng} \cdot \text{g}^{-1}$ in soil and $200 \text{ ng} \cdot \text{g}^{-1}$ in sediment were found and at the upper reaches of the Jevišovka river. The levels of other organochlorine pesticides (HCB, β -HCH, aldrin, dieldrin) were also found to be significant.

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Analysis of drilling fluid additives by pyrolysis- GC-MS with regard to their application as environmental marker

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Drilling fluids are important additives for exploration and production drilling in terrestrial and marine environments. Their usage is not a strictly closed system application, hence continuously emission of drilling fluids towards ecosystems are evident. For example, drilling cuttings as byproducts contain significant amounts of such additives and in average 25% of drilling cuttings are released during off-shore drilling. Accordingly, loss of associated drilling fluids is obvious. Further on, drilling fluids are contaminants of drilling waste, which has to be handled and cleaned. Leakages, accidents and careless handling of drilling waste might also lead to drilling fluid emissions.

To follow these emissions and to estimate the level of contamination a chemical characterisation is fundamental. Drilling fluids consist of different ingredients including inorganic and organic substances. However, many of the ingredients, in particular inorganic constituents, are not source specific (e.g. bentonite) and, therefore, cannot act as emission marker. With respect to organic substances, the dominant ingredients are technical polymers, which exhibit a high structural significance. Hence, they can be used as drilling fluid indicators in principal, but appropriate analytical methods are needed. In particular due to the low concentration in environmental systems, analytical approaches for a successful detection are still missing.

Pyrolysis-gas chromatography-mass spectrometry (Py-GC-MS) is an appropriate analytical tool to characterise and, probably, determine quantitatively organic macromolecules. Pre-conditions are the principal possibility to pyrolyse the polymers and to obtain specific pyrolytic products. Examples are reported for polyvinylpyrrolidone [1] and chemical modified polyacrylamides [2].

In the study we performed Py-GC-MS analyses of different technical formulations of drilling fluids in order to identify specific products. The polymers used in the investigated formulations are dominantly based on chemically modified cellulose (carboxymethylcellulose). Hence, first steps of our work were related to optimization pyrolysis conditions and optimum parameters concerning temperature and time have been obtained. Further on, online derivatisation by TMAH has been proven as useful tool for a more comprehensive detection of pyrolysis products.

As the most important step, the results of the pyrolysis analyses are discussed in terms of polymer specificity and probability to act as marker for following drilling fluid contamination in influenced water or solid particles. Correlation of polymer structure with the low molecular products revealed some interesting candidates with carbohydrate backbone.

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Determination of methylmercury muscle and skin of *Leuciscus cephalus*

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Mercury is a hazardous element that can be found in all components of ecosystem. It is considered to be a global pollutant of the environment [1]. Mercury represents one of the most toxic substances present in the environment and biota, because of its accumulation and persistent character [2]. The behavior of mercury in the environment depends on its chemical form and on the environment in which it is located [5]. Methylmercury is considered to be most toxic form of mercury that is produced by biomethylation or abiotic methylation of inorganic forms of mercury by some bacteria living in sediments [4]. The content of total mercury and methylmercury in aquatic organisms increases with the trophic level of the food pyramid. Fish belong to the group of bioindicating organisms and accumulate mercury compounds from the aquatic environment. [3].

Methylmercury was determined in the muscle and skin of twenty fishes (species *Leuciscus cephalus*). The sampling site was the confluence of the Svratka and Svitava rivers and the location near Rajhradice village. Wastewater treatment plant is situated between these catching places. For the determination of methylmercury, the method involves extraction of analyte, extract purification and determination by gas chromatography (Hewlett Packard 6890 Series) with electron capture detektor (^{63}Ni). The capillary column DB 17 (30 m, 250 μm I.D., 0,25 μm film) was used. The same protocol was used in order to prepare extracts of muscle and skin. Validation of the method was performed using the Certified Reference Material - tuna fish.

Before WWTP was measured 124.25 to 255.32 $\mu\text{g.kg}^{-1}$ MeHg in muscle and 34.18 to 103.98 $\mu\text{g.kg}^{-1}$ in the skin. Behind WWTP was measured 59.74 to 183.50 $\mu\text{g.kg}^{-1}$ MeHg in muscle and 13,62 to 76,88 $\mu\text{g.kg}^{-1}$ in the skin. Commission regulation (EU) No 420/2011 setting maximum levels for certain contaminants in foodstuffs indicates max limit mercury 0.50 mg.kg^{-1} fresh weight fish. The obtained results do not exceed this value.

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Isolation and characterization of bacteria from spent nuclear fuel pools in Slovakia

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This work is focused on a characterization of bacterial contamination in pool water of the Interim spent nuclear fuel storage (ISFS, JAVYS Inc.) in Slovakia. The ISFS consists of 4 interconnecting pools: 3 fuel storage pools and 1 reserve pool built from austenitic steel and permanently filled with deionized water (Fig 1). The mean specific radioactivity of pool water for β emitters was 3.9×10^5 Bq/L, for γ emitters 3.7×10^5 Bq/m³. Tritium participated by the activity 1.3×10^5 Bq/m³ and contribution of radionuclides increased in the order: $^{60}\text{Co} < ^{134}\text{Cs} < ^3\text{H} < ^{137}\text{Cs}$. From the microbiological point of view, water represents oligotrophic environment which enables the growth of mesophilic bacteria, where chronic radiation exerts selective pressure, altering both the diversity and abundance of bacteria.

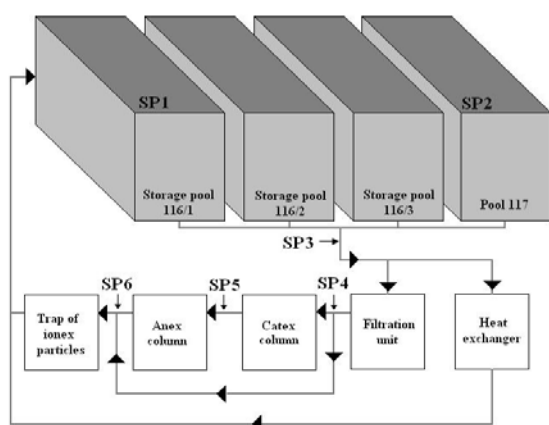


Fig. 1. Circulation system of water in storage pools at ISFS.

Bacterial content in pool waters is kept on very low level by extremely low concentration of solutes in deionized water and by both the efficient water and air filtration systems. During the last three years of monitoring, bacterial densities in the water samples from the surface of pools (SP1, 2) were within the range from 50 to 4 525 CFU/L. Viable counts in the water from the bottom of the pool SP 3 and SP4 to SP6 fluctuated between 100 and 5 500 CFU/L, although noticeable higher values were observed in August and October 2011. Observed higher values up to 55 000 CFU/L can be caused by manipulation procedures such as filling the new fuel assemblies or manipulation in filtration units. Analysis of 16S rDNA indicated that four bacterial cultures identified as *Kocuria palustris*, *Micrococcus luteus*, *Ochrobactrum* spp. and *Pseudomonas aeruginosa* are dominant in ISFS.

In laboratory experiments, the bioaccumulation of ^{137}Cs and ^{60}Co by isolated bacteria were also studied. The maximum uptake of Cs^+ after 48 h cultivation reached 7.54 ± 0.48 $\mu\text{mol/g dw.}$ (*Ochrobactrum* spp.), 19.6 ± 0.1 $\mu\text{mol/g dw.}$ (*M. luteus*) and 20.1 ± 2.2 $\mu\text{mol/g dw.}$ (*K. palustris*). The maximum uptake of Co^{2+} reached 31.1 ± 3.5 $\mu\text{mol/g dw.}$ (*Ochrobactrum* spp.), 86.6 ± 12.2 $\mu\text{mol/g dw.}$ (*M. luteus*) and 16.9 ± 1.2 $\mu\text{mol/g dw.}$ (*K. palustris*).

Isolated bacteria effectively accumulate both ^{137}Cs and ^{60}Co under growth conditions indicating that these bacteria affect the fate of radionuclides in pool water. Presented results should serve as contribution to the microbial safety of wet nuclear waste storage facilities.

The pollutant tracing in Danube river in Novi Sad

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Novi Sad municipality faces a specific problem, deriving drinking water either from the Danube River or from several groundwater reservoirs. In the Danube River, the drinking water abstraction point is located only several hundred meters downstream of the municipality's waste disposal point. Additionally, several groundwater abstraction points are used; however, all of them are located under densely populated urban areas, and one of them is located in the proximity of the oil refinery. During the previous period in Novi Sad municipality no detailed monitoring programme for the screening of emerging substances in surface water in Novi Sad municipality was performed. At present, the available information about pollution of water used for abstraction of drinking water in Novi Sad municipality are insufficient for monitoring and risk management for the protection of inhabitants. Screening approaches are either not used at all or very scarcely and most of monitoring is limited to the selected physical chemical parameters and target compounds. The aim of this work was to gather detailed information about organic contaminants present in the raw water used for drinking water production at Novi Sad.

Sampling of eight individual 1L water samples for the screening analysis was performed either directly from the collectors of sewage discharges *Cepelin*, *Beogradski kej*, *Ratno ostrvo* and *Rokov potok*, or samples of surface water from Danube River were taken at least 100 meters downstream of the each discharge. Characterisation of possible contaminants was performed by gas chromatography coupled to mass spectrometry. Organic compounds were extracted by liquid-liquid extraction and stir bar sorptive extraction. The GC analysis was performed using Agilent 7890 gas chromatograph coupled to Agilent 5975 mass spectrometric detector. The system was equipped with PTV injector system. Helium was used as carrier gas. The MSD was used in the SCAN mode for all samples.

Phthalates, PAHs, terpenes and fatty acids belong to the most frequently occurring compounds in wastewater and Danube surface water in the vicinity of Novi Sad. Phthalates are commonly used as plasticizers, industrial and lubricating oils, defoaming agents, cosmetics and insect repellents. Dibutyl phthalate, diethyl phthalate and dioctyl phthalate that are already on the NORMAN list of emerging substances, as well as di(2-ethylhexyl) phthalate that is on the priority substances list of WFD, were detected in all water samples, which confirmed their ubiquitous presence. The sources of the detected fatty acids in the aquatic environment are mainly from degradation processes of petroleum hydrocarbons or animal and vegetable fats. Special groups detected in all waste and river water samples are terpenes like nerol, citronellol, menthol, ionone and other compounds like camphor, ethyl citrate or methyljasmonate that could occur in cosmetics, care products, and home cleaning products. Wide variety of hormones, derivatives of benzene and polycyclic aromatic hydrocarbons (PAHs) were detected in water samples.

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Malachite green in suspended particulate matter and surface sediments in Germany

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Malachite green (see figure 1) is applied as an antibiotic agent against parasites and fungi in ornamental pisciculture, and not allowed to be applied by EU law in commercial fish farming (Council Regulation **2377/90/EC**). Due to the cheap costs it is utilized in China and Taiwan in aquaculture. The application is realized as salt (oxalate or chloride) with a water solubility of 40g/L (25°C) and has a low particle reactive sorption ($\log K_{ow} = 0.62$).

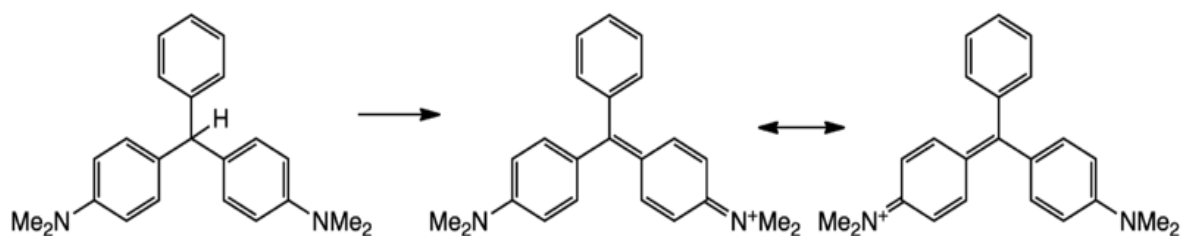


Figure 1: Structure formula of leukomalachite green (left) and malachite green cation

Within the Environmental Specimen Bank Germany (ESB), SPM samples are taken on a monthly basis by means of sedimentation boxes and yearly homogenates are created. The sampling locations of the ESB are carefully selected to represent different ecosystems and not to be influenced by local sources.

Fish analysis of samples from the ESB and of the Berlin area in 2007 revealed in specimens of the ESB and in eel from the Berlin area partially elevated concentrations of up to 0.765 $\mu\text{g MG/kg d.w.}$ in samples from the Teltow Canal (Berlin). These sampling locations are influenced by effluents of sewage treatment plants. For comparing the level of contamination with particulate samples from the same regions in 2011 sediment cores from the Berlin area and SPM samples from the ESB of 2007 and 2010 were analyzed for MG and the reduction product LMG.

SPM and sediments are collected with liner coring for sediments. For the analysis of MG and LMG the freeze-dried particulate matter was extracted with acetonitrile and hydroxylamine followed by detection via LC-MS/MS in ESI+ mode with deuterated (D5) standards.

No LMG was detected in any sample beside anoxic conditions in the first mm of the sediment cores. In the samples from the ESB remarkable increases between 2007 and 2010 are depicted, even at sampling locations with no detection in 2007. Only a few samples from the Berlin area (1-2 years in maximum old) illustrate a low level of contamination, in accordance with the fish analysis.

Generally, the origin and fate of MG in sewage treatment plants and in aquatic ecosystems is not yet elucidated. A more detailed study is warranted about the formation and the reaction kinetics of MG to LMG, the sources and fate in aquatic ecosystems and a survey of different water bodies like the Danube and other European Rivers would enhance the data base.

Assessment of the level of contamination by PCB and PBDE in aquatic ecosystem of the South Moravian region

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The present paper deals with the evaluation of the level of contamination by persistent organic pollutants (POPs) in aquatic ecosystem. The study is focused on selected watercourses of the South Moravian region.

Polychlorinated biphenyls (PCBs) and polybrominated diphenyl ethers (PBDEs), which are still included in the group of priority pollutants, were selected as monitored contaminants. The monitoring of PBDEs has recently been extended because many everyday products include commercial mixtures that contain these organic pollutants. PCBs are frequently and commonly detected organohalogen pollutants under the secondary contamination. The most negative impact of these substances on the environment is their high toxicity and persistence. These contaminants are also characterized by a high level of accumulation in biological systems [1,2].

Selected analytes were monitored in matrices that are suitable tools for the assessment of pollution in aquatic ecosystem. Water and water plants were chosen as appropriate matrices. A method of solid-phase extraction (SPE) was used for isolation of PCBs and PBDEs from these abiotic and biotic matrices, also the solid-phase microextraction (SPME) was used for the water.

The first step of this study was to optimize these methods performed on model samples. Basic metrological parameters of selected methods were determined by using analysis of model samples. After that these optimized methods were used to determine monitored analytes in real samples. Analysis of real samples also included preanalytical sample treatment consisting of extract purification and concentration, followed by an identification and quantification of selected analytes by gas chromatography with electron capture detector, for the confirmation with mass spectrometer detector.

The results obtained by optimization were used to assess the validity of these methods. The results obtained from the analysis of real samples were used to assess the level of contamination by organohalogenic pollutants in selected localities of South Moravian region.

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Problems of simultaneous preconcentration of platinum group metals by solid phase extraction and their determination by inductively coupled plasma mass spectrometry

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The problems of determination of platinum group metals (PGMs) in environmental samples is very topical because of the concentration of PGMs in the environment currently constantly increasing as a result of increasing intensity of car transport. Especially, monitoring of platinum, rhodium and palladium is important because these metals are widely used as catalysts in many branches of industry and primarily as catalytic converters in cars [1]. Moreover, the use of a number of platinum(II) complexes in medicine against various kinds of cancer has to be mentioned [2].

This study is focused on optimization of preconcentration procedure of trace amounts of PGMs by solid phase extraction (SPE). Amberlite polystyrene-divinylbenzene based sorbent (Strata SDB-L, Phenomenex) was used for this purpose.

Under the optimizing process, the following parameters were optimized: pH value of sorption; type and concentration of complex agent; concentration and type of cationic surfactant; type, pH, and volume of eluent mixture; acidity of final solution and various interfering influences (presence of various ions, matrix effects). These parameters were tested both for optimizing of instrumental method (ICP-MS) and sorption procedure.

Ammonium-pyrrolidindithiocarbamat (APDC), thiourea (TU), 4-(2-pyridylazo)resorcinol (PAR) and 8-hydroxyquinoline-5-sulfonic acid (8-HQS) were used as complexing agents for PGMs. Sorbent was conditioned using 0.001 mol.l⁻¹ cationic surfactant solution. Benzyldimethyltetradecylammonium chloride (Zephyramine), N-(α -karbethoxypentadecyl)-trimethylammonium bromide (Septonex) and benzyldimethyldodecylammonium bromide (Ajatin) were tested. Mixture of acetonitrile and 1 mol.dm⁻³ HCl (4:1) was proved as eluent.

The influences of various concentrations of hydrochloric acid during the complexation, elution and partial evaporation of the eluent prior the determination were tested. Effects of various elements and ions were studied during the sorption and retention on the above mentioned sorbent and ICP-MS determination was verified too.

Simultaneous determination of PGMs was performed by ICP-MS spectrometer Agilent 7500ce (Tokyo, Japan) using helium collision cell and internal standard which contained 100 μ g.l⁻¹ In, Re and Bi in 1% HCl. Detection limits for individual elements at discussed conditions were evaluated.

Acknowledgment

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Fast plant oils screening for total content of F-, Cl-, Br- and S-organic compounds

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Different pesticides are widely used in agriculture. Commonly used methods for plant oils pesticides content determination are based on GC or GC/MS and mainly targeted compounds to be determined. Standards of the analytes are required. These methods are time consuming and can't be used for fast oils control for pesticides (targeted and non-targeted) content.

General number of pesticides used today for different purposes is more than 1000. Therefore fast screening of plant oils for all (targeted and non-targeted) pesticides is very actual especially for potential sample customers.

The most dangerous are F-, Cl-, Br- P- and S-containing organic compounds. The same is true for pesticides.

We have developed the new method for total content determination of such compounds in plant oils which was based on liquid extraction from oil sample, injection of concentrate extract into high temperature quartz reactor in oxygen flow, absorption of conversion products, and ion chromatography analysis of F-, Cl-, Br- and SO_4^{2-} anions being formed, corresponding to determined elements.

A new approach to fast screening of oils for pesticides used in their production based on registration of respective elements (F, Cl, Br, S), using developed method, was proposed.

The possibility of fast and reliable identification of such pesticides was shown when the information about registered elements and molecular masses of pesticides (determined using gas chromatography/mass-spectrometry with chemical ionization (GC/MS-CI)) was used simultaneously.

The developed method can be used for fast plant oils samples screening for total content of respective pesticides and organization of reliable plant oils pollution control.

Characterization of environmental pollutants coming from meat industry in Vojvodina region

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The meat industry sector emerges as one of the top two or three most significant contributors to the most serious environmental problems, at every scale from local to global. Meat industry is one of the major causes of the world's most pressing environmental problems, including global warming, land degradation, air and water pollution, and loss of biodiversity. Using a methodology that considers the entire commodity chain, it estimates that meat industry is responsible for 18 percent of greenhouse gas emissions. The Food and Agriculture Organization of the United Nations report recommends a range of measures to mitigate meat industry's threats to the environment, such as land degradation, greenhouse gas emissions, water pollution and biodiversity loss. The aim of this work was to identify significant organic pollutants that are coming to water environment from meat industry in Vojvodina region, Serbia.

Within the first survey of the research, 4 individual 1 L water samples were taken from the discharges of 4 significant meat industry polluters identified on the territory of the Autonomous Province of Vojvodina. Gas chromatography coupled to mass spectrometry was used for screening analyses to identify for possible organic contaminants. Organic compounds were extracted by liquid-liquid extraction. Water samples (800 ml) were placed in a 1000 ml glass separatory funnel and extracted with two 50 ml portions of dichloromethane for 20 minutes using automatic shaker device. After extraction, both extracts were combined, dried and placed into heart-shape flask for evaporation to final volume 1 ml. Large volume injection was used for introduction of 30 µl extract to GC system. The GC analysis was performed using Agilent 7890 gas chromatograph coupled to Agilent 5975 mass spectrometric detector. The system was equipped with PTV injector system. Capillary GC analysis was performed on a 30 m x 250 mm I.D., 0.25 mm df DB-FFAP column. Helium was used as carrier gas. The MSD was used in the SCAN mode for all samples. Identification of compounds was performed using Wiley7n and NIST08 mass spectrum libraries. Based on the obtained mass spectra and retention data, many chemical structures of analytes could be proposed. The obtained results will undergo further evaluation using risk prioritization strategies in order to select toxic contaminants found at high concentration levels to present a significant hazard for the population of Novi Sad. The monitoring of the quality of waste water coming from meat industry will be discussed in details.

Acknowledgment: This research has been supported by the Ministry of Science and Technological Development of the Republic of Serbia within the project: Improvement and development of hygienic and technological procedures in production of animal originating foodstuffs with the aim of producing high-quality and safe products competitive on the global market (46009). M.S. would like to thank Visegrad fellowship program for contract number 51200592 allowing her 6 months study stay at Institute of Analytical Chemistry, Faculty of Chemical and Food Technology, STU, Bratislava, Slovakia. I.S. would like to thank SRDA project No. SK-SRB-0022-11.

Study of the complexation process by modified carbon fibers

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Carbon fibers modified with organic compounds combine the properties of the matrix and fixer-modifier reagent and can be considered as a new material with the properties different from the starting material properties. At the present time few number of works focusing on the investigation of the surface morphology of carbon fibers modified by organic chelating agents are known. Therefore the purpose of this study is the investigation of the process of complex formation between chromium ions and modified surface of hydrate-cellulose carbon fiber by using atomic force microscopy. Modified samples of carbon fibers were obtained with liquid phase oxidation by concentrated nitric acid and the treatment with 1% diphenyl carbazide solution. Investigation of the surface carbon fibers morphology has been made with *Agilent Technologies 5500 Scanning Probe Microscopy* atomic force microscope.

It has been found that carbon fiber was consisted of smaller fibers (7-8 microns diameter) which in turn are made of 400-600 nm microfibrils. As can be observed on the images, a fiber block structure shows the location of microfibrils along the fiber axis confirming published data on the structure of carbon fibers. The different sizes pores located on the fiber surface mostly have a slit-like structure. Liquid-phase oxidation of carbon fibers leads to significant increasing of meso- and macropores. Mesopores content in OACF increases to 60%, macropores – up to 22%. A diphenyl carbazide coating to the surface of the oxidized carbon fiber is accompanied by sorption of the latest in sorbent mesopores as is evidenced by the pore distribution histogram. According to a graph of integral heights, almost 70% points on the surface of modified by DPC carbon fiber have a height of 0 to 994 nm, whereas the highest points on the oxidized carbon fiber surface reach up to 482 nm and their content is slight. The interaction of chromium with analytical functional group leads to the formation of complex which molecules are equally distributed over the surface of modified carbon fiber. Circular form complexes and their associates have size of 50 to 100 nm. The graph of the integral of the histogram on the heights shows that almost 98% of points on the adsorbent surface with surface complexes of chromium have a height 900-1000 nm.

Extraction of unbiased mass spectra in case of unresolved chromatographic peaks

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Library search against electron ionization mass spectral databases is the most popular, easy and quick approach used for tentative identification of unknown organic compounds. Success of library search depends greatly on quality of experimental mass spectrum. Gas chromatography coupled to mass spectrometry allows analyzing complex samples (containing hundreds of components). However overlapping of chromatographic peaks complicates extraction of unbiased mass spectra and decreases reliability of library search results. Therefore a lot of mathematical approaches were developed to simplify extraction of “pure” mass spectra of coeluting components.

We have compared four approaches applied for mass spectra purification: background subtraction, AMDIS software (NIST), ChromaTOF software (Leco) and Procrustes analysis (which is based on using principal component analysis). In the work experimental and simulated GC/MS data were considered. In case of simulated data a lot of parameters were varied: the number of coeluting components, chromatographic resolution, ratio of component concentrations, the number of common m/z values (presented in mass spectra of coeluting components) and noise level.

Acknowledgements

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Microelement composition of some hydrobionts tissues of the Japan Sea

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Current status of coastal waters of the Far East, especially the Japan Sea, is determined by considerable anthropogenic and technogenic influence that results in disturbance of the natural background of many elements in the aquatic environment and marine organisms.

The present work is dedicated to study of some microelement contents in soft tissues, gills and liver of flounder (*Cleisthenes herzensteini*) and saffron (*Eleginus gracilis*) and in shells and muscles of mussel (*Mytilus trossulus*) and scallop (*Mizuhopecten yessoensis*) selected from the Peter the Great Bay (the Japan Sea). Analysis of all 60 samples was subjected to the organs and tissues of fish and shellfish. Samples were digested in a microwave reactor Milestone UltraClave with hydrochloric and nitric acids mixture (1:2). From the resulting solution 30 µl was applied on the polished quartz support. Elemental analysis was performed by Total Reflection X-ray Fluorescence spectrometry (TXRF 8030C). The results are presented in the Table.

Microelement concentration in hydrobiont tissues, mg/kg dry mass

| | <i>Cleisthenes herzensteini</i> | | | <i>Eleginus gracilis</i> | | | <i>Mytilus trossulus</i> | | <i>Mizuhopecten yessoensis</i> | |
|----|---------------------------------|-------|-------|--------------------------|-------|-------|--------------------------|------|--------------------------------|------|
| | | | | | | | | | | |
| P | 4170 | 2180 | 6590 | 2070 | 1810 | 9540 | - | 2700 | - | 2800 |
| S | 2480 | 2330 | 1870 | 1800 | 2190 | 2970 | - | 2900 | - | 4100 |
| K | 2090 | 2330 | 1140 | 1400 | 1690 | 2170 | - | 300 | - | 300 |
| Ca | 74.67 | 82.10 | 7844 | 220 | 260 | 16600 | 96000 | 5200 | 92000 | 2900 |
| Fe | 223 | 9.01 | 95.87 | 40.6 | 6.75 | 153 | - | 101 | - | 325 |
| Cu | 7.39 | 0.598 | 1.53 | 3.02 | 0.553 | 3.4 | - | 3.9 | - | 6.93 |
| Zn | 33.75 | 7.46 | 35.58 | 23.89 | 9.08 | 48.1 | - | 58.1 | - | 116 |
| As | 3.54 | 3.43 | - | 3.46 | 3.08 | - | - | - | - | - |
| Se | 2.33 | 0.593 | - | 1.26 | 0.510 | 2.07 | - | 1.94 | - | 4.2 |
| Br | 0.629 | 0.377 | - | 0.536 | 0.401 | 3.61 | - | 1.78 | - | 3.86 |
| Sr | 1.41 | 0.875 | 59.54 | 2.16 | 2.82 | 97.3 | 1100 | 42.6 | 800 | 51.7 |
| Mn | - | - | 9.05 | 1.61 | 1.43 | - | - | 12.9 | - | 35.6 |
| Ni | - | 1.01 | - | - | - | 4.35 | - | - | - | 7.6 |
| Cr | - | - | - | - | - | - | - | - | - | - |
| Ti | - | - | - | - | - | - | - | 29.5 | - | 32.1 |
| Cd | - | - | - | - | - | - | - | - | - | 5.89 |

Thus, it was shown that a large number of microelements may be determined from one sample using the Total Reflection X-Ray Fluorescence method.

Combination of high resolution ortho-TOF MS and the ion source with ionization of a pattern by both active particles and irradiation from glow discharge

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One of the most powerful methods for monitoring of the environmental pollution as well as air pollution in the manufacturing process and security systems is mass spectrometry. Distinctive feature of modern mass spectrometer is possibility for real time analysis of chemical composition of the environment and the process technology. Here, key characteristics are the recording rate, sensitivity and resolution of the instrument. On the basis of electrodeless glow discharge, a new version of the ion source is developed and designed to ionize a gas pattern. The discharge and ionization regions can be spatially separated. Thus, using the same ion source, different ionization mechanisms can be realized. By introducing a gas-reactant in the glow discharge region, the ionization occurs via ion-molecular reactions with a proton transfer. In the case of the glow discharge in a pure rare gas, e. g. Ar or He, the ionization of a pattern will take place under mutual action of high excited metastable atoms of inert gas and hard ultraviolet radiation from the discharge.

Different geometries of introducing a gas-phase pattern into the ion source as well as focusing and extracting the ions from an ionization region are tested. Ionization occurs at a pressure of buffer gas in the range of 0.1 – 2 mbar. When the discharge and ionization regions are spatially separated, the mass spectra obtained look like those of electron ionization with reduced energy. When these regions are combined, the sensitivity of the instrument to the organic impurities is higher but views of the mass spectra are more complicated because of a variety of ion-molecular reactions which occur with participation of primary ion-radicals from impurities.

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Determination of the elemental composition of the East Arctic Seas sediments by energy dispersive X-ray fluorescence analysis

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The method of energy dispersive X-ray fluorescence analysis was applied to determine the qualitative and quantitative composition of 78 samples of sediments obtained during the 45-day cruise onboard RV "Academician Lavrentiev" in the East sector of the Arctic Sea (02.09.2011 - 17.10.2011., the expedition manager D.Sc. Igor P. Semiletov). The test samples were dried at 105°C, milled in a planetary mill to an average particle size of 200 microns and pressed to obtain emitters of a diameter of 20 mm. The measurements were performed using a Shimadzu EDX-800HS spectrometer (Rh- anode, vacuum, exposure time 200 sec.) The elements concentrations were calculated by the fundamental parameters method. The accuracy of determination was controlled using certified sediment reference materials (SDO-2, SDO-4, SDO-6). The following elements were found in all the samples: Si, Ca, Na, K, Mg, Al, S, Fe, Mn, Cr, Zn, Ni, Ti, Cu, Rb, Sr, Y, Zr, Ba. Some samples also contained As, Br, Nb, Mo, Sn and Pb. The silicon content varied from 50 to 70 wt. %, the iron content varied from 8 to 20 wt. %, the potassium and aluminum contents were within the range 10-15 wt.%. Calcium, sodium, magnesium and titanium were present in amounts 1-3 wt. %. The concentrations of other elements did not exceed 1 wt. %.

To sum up, within the scopes of the program of studies of physical-chemical characteristics of the gas hydrate mega-pool of the underwater permafrost of the East Siberian Shelf, we determined the element composition of sediment samples taken in the Laptev Sea, East Siberian and Chukchi seas, and the north-western part of the Bering Sea.

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Polybrominated diphenylethers in indoor and outdoor air and dust samples in Russian Federation

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Brominated Flame Retardants (BFRs) are a group of chemicals that have attracted increasing attention from scientists in recent years. The most used BFRs are polybrominated diphenylethers (PBDEs). These chemicals are added to polyurethane furniture foam, textiles, high impact cases, printed circuit boards used in televisions and computers and other materials to prevent fire damage and harm[1]. Flame retardants are physically combined with the polymer material. This means that there is a possibility that the flame retardant may diffuse out of the treated material to some extent. The increased use of PBDEs in consumer products has resulted in the ubiquitous presence of these compounds in private housing, offices, public buildings, other work environments and the outdoor environment. PBDEs exhibit toxic properties that are similar to persistent organic pollutants that have been banned or restricted, such as dioxins and polychlorinated biphenyls. Findings that PBDEs are widely distributed in the environment and are present at increasing levels in humans have raised concerns about the potential risks of exposure to human health and the environment [2]. Transport of PBDEs mostly takes place in the atmosphere and their transfer to humans basically occurs through inhalation and ingestion pathways.

The objectives of this research were determination of PBDEs concentration in air and dust samples in a wide variety buildings such as commercial, residences (old and new buildings) and garages. The experimental work included collection of indoor and outdoor air (vapor and particulate fractions) and dust samples, characterization and comparison PBDEs levels in microenvironments and study of air across a northern gradient in Russia (sampling sites: Obninsk, Moscow, Arkhangelsk and Amderma).

Air and dust samples were Soxhlet-extracted, cleaned and fractionated, and analyzed for 18 PBDE congeners using GC/MS operating in negative chemical ionization mode. The following quality control samples were processed: blanks and standard reference dust were analyzed with each sample batch. Linearity, drift check, surrogate and spike recovery analyses were carried out.

The results of the study show that low brominated BDEs were detected in every air and dust sample. Levels of PBDE were the highest in dust with average concentrations 9 to 458 ng/g dry wet. Predominant congeners were PBDE-47 and 99. Deca-BDEs was detected in every dust sample. Major congeners found in dust samples are reflected the commercial penta- and deca-formula.

The urban/industrial air samples higher concentration in the particulate phase, including PBDE-209 and PBDE-208. The remote Arkhangelsk and Amderma sites show generally low levels and vapor phase fraction dominates.

The observation that PBDE concentrations were higher in an commercial and residences environment than outdoors at a control site suggests that people are more likely to be exposed to higher PBDE concentrations in the indoor environment.

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Voltammetric systems such as “electronic tongue” for express identification of the composition and the nature of wastewater

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Many of the problems of voltammetry when using in electroanalytical control due to the lack of signal selectivity can be solved by use of multiple electrodes with different signal characteristics instead of a single electrode. Such systems are named “multielectrode systems” or “electronic tongue”. The motives for using these systems are:

- The expansion of the list of determining compounds;
- Simultaneous determination of several compounds whose signals are partially overlapped with each other and with the signals of the matrix or interfering components;
- The determination of the signals for several components which are influence each other;
- Obtaining of nonparametric information related to the chemical composition and quality of the object of analysis.

The first two systems have no difference from traditional voltammetric systems. Others suggest processing of measurements data array using chemometric methods, especially in the case of nonlinear and multi-parameter signal-concentration relation, and also the isolation of signals of individual compounds. The voltammetric systems designed for solving the problems related to the determination of objects differences and similarities by use of priori or a posteriori criteria which are using in expert systems such as “electronic tongue” are of particular interest.

The report covers the most frequently used in environmental control “intelligent” voltammetric systems, the examples of data processing of voltammetric measurements based on mathematical and statistical modeling [1, 2]: feedforward neural networks, artificial neural networks based on the adaptive resonance theory, the principal component analysis and etc. Special attention is paid to the voltammetric devices such as “electronic tongue”, the examples of their use in electrochemical analysis for the identification of the nature and the composition of multicomponent solutions of electroactive and non-electroactive substances and wastewater are represented, the prospects of the research development in this area, electrodes used, the methods of their modifying, signal modulating, equipment are considered.

Examples of the flow-through voltammetric systems such as “electronic tongue” in the control of the production processes on line and in line, including wastewater of pulp and paper mill, are also considered.

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Radio-frequency time-of-flight mass-reflectron

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The pollution of the environment is the major problem of the XXI century. Range of anthropogenic pollution of water and soil ecosystems is wide. Most effective in dealing with environmental problems are devices with mass spectrometric (MS) analyzer to detect and identify micro-level pollution concentrations.

The TOF MS with static fields used have a narrow range of energies and ion in-flight angles. In them the phase space of ion packs is limited by the space charge. Devices with quadrupole RF fields, i.e. mass filters and ion traps, are also employed in mass-spectrometry. Their mass sweep is sequential and as a consequence the analysis rate is not high. Selective qualities of the quadrupole RF fields are not restricted only by the separation of ions into stable and unstable ones. The spectrum formulation of oscillations in quadrupole RF fields depends solely upon the ratio of the charge to the mass of the particles e/m . This property can be used for space-time focusing and time-of-flight mass analysis of ions.

The suggested procedure of TOF mass analysis of ions in quadrupole RF fields is based on peculiarities of solutions to Mathieu's equations at small values of the parameters a and q [1]. With $a=0$ ion oscillations along the X and Y axes involve a harmonic with a circular frequency and a set of higher harmonics. With $q<0.1$ the level of the higher harmonics diminishes rapidly as the number of the harmonics n grows. Ion oscillations with $q<0.1$ are described rather accurately by the first three harmonics. At $q=0$ ion oscillations along the X and Y axes degenerate into monochromatic ones with a circular frequency. The period of circular oscillations does not depend on initial parameters of ion movements. In the time $t_0=T/2$ the coordinates of ions change to the opposite. This means that in the $y=kx$ planes quadrupole RF fields effect a periodic space-time focusing of ions with $y_0=kx_0$ initial coordinates. The independence of the time of the reciprocal movement t_0 from the initial coordinates and the ion velocities x_0, v_{0x}, y_0, v_{0y} point to the isochrone and isotope character of quadrupole RF field focusing properties. These qualities prove to be essential for the TOF mass analysis of non-monoenergetic ions.

For the TOF MS the version of focusing ions in the planes of the zeroth potential proves to be the best. In the quadrupole field such as these are the $y=\pm x$ planes. With the turn of the system of coordinates XOY through the 45° angle the focusing planes $Y=0$ match the asymptotes of the quadrupole. In the new system potential distributions along the X and Y axes become linear. Such distributions are formed in the hyperbolic dipole as well as in the system of plane electrodes with one-dimensional linear distributions of the potential. In them the character of circular oscillations of ions is preserved whereas the structure of the RF partials changes. A correction to the drift time t_0 for this occasion dt depends on initial parameters of ions [2]. The obtained results serve the basis for developing a new type of TOF MS, i.e. the radio-frequency time-of-flight mass-reflectron.

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Analysis of kraft pulp wastewater by gas chromatography with mass detection

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Wastewater of pulp and paper mills belongs to complex multi-component analytical systems, which qualitative indices are determined both as features of chemical milling process and as proportion of basic groups of components defining their composition.

North-western part of Russia is characterized by significant marsh watershed and high content of organic compounds (humic and fulvic acid, water soluble lignin) into surface water. These high-molecular compounds determine the natural background concentration of contaminants in the northern rivers and may have a significant interfering effect on the accuracy and reliability of methods for the quantitative determination of some indices, which characterize the effect of pulp and paper mills wastewater on the surface water quality.

Thus, in order to create the system of wastewater quality analytical control of pulp and paper effluents it is necessary to determine these components groups. Content of extractives is considered as priority index for water quality control. The aim of this research is identification of organic components of kraft pulp wastewater by chromatography method.

Biologically untreated kraft pulp wastewater was chosen as the research object. The schema of sample preparation with high content of natural background concentration of humic and lignin substances was drawn up. The schema includes the following stages: removal of suspended substances, volatiles and lignin substance.

Wastewater samples were extracted by two variants as follows: variant A (extraction by diethyl ether, derivatization by methanol and N,O-Bis(trimethylsilyl)trifluoroacetamide (BSTFA)), variant B (extraction by chloroform, derivatization by methanol and BSTFA);

Qualitative analysis of extract composition is performed by chromatography-mass spectrometry method using the following equipment: gas chromatograph Agilent 6850 equipped with mass spectrometric detector Agilent 5973N. Compounds are identified by comparison of compound mass spectra using database NIST 2005 and gas chromatograph-mass-spectrometer Shimadzu QP2010S. Compounds are identified by comparison of compound mass spectra with library mass-spectra MS08.

It was determined experimentally:

1. Extracts of kraft pulp wastewater are multicomponent mixture of organic compounds, which bases is phenol derivatives;
2. Chloroform used for extraction doesn't allow separating particle of organic substances of kraft pulp wastewater;
3. Derivatization of extracts by BSTFA allows determining wide range of carboxylic acids.

Acknowledgments

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Production of the wood fiber semi-products: features of effluents' composition

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At the present time preferred direction for development of complex wood processing enterprise is implementation of various modifications of high yield semi-products, which processes allow increasing output of useful product almost twice in comparison with pulp manufacturing, significant decreasing chemical agent consumption, as well as reducing number of industrial emissions[1]. However, as a result of thermomechanical effect on wood and using of chemicalson stages of impregnation and bleaching of pulp, dissolved organic substances consisting of decomposition products of hemicelluloses, partially lignin, extractives and also mineralcomponentsget into effluents. Theseeffluents arehigh polluted (COD approaches 5000 $\mu\text{O}_2/\text{l}$) and including groups of organic and mineral substances in dissolved and suspended state.

The purpose of this paper is analysis of qualitative and quantitative composition of dissolved substances of high yield fiber semi-products effluents; separation of representative groups of organic substances (volatile with steamsubstances, lignin substances, neutral substances, phenols, extractives) and determination of contribution of different natures contaminants into wastewater pollution.

Chemithermomechanical pulp production effluents were taken for our investigation.

According to method of high-efficiency liquid chromatographymain mineral componentsaresulfur compounds.Using developed diagram for fractionating organic components [2] representative groups of organic substances wereseparated and quantitystudied.

Being that COD is a general measure of water pollution with components of various chemical nature and aggregative state, it was chosen as preferred index for evaluation of wastewater quality.

Our research has shown that suspended solids of CTMP effluents have the most contribution to COD, which is approximately at level of 42–46 rel.%. Contribution of dissolved mineral substances obtains 38–40 rel.%. Contribution of dissolved organic substances obtains 17–19 rel.% of total COD. From them the fractions of volatile components and lignin substances make the largest contribution to organic part of COD. Contribution of these fractions for analyzed effluents to total COD obtains 3.8 % and 9.1 % accordingly. Therefore, it is necessary to provide prior local treatment, ensuring the removal of suspended solids and mineral components.

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Ultratrace and isotopic analysis of uranium in environmental samples by Inductively coupled plasma mass spectrometry using high efficiency sample introduction

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The ICP-MS technique has a wide application both for analysis of environmental samples and uranium materials in the Analytical Center (AC) of UEIP. Modern mass-spectrometric instrumentation, analytical procedures and high professional skill of the personnel permits to cope with the contemporary analytical tasks rapidly and qualitatively. The sample introduction system is one of the most important components of the entire ICP-MS system that influences on analytical performances such as sensitivity, matrix effects, background level and sample memory.

Nowadays cross-flow nebulizers, due to their high inertness, are used in the most ICP-MS analytical procedures developed in the AC. These nebulizers operate at high uptake flows (approx. $1\text{--}1.5\text{ ml}\cdot\text{min}^{-1}$), with reduced efficiency (approx. 2%) and more signal loss. The possibilities of ICP mass spectrometers are restricted for analysis where high sensitivity is required or the sample volume available is small.

The application for sample introduction MCN-100 micro concentric nebulizer and U6000AT+ ultrasonic nebulizer/membrane desolvator (Cetac Technologies) provides better sensitivity at much lower flow rates (typically $0.02\text{--}0.1\text{ ml}\cdot\text{min}^{-1}$) due to their greater efficiency (up to 35%).

The proper choice of sample introduction system for specific applications is impossible without the regard of their properties. Therefore, the main aim of this paper was investigation the capabilities of micro concentric and ultrasonic/membrane desolvator nebulizers for ultratrace ICP-MS determination of uranium isotopes in environmental samples, effluents and emissions.

In this paper the effect of nebulizing operational parameters on signal intensity of uranium isotopes and on the formation of polyatomic and doubly charged species was investigated. Such instrumental conditions as RF forward power, nebulizer gas flow and sample flow rates, lens voltage were optimized. Experimental data on matrix effects of concentration and composition of solutions on uranium isotopes measurement conditions was obtained. Sample memory effect was evaluated. Finally, a rapid and sensitive analytical procedure for uranium isotopes measurement in environmental samples based on inductively coupled plasma quadrupole mass spectrometry with using high efficiency introduction system was developed. The estimation of detection limits, lower range limit and the random inaccuracy characteristic of uranium isotopes determination were provided. It was found that the application of ultrasonic nebulizer/membrane desolvation improves the limits of detection for a factor of 3.

The principles of organization of the system of monitoring pollutions on industrial-urban areas

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The natural complex industrial-urban areas of Russia gradually degrades and loses natural functions, almost everywhere there is a high level of pollution of the urban environment, and the situation of waste production and consumption becomes an almost insoluble problem. Despite notable achievements in the creation of resource saving and environmentally friendly technologies in the industry, energy and transport sectors, a major risk factor for most of the country is the level and extent of air pollution. In this regard, the study of source and component-concentration of atmospheric pollution are particularly important to assess the overall environmental situation of industrial and urban areas.

In this report, based on a comprehensive analysis of existing environmental monitoring systems discusses the features of construction, structure, and hardware and equipment methodical monitoring of large industrial and urban areas (cities, industrial centers, regions). [1] It is shown that the territorial monitoring system should be aimed at addressing the major challenges of the definition of "hot spots" (industrial facilities with high pollution emissions) on the map of the region. Justification of the list of priority pollutants subject to mandatory control in the environment should be based on a study of the formation and transport of contaminants, and to identify patterns of their spatial and temporal distribution in controlled areas

As part of the regional level should increase use methods of operational control, including hand-held devices, mobile laboratories and remote sensing [2,3]. In particular, this approach can be very effective in solving problems monitoring of pollution of the environment of Moscow in connection with a major expansion of its borders. The authors substantiate the set of methods and apparatus for use as a part of a city at the present time environmental monitoring of the capital and across the Moscow region.

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Useful of new preconcentration techniques in CE to effectively focus of bioactive analytes in complex biological mixtures

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Although CE holds great promise as the method of choice for high resolution of biological and environmental samples, it suffers from poor concentration sensitivity, particularly when UV detection is used. Diagnostically important analytes, such as catecholamines, steroids, amino acids found in biological matrix at $10^{-9} - 10^{-12}$ M. *On-line* preconcentration in CE is a very useful way to solve this problem.

We have investigated different techniques of *on-line* concentration (*stacking*, *dynamic pH-junction*, *sweeping*) for ionogenic and neutral analytes (proteins, biogenic amines, neurotransmitter amino acids, steroids) in biological objects by different modes of capillary electrophoresis: zone (CZE) and micellar (micellar electrokinetic chromatography MEKC) modes with normal and reversed polarity.

We have developed a novel *on-line* concentration technique in MEKC with reversed polarity for catecholamines and their metabolites with 18-crown-6 (4mM) and cyclohexilamine (5 mM) in the sample matrix. It was achieved 900-1500-fold sensitivity enhancement factor.

It was observed, that dynamic preconcentration techniques (*sweeping* and *stacking*) has provided 20-fold increases in detection sensitivity for steroids by stacking, and for sweeping with the use of β -cyclodextrin in sample matrix – 120-fold.

It was found that the use of different options *on-line* with the polymer solution PEO allows to determine albumin in real biological systems with a detection limit of 15 and 10 $\mu\text{g/ml}$, respectively.

In this study we investigated the potential of using hyperbranched polymers (hbp) polyethylenimins, functionalized with maltose (PEI-Mal), with different molecular weights (5 and 25 kDa) and degree of modification with maltose, as a stationary phases in electrophoretic separation of bio-active substances. It was performed columns with PEI-Mal covalently bonded to the interior of a capillary as a stationary phase, etc. *PLOT*-column.

PEI coating of capillary column reverse the direction of the EOF at acidic pH (2.2) and perform a good conditions for *on-line* preconcentration - the large volume sample stacking (LVSS) without polarity switching.

We have compared the three sample stacking methods, including **LVSS**, **HC-LVSS**, **FESI** with **LVSS**. We founded that using a combination of focusing principles of sample stacking with electrokinetic injection (FESI) and LVSS to analyze proteins resulted in a 1100-fold improvement in sensitivity. The LOD was achieved about 0,1 $\mu\text{g/ml}$ for analytes.

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Application of regular multimolecular sorbent based on Fe(III) stearate for mass spectrometric determination of residual contamination of natural waters by perfluorooctanoic acid

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Perfluorooctanesulfonic acid (PFOS, C₈HF₁₇O₃S) is persistent organic environmental pollutant. Extremely stable in the environment, perfluorooctanesulfonic acid is almost completely not subjected to biodegradation. Its carcinogenic properties are proved [1]. Currently the most commonly used method for sample preparation for the determination of trace amounts of perfluorooctanesulfonate is solid-phase extraction on reversed-phase sorbents. Although widely used commercial sorbents do not always provide a high degree of extraction of the analyte while reducing matrix effects. Immobilized metal-affinity chromatography (IMAC) is highly specific method of sample preparation. According to the Pearson's HSAB concept one can expect that such a metal as iron (hard Lewis base) will interact with oxygen of sulfonic group or fluorine (hard Lewis acid), comprising the perfluorooctanoic acid. Therefore, we can expect high recovery and great specificity in the solid-phase extraction if metal-affinity sorbent containing iron ions will be used. It should be noted that the existing IMAC sorbents are of a high cost since manufactured abroad and they are adapted only to selected groups of substances. It has recently been suggested to utilize a) Langmuir-Blodgett films based on iron(III) stearate [2] and b) Fe₂O₃, obtained by the sol-gel method combined with microwave-induced self-propagating synthesis, as metal-affinity sorbents [3].

At first the possibility of PFOS sorption by new sorbents was studied using BATCH chromatography. Qualitative estimation was run by MALDI method. Both new sorbents were used for the extraction of PFOS from the small volume of sample with relatively high concentration (50ng/ml). Sorption was carried out at pH 3 in the spin column filled with sorbent and eluted consecutively with different complex solvents. Mass spectrometry experiments showed that the signal corresponding to PFOS was observed in the same fraction of eluate as in BATCH experiment. In order to investigate the possibility of PFOS concentration from large sample volume, model system (exact analyte amount, equal to 50ng, in DI water) and sorbent based on iron(III) stearate were used. Sorption was carried out by flow method in standard SPE conditions with consecutive elution as in previous experiments described above. In parallel, the same amount of PFOS was extracted from the solution using a standard reverse-phase sorbent. Quantitative analysis of PFOS was conducted on LCMS-IT-TOF instrument. The experiment showed that while the weight of the standard sorbent was 6-fold higher, amounts of extracted PFOS were almost equal for the both phases. Thus the principle possibility of extracting perfluorooctanoic acid by metal-affinity chromatography on the new sorbents containing iron (III) ions was shown.

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LC-MS TOF analysis of erythromycin, related substances and degradation products

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In previous works a separation of Erythromycin A (EA), Erythromycin B (EB), Erythromycin C (EC) and main degradation products was performed on xTerra RP C18 column using mobile phase consisting of acetonitrile – 0.2M potassium phosphate and UV detection [1,2].

The aim of our work was developing a method valid for mass spectrometry using a volatile buffer solution. We suggested a sensitive, selective isocratic LC-MS method for the analysis of erythromycin and related substances to analyze solutions with substantially lower concentration than required for UV detection.

A commercial erythromycin sample (Phenix, Belgium) is known to contain the following impurities: EANO (0.5%), EF (1.4%), NdMeEA (0.6%), EC (2.2%), EE (2.4%), E A (81.8%), AEA (2.5%) and EB (3.3). In the present work EA was full-separated from related substances EB and EC. The main degradation products were eluted separately.

Components were resolved using xTerra PR C18 column. The mobile phase was a mixture of methanol and 2mM ammonium formate solution. Detection was measured by Waters LCT TOF mass spectrometer operated in the positive-ion electrospray mode. Full scans were acquired from m/z 50 to 1000 at 1 scan per second. The molecular weight was confirmed as protonated molecules at a capillary exit voltage of +100 V, and samples were reanalyzed with a capillary exit voltage of +200 V for the fragmentation by in-source collision-induced dissociation. The individual chromatogram of each compound was obtained by selected ion monitoring. The method was completely validated and allowed to quantitative erythromycin analysis.

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Evaluation of the anodic stripping voltammetry to study heavy metals removal by grape stalk waste in fixed-bed column

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Heavy metals are used in various industries due to their technological importance. But, imperfect treatment of waste products from these industries may lead to both human health and environmental issues. Considering the harmful effects of heavy metals, it becomes important to remove them from liquid wastes at least to a limit accepted by the regulations.

The ability of biological materials to sorb metal ions has received considerable attention for the development of an efficient, clean and cheap technology for wastewater metal removal. One of these sorbents is grape stalk wastes generated in the wine production process, which has been satisfactorily applied in fixed-bed column to remove heavy metals from high concentration liquid effluents.

In these works were evaluated the removal of Cu^{2+} , Ni^{2+} , Pb^{2+} and Cd^{2+} from aqueous solutions with initial metal concentration around 5×10^{-4} M with limit of detection (LOD) of 10^{-5} M. The influence of the initial concentration, the sorbent particle size and the regeneration process were also evaluated.

The present work studies the removal of Cu^{2+} , Zn^{2+} , Cd^{2+} and Pb^{2+} and their mixtures from aqueous solutions by using grape stalk wastes in a fixed-bed configuration. The experiments were carried out with low metal concentration (2.3×10^{-5} M with LOD around 1×10^{-7} M) and it was necessary the use of the anodic stripping voltammetry (ASV) to analyze all collected samples.

The results obtained in sorption experiments show the existence of a competitive ion exchange process which leads to the overshooting phenomenon which represents the desorption of the low affinity metal in front to the metal with higher affinity for the biosorbent as can be seen in Figure 1.

The results also showed that the ASV method is useful to quantify simultaneously low concentrated metal ions which can be of great interest in the removal of heavy metals from industrial wastewater. Moreover, the technique requires small amounts of sample and the results obtained are quite exact for a wide variety of metal cations.

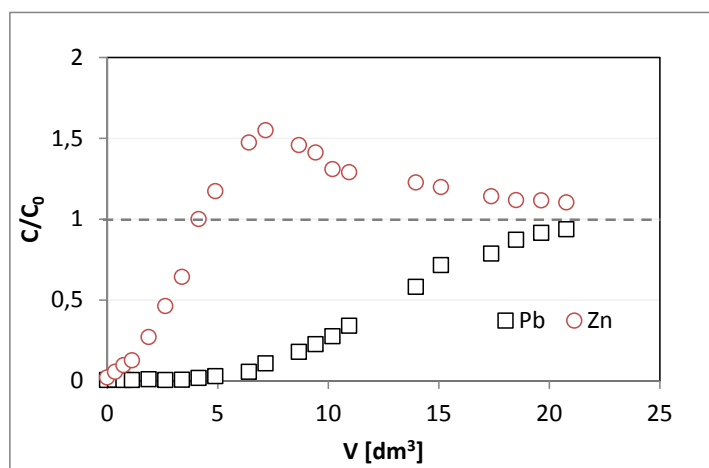


Figure 1. Sorption of Pb/Zn binary system onto grape stalks in fixed-bed column.

Options for isolation and determination of selected pharmaceuticals from livestock excrements

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Antibiotics, including sulfonamides, are in both human and animal body metabolized and excreted in the urine or faeces, while 30 to 90 % of them are excreted in active form. In this way, antibiotics in their original or metabolized form can enter the environment. Veterinary antibiotics are very often more hazardous than those used to treat people. Animals consume up to 60 % of antibiotics not only for veterinary treatment but in some countries also as a feed supplement. Livestock excrements may then be used as manure on fields which is one of the way how residues of pharmaceuticals could enter to different components of the environment such as soil or water ecosystem, including aquatic organisms. The occurrence of residual antibiotics in the environment then results in an increased incidence of resistant bacteria, which may in future become a potential threat to human health [1, 2, 3].

The work was focused on the selection of suitable method for the isolation and determination of pharmaceutical residues from the group of sulfonamide antibiotics in samples of livestock excrements. Pharmaceuticals investigated included ten sulfonamides (sulfaguandine, sulfadiazine, sulfathiazole, sulfapyridine, sulfamerazine, sulfadimidine, sulfamethoxazole, sulfadoxine, sulfaclozine and sulfadimethoxine). Pre-analytical procedures as well as final analytical determination were optimized. Dried animal manure was extracted into methanol using PSE (Pressurized Solvent Extraction). Several conditions of different pressures and temperatures were used for optimization of extraction part. The method further involved pre-concentration and purification by SPE (Solid Phase Extraction) using different extraction cartridges, including Oasis HLB (Waters), Cleanert PEP Plus (GS-Tek) or Supel-Select HLB (Supelco). Final analysis of the selected pharmaceutical compounds was carried out by high-performance liquid chromatography (HPLC) coupled with diode array detector (DAD). The efficiency of the method was verified using analytical standards of selected pharmaceuticals while recoveries were counted. The optimized method was applied to the determination of selected sulfonamides in real samples of livestock excrements originating from veterinary medical clinic situated at VFU Brno [4].

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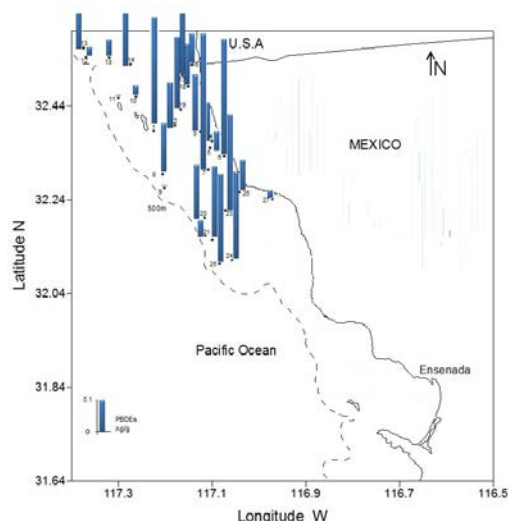
PBDEs and POPs at the southern end of the Southern California Bight

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Around the world, contaminants old and new are both of great concern for human and ecological reasons. Among those new contaminants of emerging concern, we are analyzing the brominated flame-retardants as they have been reported with a strong presence in the north of the southern California Bight (SCB) [1]. These and other contaminants of emerging concern (CEC) along with legacy POPs are frequently found in coastal marine sediments. The effects of both, CEC and legacy POPs on marine organisms and humans have been already documented [2,3,4]. We are reporting here, for the first time, PBDEs in the southern end of the SCB in Mexican Coastal marine sediments along with DDTs.

Our concern over the presence and distribution of PBDEs in recent marine sediments originated in the reports generated at the north of our study area. Those studies indicate that concentrations for these chemicals are among the largest in the world in *Mytilus* sp. tissue [5], and even in human tissue [5]. Because of this, and using the samples collected under the same monitoring program in parallel to that of SCB in the US, we used the sample from 2008 and are reporting both PBDEs and DDTs. PBDEs were measured by GC-MS using Negative Chemical Ionization with methane as reacting gas. The most frequent PBDEs found so far, have been the PBDE 47, the PBDE 99 and the PBDE 100. It has been mentioned that 209 is the most frequently found in the USA side of the SCB [1], however, we have not measured that particular compound, as it requires a shorter column. It is surprising that the distributions found for PBDEs is different than that of DDTs (not shown). The distribution of DDTs appears to be more related to zones where organic material or small size sediment accumulates. On the contrary, the distribution for PBDEs, appears to be more associated to coastal areas where discharges are taking place from land.



The concentrations for PBDEs are however far less than those reported for the San Diego area. The maximum concentration 431 pg/g dry weight, with an average concentration of only 174 pg/g. These concentrations are more similar to those reported for other parts of the world. This results may imply that the main route of transport into the local coastal environment is the wastewater discharges along with the creeks and rain wash-out and not so much atmospheric given the near the coast distribution and the fact that little impact appears to derive so far, from the larger concentrations found just a few miles

north from our location. These are only partial results to be presented at the meeting.

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2. C. Lam, R. Newman, P.K.S. Shin, D.W.T. Au, P.Y. Qian, R. Wu. *Environ. Sci & Technol.*, vol. 44, 2010, pp. 7130-7137.
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Analytical methods for the detection of dimethyl thallium in water samples at low concentration levels

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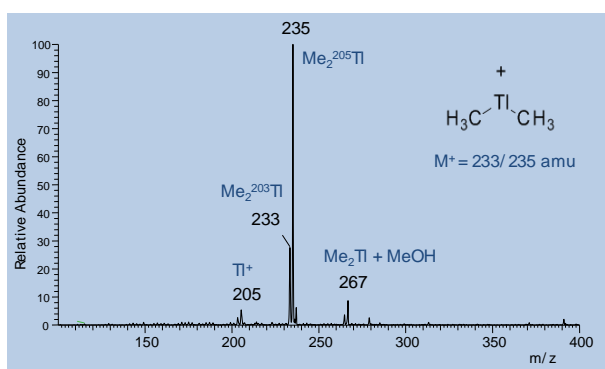
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Thallium exhibits a high environmental relevance due to its elevated toxicity. It is emitted by various sources comprising industry, mining and waste handling. Usually, the inorganic species of thallium are considered in environmental studies. However, a very few investigations currently pointed to the occurrence of an organic species of thallium in marine ecosystems, the dimethyl thallium cation [e.g. 1]. Knowledge on the environmental relevance of this organometallic compound is very restricted, primarily due to the fact, that analytical methods to determine dimethyl thallium, in particular at low concentration levels, are lacking.

Therefore, this study aims at the development of appropriate analytical methods for the determination of dimethyl thallium at trace levels. Two different approaches have been investigated, a LC/MS based technique and ion chromatography linked with ICP/MS. For optimization and specification of these analytical approaches a Tl (CH₃)₂⁺ standard has been synthesized.

Firstly, the Tl-species Tl⁺ and Tl (CH₃)₂⁺ were determined simultaneously in river water and hydrous extracts of street dust applying ion chromatography combined with inductively coupled plasma mass spectrometry (IC-ICP-MS). The system consisted of a Metrohm 709 IC pump, a Vici injection valve with 250 µl loop, a Metrohm Metrosep C4 250/4.0 column with a Metrosep C4 guard column and a Perkin Elmer Elan DRCe quadrupole ICP-MS. A 1.7 mmol/L HNO₃ was used as eluent. The retention time of Tl (CH₃)₂⁺ was significantly shorter than that of Tl⁺ and the detection limit is < 1 µg/L Tl. First results show that Tl (CH₃)₂⁺ occurs in river water during summer time, possibly due to enhanced production of organic matter. The Tl-fraction, which is easily mobilized from street dust by water, exclusively contains the Tl⁺-species.



Secondly, 1L water samples have been reduced in volume by evaporation to final volumes of approx. 2 mL. From these concentrated samples aliquots of 5 µL have been measured by LC/MS using a reversed phase column and acidified water/methanol mixtures as eluent. Mass spectrometric detection has been performed with both ESI and APCI sources at different ionization parameters. However, best results were obtained using the APCI device. Limit of detection was also

in the range of 1 µg/L. Analyses of surface water samples derived from a contaminated area revealed concentrations of up to 160 µg/L of Tl (CH₃)₂⁺.

In summary, two independent analytical methods have been developed to determine successfully dimethyl thallium species in water samples at concentration levels relevant for environmental studies.

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Trace and major metal abundances in the shale and coal of various seams at Okaba coal mine, Kogi State, Nigeria

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The distribution of a number of trace and major elements in the shale and coal of differing seams in Okaba, Kogi State, Nigeria was studied using energy dispersive x-ray fluorescence spectrometer. Major elements of Al, K, Ca and Fe showed concentration ranges of 5.93 ± 2.49 – 8.42 ± 0.003 mg/g, 0.18 ± 0.46 – 2.16 ± 0.0 mg/g, 0.53 ± 0.41 – 2.23 ± 0.35 mg/g and 6.05 ± 0.004 – 18.28 ± 1.2 mg/g respectively. The mean concentrations are 7.24mg/g (Al), 1.25mg/g (K), 0.91mg/g (Ca) and 11.86mg/g (Fe). These values are clearly above the recommended concentrations in coal quality standards and for air emission standards by the World health organization. Trace metals of Ti, Cr, Mn, V, Ni and Cu showed concentration range of 0.84 ± 0.007 – 2.98 ± 0.007 mg/g, 0.03 ± 0.0 – 0.12 ± 0.025 mg/g, 0.02 ± 0.11 – 0.30 ± 0.02 mg/g, 0.02 ± 0.44 – 0.2 ± 0.05 mg/g, 0.01 ± 0.075 – 0.12 ± 0.001 mg/g and 0.03 ± 0.02 – 0.62 ± 0.001 mg/g respectively. These results indicate that Okaba coal and shale is enriched in the major elements analysed in comparison to worldwide averages of coal while the trace elements with exception of Ti are below the coal quality standards. Correlations between the various metals were also established. The S content correlated inversely well with the K content of both the shale and coal. Expectedly the % Si content was high in the shale1 (26.70%) and shale2 (26.38%) while the lowest concentration was recorded at Okaba coal seam 5 (6.58%). The absence of Cl, Br, Na, and Mg in the samples clearly indicates the extent of surface leaching on the study area. This is evident by the various mountainous depressions in the study area.

Determination of volatile compounds in water, soil and sediment by Head Space-SPME-GC/MS

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Head-Space-SPME coupled with GC/MS was used for the identification and quantitation of volatile compounds in water, soil and sediments.

There are two approaches to quantitation in SPME. The first is to isolate a small amount of the equilibrium gas phase and complete adsorption all analytes. Second - adsorption analytes from a large volume of equilibrium in a relatively short time, so that over the time the concentration of analytes did not change much.

Quantitation in SPME is possible without reaching equilibrium, if the conditions are constant. This requires a calibration or calculation of the calibration factors on the basis of physical and chemical properties.

It is known that there is a correlation between distribution coefficients K between air and solid phase poly(dimethylsiloxan) fibre for SPME and retention index at temperature programmed GC. Therefore, K can be determined for each peak in the chromatogram using experimental or literature data of retention indices. For determination of volatile hydrocarbons in soil or water, the distribution of compounds between the solid phase (liquid) and a gas phase, on the one hand, must be considered, and between the gas phase and the adsorbent, on the other hand. The distribution between the solid (liquid) phase and a gas phase depends on the nature of the solid (liquid) phase and temperature: the higher the temperature, the more the equilibrium concentration in the gas phase. Since the control of all these processes is difficult, way out of this situation would be the use of an internal standard, adding to the analyzed object. The internal standard must have the same nature as the analyte.

Quantitation the volatile compounds including the total content of low-boiling petroleum products can be produced using internal standards and calibration on n-alkanes. This method was used for determination of volatile components of oil in the settling pond sediments, and the volatile compounds in the air, natural and waste waters.

Towards on site MS microbe assay in portable microbe enrichment unit with metal oxide sensors

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Microbe identification should be fast and preferably done on site as the health of environment and also humans is in danger. At present sampling, sample transfers as also routine cultivations are slow. Whenever bacteria, yeasts and moulds grow they produce volatiles, which provides rapid means for monitoring microbial species and their metabolism. We have integrated the portable enrichment cultivation units (PMEU) with high speed gas detection using metal oxide sensors. In connection with this, also radioisotope ionization activated ion mobility spectrometry is used in volatile identification in field conditions and also in laboratory screening (PMEU Scentrion®) equipment. This technology has been applied for detecting blood contaminations, monitoring urinary tract infections, fecal microbiological analysis, screening hygiene indicator bacteria and pathogens from waters, measuring the effects of antibiotics or antimicrobial peptides on various strains, air quality sampling (eg. in estimated damages to buildings caused by microbes), simulating intestinal ecosystems and food microbiology.

Improved analytical services and their increased performance produce security in healthcare, food and water production, and in the environment. The mass spectroscopy is offering tools for these uses but further product development is still needed to make them more compact for microbiological field and also laboratory analysis. At present the sensors we have used based on ion mobility spectrometry to make the whole system easier to be moved to field on the site of problems.

Response of *Pseudomonas syringae* isolated from clouds to cold stress. A metabolomic study

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Metabolomics has emerged more than ten years ago, and papers related to this approach have increased tremendously recently. This approach allows to study the response of the whole microbial metabolome to various environmental factors such as oxidative stresses, cold or heat stresses, lack of nutrients, presence of xenobiotics etc... "Ecological metabolomics" is still in the infancy but represents a great challenge for understanding new environmental questions such as climate change, ecosystem biodiversity evolution...

In this paper we present our latest results, they concern the response of the bacterial strain *Pseudomonas syringae* isolated from clouds at the Puy de Dome station to cold stress. The objective is to understand the adaptation of microorganisms to the hostile atmospheric environment where temperature is changing permanently. The bacterial strain has been incubated at two different temperatures, 17°C (average temperature in summertime) and 5°C (average annual temperature). The intracellular metabolites have been extracted by MeOH/Water/CHCl₃. The extracts (12 biological replicates for each temperature) were then analyzed by UPLC-MS (ESI+) and on line ¹H NMR thanks to the integrated platform "Metabolic Profiler" from Bruker.

The most discriminant metabolites show that the bacterium modifies its membrane fluidly, its energetic metabolism and synthesizes cryoprotectants in order to adapt to cold temperatures.

Some reviews of interest:

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Enantioselective and stable carbon isotope analyses following microbial assisted processes in soil: bound residue formation and degradation of the herbicide metalaxyl

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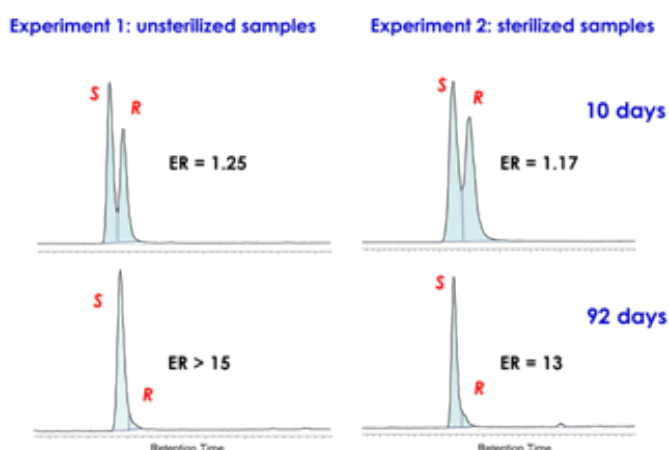
Formation of non-extractable residues (NER) in soils is a process at biogeochemical interfaces with a high environmental relevance, since NER influence bioavailability and, thus, (eco)toxicological properties of contaminations. Hence, we investigated NER formation of the fungicide metalaxyl in organic rich soil subfractions from Ultuna (Sweden) with a special focus on covalent linkages.

Stereochemical properties of chiral compounds such as metalaxyl are highly influenced by environmental processes, in which microbial activity is involved [1]. For biotic degradation in aerobic soils with pH > 5 a selective depletion of the metalaxyl (–)-(R)-enantiomer has been described. However, knowledge on the stereochemical effect of NER formation on metalaxyl has not been studied so far. Beside the stereochemistry also isotopic properties are changed by enzymatic processes. Hence, composition of stable carbon isotopes reveals also insights into microbial assisted NER formation processes.

Therefore, enantioselective analysis as well as compound specific stable carbon isotope analysis (CSIA), using *chiral*-GC/MS and GC/irmMS, respectively, have been applied to different soil fractions obtained from incubation experiments. The water soluble fraction of applied metalaxyl, derived from particle-size fractionation process-water, as well as solvent-extractable proportions from separated sand, silt and clay subfractions have been analysed.

The results show a significant depletion of (–)-(R)-enantiomere during an incubation time of 10 to 92 days for sterilized and unsterilized samples. This accounts not only for the water

soluble fraction but also for the particle associated extractable fraction. Hence, a high chiral selectivity of the active microbes and/or extracellular enzymes in the soil has been demonstrated. Further on, GC/irmMS analyses revealed a significant shift in $\delta^{13}\text{C}(\text{‰})$ values. In unsterilized samples an increase in $\delta^{13}\text{C}$ value of water soluble metalaxyl from 10 days to 92 days gave evidence for a microbial assistant isotopic fractionation. This observation was confirmed by measurements of



sterilized samples, in which no isotopic shift was detected.

All results demonstrated the usefulness of enantioselective and isotopic analysis for characterization of microbial assisted processes at biogeochemical interfaces in soil. Data showed, that this accounts for intra- as well as extracellular activities. Further on, the implications for the environment fate of organic pollutants in soil will be discussed.

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Siderophore production in cloud water

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Cloud water hosts microbial populations that have been found metabolically active in spite of stressful conditions (low temperature, desiccation, oxidation, UV radiation, acidic pH in aqueous phase etc...). Microbial activity in cloud water containing organic compounds such as carboxylic acids, formaldehyde and methanol has been measured and inferred estimations have shown that it probably affects the chemistry of these compounds in warm clouds (17°C), and could even drive their reactivity during the night [1-3].

Bacterial metabolism could then be considered as an alternative to chemical processes in atmosphere liquid phase.

These processes, mostly photochemical and/or driven by iron complexes, produce hydroxyl radicals which are powerful oxidants. Iron is also involved in bacterial metabolism since lots of enzymatic reactions are catalyzed by iron metalloenzymes.

We have been collecting cloud water to the summit of the Puy de Dôme mountain for several years and we possess now a collection of about 400 strains of microorganisms isolated from cloud water. This bank has been screened for siderophore production in order to check if this activity is a survival factor in clouds. Results will permit to study interactions between iron and microorganisms.

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Mesotrione adsorption on vertisol (Limagne plain, France): effect of soil properties

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The aim of this study was to investigate the adsorption of mesotrione (triketone family herbicide) on various fractions of a topsoil of Limagne plain. This soil is a silty-loam in texture, rich in organic matter (1.70 % of organic carbon – OC) , alkaline , with a montmorillonite as a principal clay mineral. To evaluate the role of mineralogy (clay vs “coarse” minerals) and different organic matter pools in herbicide behavior , additionally to the bulk soil sample mesotrione adsorption on particle size fractions knowingly different in mineralogy and organic matter (OM) content, structure and functions : < 2, 2-20 , 20-75 and 75- 500 µm , has been done. The role of OM in mesotrione adsorption was estimated also by adsorption experiments on topsoil treated with H₂O₂. The properties of all mentioned soil constituents were studied using the complex of methods: XRF, XRD, FT-IR, solid state ¹³C-NMR.

Pure mesotrione used is an analytical-grade powder (purity 99.8%, Buchs SG, Switzerland). Adsorption experiments have been done for 1-10 µM /l mesotrione concentrations using batch equilibration technique at room temperature for 24 h and 1 : 3 solid to liquid ratio, at fixed pH (7). After 24h pesticide adsorption and centrifugation supernatants were filtered using PVDF syringe filters with the pore size 0.45 µm. Mesotrione concentration in filtrate was determined by HPLC analysis.

Isotherms of mesotrione adsorption on all soil constituents are well described by Freundlich equation ($R^2=0.957-0.996$). Mean K_d values were within 0.59-1.52 l/kg range. The smallest value was obtained for 20-75 µm fraction ; the largest – for clay fraction. K_{oc} values calculated as $(100K_d)/OC$ were 60-200. The smallest was for 20-75 µm fraction, the largest – for bulk soil after H₂O₂ treatment and clay fraction.

The obtained data show that both mineralogy and OM content and characteristics are important components influencing the adsorption of this weak acid herbicide. Good positive correlations exist between K_d and CEC ($R^2=0.807$), and OC ($R^2=0.957$). Good negative correlation has been found between K_d and C/N ratio of OM ($R^2=0.723$). ¹³C-NMR spectra of studied samples show the predominance of aliphatic groups (60-65 %) ; the aromaticity index was 30-42 %. Clay fraction , which demonstrates the best adsorption characteristics is enriched in alkyls (31 %) and carboxyl groups (15 %). Overall K_d showed good positive correlations with the content of carboxyl groups and alkyls and is negatively correlated with the aromaticity index and acetal groups content.

Marine aerosol as a source of halogens in the troposphere

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Using two identical coated-insert flow tube reactors coupled to a mass spectrometer with molecular beam sampling and to ESR spectrometer with matrix isolation, a reactive uptake of NO₃ radicals as the “night-time oxidants” as well as NO₂ and ClONO₂ molecules on polycrystalline saline films was studied. The studies were carried out for the uptake of NO₂ molecules on NaCl films, ClONO₂ molecules on NaCl, MgCl₂ and NaCl doped with MgCl₂, and NO₃ radicals on NaCl, NaBr, NaI, MgCl₂, MgBr₂ as well as on NaCl doped with NaBr, NaI, MgCl₂, MgBr₂ and natural sea salt films under conditions of varying humidity up to 10¹⁶ molecules cm⁻³ and the reactant concentrations ranging between 10¹⁰ and 10¹⁴ molecules cm⁻³. The dependences of the uptake coefficient γ on (i) the reactant concentration at a fixed humidity; (ii) humidity at a fixed gas-phase reactant concentration; (iii) temperature; (iv) admixture of a doped salt in NaCl were measured. Under the same conditions, the reaction gas-phase products were detected and their branching ratio in the total uptake was determined.

In the reaction $\text{NO}_3 + \text{NaX} \rightarrow \text{X} + \text{NaNO}_3$ where X = Cl, Br, and I, chlorine atoms are established to be adsorbed whereas Br and I atoms leave the surface. Further fate of the Cl adatoms depends on mixing ratio of the surrounding reactive gases and their reactions. Under laboratory conditions at high NO₃ concentration, Cl adatoms change into NO₂ products in the fast secondary reaction $\text{Cl}_{\text{ad}} + \text{NO}_3 \rightarrow \text{ClO}(\text{g}) + \text{NO}_2(\text{g})$. In the troposphere, the secondary reaction is likely to be $\text{Cl}_{\text{ad}} + \text{O}_3 \rightarrow \text{ClO}(\text{g}) + \text{O}_2$.

For the first time, the reaction $2\text{ClONO}_2 + \text{MgCl}_2 \rightarrow 2\text{Cl}_2 + \text{new salt}$ is proposed and investigated. The reaction is considered to be an additional source of chlorine in the troposphere.

Over initial treatment of all fresh saline films with the reactant flux, the uptake coefficient $\gamma(t) = \gamma_{\text{ini}} \exp(-t/\tau) + \gamma_{\text{ss}}$ is found to decrease exponentially in time from an initial γ_{ini} down to some steady-state γ_{ss} , the parameters γ_{ini} , γ_{ss} , and τ being determined by the salt, the reactant volume concentration, and relative humidity.

Quantitative correlation between surface density of the salt components and their mole fractions in the bulk is determined by varying mole fraction in the source aqueous solution deposited as a film coating and by measuring the reactant uptake and the gas-phase products. Based on experimental dependencies, a conclusion is drawn about a dominant role of the doping agents in forming the coating surface of binary salts and natural sea salt.

On the basis of our experimental dependences and an analysis of literature data, a kinetic model of the uptake is proposed. The main outcome of the model is an analytical representation of the uptake coefficient in terms of some elementary parameters and the rate coefficients for elementary processes such as reversible adsorption of the reactants and the elementary heterogeneous reactions.

By handling of experimental data with the proposed model, some elementary rate coefficients were evaluated, i.e., the desorption rate coefficients and the adsorption heats, the rate coefficients of elementary heterogeneous reactions and their activation energies. The model allows us to extrapolate the laboratory data to real tropospheric conditions and to elucidate which of the uptake coefficients, i.e., γ_{ini} or γ_{ss} has to be used in the databases for chemical modeling of the troposphere.

Temperature dependent ozonation reaction of 1,1-diphenylethylene on artificial snow grains

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Temperature dependence of heterogeneous chemistry of 1,1-diphenylethylene (DPE) with ozone on artificially prepared snow grain surface was studied. Artificial snow was produced by shock freezing of the aqueous solutions of DPE (35g L⁻¹) in liquid nitrogen or by adsorption of DPE vapors on the ice surface. The calculated availability surface area of artificially produced snow grains were comparable and in good agreement with that determined by other physical methods. The values were found to increase with decreasing snow surface temperature. The reaction kinetics has already been described by Langmuir-Hinshelwood mechanism at -15 °C [1]. At -85 °C, ozonation kinetics was found to follow the Eley-Rideal mechanism. Our results can be beneficial for understanding heterogeneous reactivity of volatile and semi-volatile organic compounds on the ice surface.

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Environmental levels of lead and nitrogen dioxide in urban Atlanta, Georgia, United States of America (USA): methods and preliminary results

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Urban soil and road dust are well-known reservoirs of Pb from past use of leaded gasoline (petrol) and lead-based paint. This study was conducted to determine the quantity and form of Pb in urban Atlanta, GA, U.S.A., using methodologies from geochemical, microanalytical, and statistical techniques. Complementary soil and road dust samples were taken from 150 sites and the Pb, Zn, and Cu contents for all 300 samples were determined using energy-dispersive X-ray fluorescence (XRF); the bulk road dust samples were sieved to <250 μ m size portions and were re-tested. Samples with the highest lead content were analyzed using X-ray diffraction (XRD) and scanning electron microscopy (SEM). The median soil, bulk dust, and <250 μ m dust Pb concentrations were 70 mg/kg, 53mg/kg, and 74 mg/kg respectively, with the highest value, 968 mg/kg, found in a road dust sample. Evidently bulk dust and <250 μ m dust Pb levels are strongly correlated, however bulk soil and bulk dust are not—suggesting different sources, modes of transport and deposition of Pb. The road dust sieved at <250 μ m were found to have the highest Pb concentrations, which consequently hold the greatest potential to become airborne.

Atlanta has a built environment including multiple major interstates which provide substantial sources of nitrogen dioxide (NO₂) in urban Atlanta. Passive air monitors were installed in twenty-six sites for a period of seven days. Ultraviolet-visible spectroscopy (UV/Vis) absorbance was calibrated with nitrite solutions and then used to determine the levels of NO₂ the monitors collected. Geospatial analysis displayed higher nitrogen dioxide concentrations with closer proximity to highways ranging from 6 to 21 ppb. No samples exceeded the United States Environmental Protection Agency's (EPA) standard of 53 ppb. Mann-Whitney U tests showed that concentrations measured \leq 400 m from major interstates were higher than concentrations \geq 400 m away.

Occurrence of arsenic pollution in airborne pm in the area of gran bilbao (Northern Spain)

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Arsenic pollution and its effect on human health has been reported worldwide [1]. Main anthropogenic sources are: metallurgic industry, combustion of fossil fuels, use of weed killers, and wood treatment products. Although not forming organic gaseous species when burnt, it is present in the air in the fine particulate matter (PM), where the burning of fossil fuels is the main source. In the atmosphere, As exists mainly absorbed on PM in the form of As(III) and As(IV). Target As daily average value set by the European Union for 2013 in air amounts to 6 ng/m³ [2]. Results indicate that airborne PM chemical and physical composition can significantly vary depending on location, period of the year and climatologic conditions. In this sense, occurrence, speciation and mobility of arsenic have received significant attention in recent years and, therefore, knowledge of factors affecting As occurrence in the environment is necessary. The present study covers a four-year period of sampling in two different sites in the area of Gran Bilbao, with more than 1,300 samples analysed, aiming to show the air concentration of PM₁₀, PM_{2.5} and As. Temporal variations of these pollutants are related to main gaseous pollutants (CO, NO₂, NO, O₃ and SO₂) and atmospheric conditions (temperature, relative humidity, wind direction and rain), considering topography and relative position of the main sources. Figure 1 shows the relative average concentrations of As, PM₁₀, CO, NO₂, NO, O₃ and SO₂ on site 1 (grey surface, city centre) and site 2 (white surface, industrial zone) in dry conditions as a function of the wind direction. In general, As values measured in both sites can be deemed as low, of a clear anthropogenic origin, and with a high temporal variability, although average values are not very different. In site 1, As is mostly associated to PM_{2.5} which, combined with the behaviour of the other measured pollutants, points to traffic, while in site 2, higher levels of PM₁₀ and SO₂ point to industrial-related origin, with at least two main sources contributing to the observed values.

The authors want to acknowledge the economic support of the Basque Government (Dpto. M.A., P.T., A. y P.) and the DFB/BFA (Project DIPE07/15).

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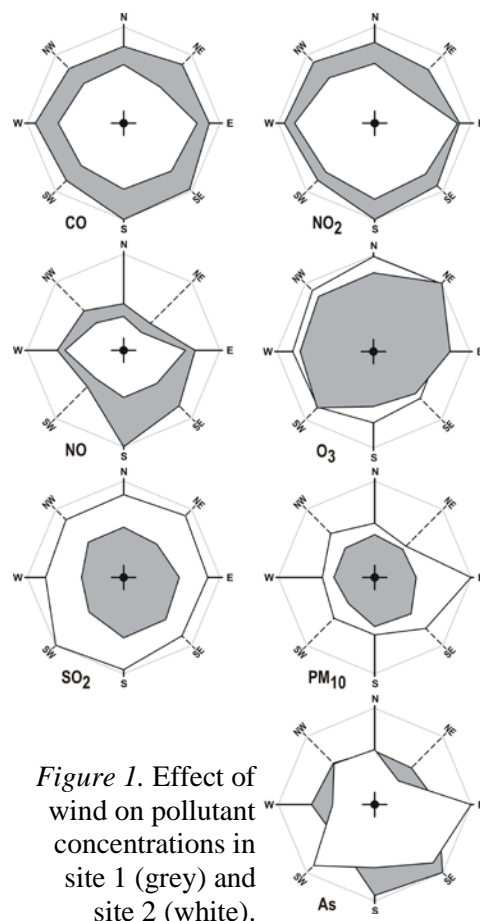


Figure 1. Effect of wind on pollutant concentrations in site 1 (grey) and site 2 (white).

The viable microorganisms of clouds

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Despite the enormous volume they represent and the importance they have for Earth's climate, clouds remain environments where the microbiological features are still obscure. Since 2003, we sampled and analyzed about 40 non-precipitating cloud events from the summit of the puy de Dôme Mountain (1465 m above sea level, France).

For investigating the participation of cloud's microflora to the chemical reactivity of clouds, we conducted microcosm experiments involving intact (non-amended and containing indigenous microflora) or filter-sterilized cloud water. Results demonstrated that both biological and photochemical activities are responsible for the net degradation of organic species in liquid clouds, with respective participations ranging from 0 to 100% depending on the chemical species. At global scale, conservative estimations suggest that bacterial cells living in cloud water could be responsible for the transformation of $\sim 10^6$ tonnes of organic carbon each year.

More than 200 strains of bacteria and 150 of yeasts were isolated from our cloud samples; they included members of Alpha-, Beta- and Gamma-Proteobacteria, Bacteroidetes, Firmicutes and Actinobacteria, and Basidiomycetous and Ascomycetous yeasts [1]. Interestingly a few genera largely dominated the pool of viable heterotrophic aerobic microorganisms: *Pseudomonas* and *Sphingomonas* in bacteria, which were detected viable in more than 40% of the clouds sampled, and *Dioszegia* and *Udeniomyces* in yeast, detected in more than 60% of the samples. The *Pseudomonas*-like isolates were screened for ice nucleation ability: 16% were found active at -8°C . Two of them could induce freezing of supercooled water at a temperature as warm as -2°C , positioning them among the most active ice nucleators described so far. In laboratory, we showed that the IN activity of *Pseudomonas* species is probably negatively affected in clouds by Human emissions (i.e., pH ~ 4 or less). Though their presence was suspected, this is the first evidence for the presence of ice nucleation active bacteria in clouds and it supports the bioprecipitation theory. In ecological aspects, the recurring presence of particular groups of microorganisms suggests that they elaborated strategies compatible with increased survival in the atmosphere and clouds, and that they are consequently likely to disseminate over long distances.

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Survival of microorganisms to the main stress factors encountered in clouds

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Microorganisms are present in low altitude clouds at concentrations of $\sim 10^4$ bacteria per mL and $\sim 10^3$ fungi per mL. The microbiological monitoring of cloud water since 2003 at the puy de Dôme station (1465 m a.s.l., France) revealed the presence of recurrent microorganisms among the cultivable bacterial community: *Pseudomonas* spp. and *Sphingomonas* spp. notably were present in 55% and 45% of the samples collected respectively, and they represented 30% of the total heterotrophic bacteria cultivable at 17°C [1].

Clouds represent nearly obligate ways to the redeposition of micrometer-sized aerosols such as microorganisms onto the ground. Even though they are believed to be less aggressive environments than dry air, clouds likely remain harsh and probably operate as environmental filters to airborne microorganisms through various selection factors: solar radiation, oxidants, low temperature, acidity, osmotic shocks... etc...

In order to test this hypothesis, we selected five bacterial or yeast strains isolated from cloud water (*Arthrobacter* sp. AJ551167 ; *Pseudomonas syringae* AB001440 and HQ256872 ; *Sphingomonas* sp. HQ256831 ; *Bullera armenica* JF706549). These strains were chosen to offer a good representation of the particularities of the culture collection (Gram-positive and Gram-negative bacteria, pigmented or not, ice nucleation active or not). In parallel, an *Escherichia coli* strain (ATCC10798) was chosen as reference as none was found viable among our cloud samples.

The survival rates of each of these strains to four factors of stress consistent with the conditions encountered in clouds were investigated: osmotic shock, which occurs when water vapour condenses or evaporates around airborne microorganisms, freeze-thaw cycles, presence of toxic compounds such as hydrogen peroxide, and solar radiation. The first results demonstrated that the strains originally isolated from clouds were not particularly resistant to these four treatments, compared with *E. coli*. Hence those selective factors are not sufficient to explain the composition of the viable community in clouds.

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Improving Water quality by using some Bulitant removals

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Water deficiency in arid region become an important issue and need special attention from researchers. Saudi Arabia has very low rainfall and the decline of ground water has increased annually. Due to the ignorance of farmer using high amount of fertilizer there has been found high amount of P in drain water. In this article various soil samples were used to study sorption of bulitant from draining water. The P adsorption was measured at 0-60 $\mu\text{g ml}^{-1}$. Most soil samples showed a high affinity for P sorption at low solution concentrations. At higher P solution concentration, P sorption was accompanied by a change in the slope of the isotherms. The higher P, the lower pH values were gained. The reduction in the final pH was related to the amount of P sorbed. The reference sample showed only a small adsorption capacity for P. Since the equilibrium solution background is CaCl_2 , the adsorption of P by minerals is that probably some of the exchangeable site occupied by Ca.

Evaluation and distribution of arsenic trioxide in seawater pollution scenario

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The maritime transport of chemicals substances has increased in the last decades due to the continuous development of the chemical industry and the need to transport in massive quantities. Accidental releases can occur as a result of natural disasters, human errors, or due to technical and mechanical failures in chemical transfer and storage equipment. When solids enter the marine environment various types of behaviour are possible. Substances can float on the surface, dissolve in the water column, sink to the bottom, or show combinations of these. The behaviour in the marine environment depends on the solubility and density of the released chemical substance as well as the interactions (equilibrium) to other compartments, i.e. sediments.

The present work evaluates the behaviour of arsenic trioxide in contact with seawater. Based on the physical properties of the inorganic compound and the mediterranean seawater conditions, it is possible to determine its distribution and fate into the seawater.

The experimental set-up was performed by using a vessel reactor with temperature and pressure control attempting to reproduce the sea conditions at laboratory scale. The rate constant of solubility was determined under different experimental conditions (pressure and temperature) and the maximum solubility was estimated as a function of the salinity concentration and the temperature. The kinetic and equilibrium sorption of arsenic trioxide on sediments were evaluated in view of the theoretical behaviour expected for this organic compound and its potential to sink and interact with bottom sediments. The Markov model was applied to predict the fate of the arsenic trioxide in seawater by taking into account the parameter previously determined.

Assessment of large industrial zone effect on element redistribution in soil profile

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This paper considers the anthropogenic impact on soil conditions caused by the activity of a large industrial zone under conditions of sharp extreme continental climate. Specific character of anthropogenic effect in this case is attributed to dust-gas emissions from large industrial enterprises into the environment. A small industrial city located 65 km north-west of Lake Baikal (Russia) as a model has been selected for testing methods on identification of industrial sources of pollution. The industrial and residential areas of the city are situated on the rather flat terrain. The main sources of anthropogenic emissions (95%) in the city are a large aluminum plant and a heating plant. Aluminum and sodium were chosen as contaminant indicators at the aluminum plant, and fuel vanadium and calcium at the heating plant working on organic fuel.

The aims of the work were to assess the impact of the large industrial zone on grey wood and meadow-chernozem soils taking into account their natural ability to self-purification and to identify sources of pollution. In our work we used and developed recent methods based on systematic analysis of transfer, transformation, and quantitative assessment of substances (pollutants) from air emissions to micro-vertical migration in the soil profile. Soil was sampled at the background site and in some areas under anthropogenic impact of different intensity level. The ICP-MS was used to analyze total composition and elements extracted with ammonium acetate solution (pH 7 and 5.5). Microelement migration patterns were studied in the micro-vertical soil profile. Behavioral trends of individual elements were determined in soil catena. The studies showed that natural downward current of all mobile elements (Ca, Na, V, etc.) occurs in all soil profiles sampled and pollutants (Al, Si, etc.) which are not involved in soil processes the accumulate in humus layers.

The analysis of soil cover showed that contamination is of local character and decreases significantly with distance from the source. The results obtained made allowed us to identify major sources of pollution and distinguish zones of maximal environmental load from a particular source in the study area. In further studies, it is planned to use these assessments and methods to predict changes in the environment in case of placement of large-scale industrial production for the territories of East Siberia.

Humates as transportation agents of surfactants and amino acids

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According to the modern viewpoint humic substances are considered as sets of various and relatively low molecular mass components that form dynamic associates stabilized by hydrophobic interactions and hydrogen bonds [1, 2]. Salts of humic acids have been found to reveal surface activity in aqueous solutions decreasing surface tension of water, and humates may be considered as anionic surfactants of natural origin. The possibility of their self-organization into micellar structures in aqueous media can be proved by the methods used to study conventional surfactants i.e. tensiometry and conductometry. Surface tension isotherms permit to determine critical micelle concentration, conductivity polytherms allow to find the minimal temperature at which the micellization becomes possible (Krafft point). Furthermore, the colloid-chemical characteristics can be used to study interactions in mixtures of humates with surfactants, amino acids and other components.

The aim of this work was to study colloid-chemical properties of humates in aqueous solutions and to investigate interactions in mixtures of humates with some conventional surfactants as well as with some amino acids in particular with lysine.

Salts of humic acids extracted from soil, coal and peat were investigated. Surface tension isotherms were obtained by the Du Noüy ring method. Conductometry and UV-spectroscopy were also used. Surface tension isotherms and conductivity polytherms were found to demonstrate the same character as those for conventional ionic surfactants. The self-organization (micellization) of the humates in aqueous media can take place at the concentration more than 0,5% and the temperature above 44-48 °C, that is higher than vegetation temperature.

On the base of surface tension isotherms and UV-spectra the binding of components in binary mixtures containing lysine and humates has been revealed. The formation of the lysine/humate complex has been investigated; its composition and colloid-chemical characteristics have been determined. The addition of lysine to the humate solutions was shown to decrease the colour intensity of the solutions and to increase the solubility of the humate as well as to reduce the Krafft temperature (33°C). It appears that the binding of the components is due to a change of conformational structure of humates.

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Isomers of hexachlorocyclohexane in water and sediment of the Elbe and Mulde River

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Isomers of hexachlorocyclohexane (HCH) are a relevant group of contaminations in the Elbe River. Past industrial production and disposal of undesirable side products resulted in highly contaminated areas, in particular in Bitterfeld-Wolfen region. Any discharge from these numerous point sources had a high impact on the water and sediment quality not only of the direct affected surface water systems, the Spittelwasser River, and the adjacent Mulde River, but also to the Elbe River. Although industrial activities have been stopped 25 years ago, a continuous emission of HCH to the river systems is evident. Acute risk is present especially during flood events, where remobilized contaminated particulate matter is distributed not only along the river but also transported to terrestrial compartments. Interestingly, the isomeric pattern in samples of the Elbe River sediment differs considerably from the industrial mixture, shifting the dominance to the β -isomer. Hence,

This study focuses on the environmental processes, which change the isomeric composition of HCH, and on the understanding of isomer-specific distribution, transport and transfer processes. For these purposes several transfer process experiments in the systems water-sediment, water-biota and sediment-biota have been created and performed to investigate the isomer specific HCH behavior related to transformation, mobility, accumulation and magnification. Experiments were performed to follow isomer and enantio-specific distribution on water and sediment samples. In addition to this laboratory experiments, analyses have been conducted on natural systems of the Mulde River drainage basin to verify these findings under natural conditions.

Specific results will be discussed in detail with regard to the behavior of HCH isomers in riverine areas.

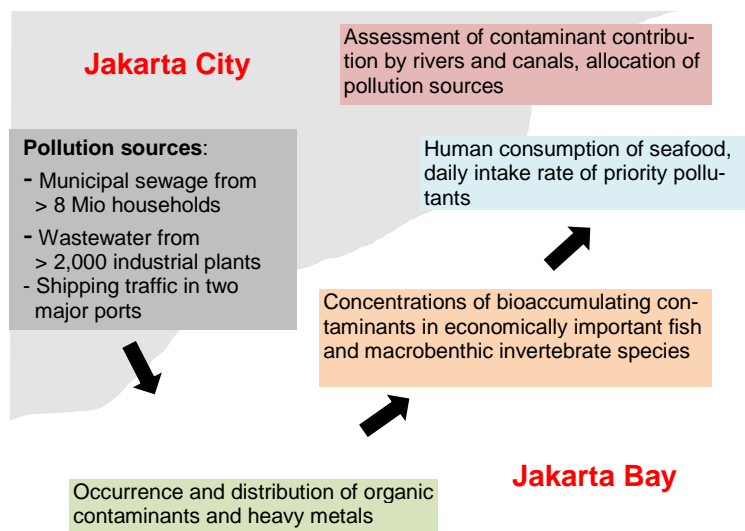
Sources and risks of organic contaminant and heavy metal burden in seafood from Jakarta Bay

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Seafood is the main protein source and an important income basis for many local communities in coastal areas of Indonesia. But seafood consumption is also an important route of human exposure to contaminants. Commercially important fish and benthos species from densely populated and industrialized coastal areas with inputs of untreated sewage such as Jakarta Bay may contain potentially harmful organic contaminants and heavy metals in levels which are exceeding international safety thresholds. This is probably posing a risk to human health, in particular with respect to bioaccumulating contaminants. It is therefore necessary to evaluate the quality of seafood from such Indonesian coastal systems in terms of contaminant burden.



The aim of this project is a *source-to-cell* approach to state of pollution in Jakarta Bay and its implication for human food resources. It traces the implications of harmful substance loads from their primary emission sources via food chains to the consumed seafood.

The project is based on previously extended organic geochemical analyses applied on sediments, water and biota samples from the Segara Anakan Lagoon in Indonesia. This first study exemplified the usefulness of a more comprehensive ana-

lytical approach for reflecting the state and dynamic of pollution and its possible implication for anthropogenic usage of local natural resources [1]. It revealed an individual description of the lagoon pollution and the uptake of relevant substances by benthic species. Beside relevant priority pollutants (e.g. PCBs and selected PAHs) in particular new emerging contaminants were identified (e.g. triphenylphosphine sulfide), that were observed to bioaccumulate in mangrove macroinvertebrates and fishes.

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Heavy metals in structure components of cryometamorphic soils in forest-tundra ecotone

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The aim of the research is to assess heavy metal (HM) content in the structure components of the soil mass such as inner aggregate mass (IAM) and skeleton (SK). Studied cryometamorphic soils are formed in the northern forest-tundra subzone under tundra vegetation. For the total soil mass and its structure components heavy metal contents (Cu, Pb, Cd, Zn, Co) have been determined at accredited laboratory “Ecoanalit” of Institute of biology Komi SC UB RAS.

Study showed that virgin cryometamorphic soils are characterized by average and low content in Cu (7.4-16.0 mg/kg) and Zn (25-47 mg/kg), average content in Pb (6.4-14.0 mg/kg), higher concentrations of Cd (0.23-0.36 mg/kg). Revealed variables are not higher than MAC (approximate permissible concentration) for acidic loamy soils. In the soils content in Co ranges between 5.1 mg/kg and 11 mg/kg which is 1-2.2 MAC.

There is a predominant HM accumulation in IAM with concentration 1.4-2.2 higher as compared to SK in cryometamorphic soils. Profile distribution pattern of trace elements (Zn, Cu and Co) is quite identical. There is a relatively equal Co distribution and gradual decrease in Cu and Zn content in IAM down the profile. At gleyic CRMg horizon skeleton is impoverished by these elements and relative accumulation of elements are noticed in underlying cryometamorphic CRM1 horizon. According to Pb content the structural components are almost undifferentiated except for CRMg horizon where a higher content in IAM (14 mg/kg) and lower content in SK (6.4 mg/kg) are revealed.

The study is supported by Program of UB RAS, project No 12-T-4-1006 “Ecological quality of reference soils in the European North-East of Russia and soil bioorganic potential as a criterion of soil productivity and protection in the background of the being prepared Soil Red List for the Komi Republic”.

Chemical palaeomonitoring of lake ecosystem

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Sediments are the unique natural sources of information on genesis of lakes and dynamics of their development for an appreciable length of time. In world practice such approach becomes more and more popular and used at monitoring researches of water objects. More often such approach use for definition of background maintenance of elements in ground deposits and an assessment of extent of anthropogenous impact on water objects. However, in our opinion, the number of received information can be expanded at a comprehensive approach to research of ground deposits. Studying of level-by-level distribution of elements and substances, and also forms of their stay in ground deposits of lakes, dating of layers and feature of grain size, will allow to expand considerably number of paleoecological and paleoclimatic information on conditions of formation of layers. Combination of chemical methods with biological methods will allow to increase reliability of received information.

For the solution of this problem we selected and studied columns of ground deposits of two lakes (Langatibeyto and Goltsovoye), located in a tundra zone of the Tyumen region (the peninsula of Yamal and the Gydansky peninsula, respectively).

The selected columns were divided into layers with a step of 1 cm, led up at room temperature to an air and dry condition, sifted through a sieve set for definition of dynamics of grain size of ground deposits in process of their formation

The received results allowed to reveal some regularities of formation of ground deposits in these climatic conditions. The grain size of ground deposits of Langatibeyto and Goltsovoye Lake on different depths has similar character: absolute prevalence of particles with the sizes 100-200µm (from 40 to 70 % and from 20 to 90 %, respectively) is observed. Fractions with the sizes of particles of 50-80 microns (10÷30 are considerably presented to %) and 80-100 microns (10÷28 in %) in both lakes. The maintenance of other fractions doesn't exceed 5-10 %.

The average content of organic substance in ground deposits of lakes are quite close, that it is impossible to tell about regularities of their distribution and forms of finding of carbon and nitrogen on depth of a column.

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The objects and methods for atmospheric monitoring

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The state of environment of the large cities is usually estimated on a condition of its separate components: atmospheric air, surface and underground water, soils and vegetative cover, health of citizens. The most dynamic and consequently the most difficult for the analysis is the atmosphere which makes essential impact on a condition of all components of an ecosystem. For monitoring of the atmosphere it is possible to use various objects and analysis methods, each of which has the restrictions and advantages. It is more rational to use other objects of the analysis which allow to carry out seasonal (snow, leaves), multiannual (on rings of trees) and centuries-old monitoring (on riding peatlands, ground deposits). Such variety of objects of the analysis allows to solve various problems of monitoring with different extent of integration of results, their relative independence. The purpose of our work was development of a comprehensive approach to monitoring of atmospheric air with use of various objects of the analysis and any extraction of information on a condition of the atmosphere and components polluting it, sources of their receipt and distribution area.

The carried-out researches showed that an objective indicator of quality of atmospheric air in the city during the winter period of time is the maintenance of various pollutants in snow cover. Concentration of polluting substances in snow on 2-3 orders is higher, than in atmospheric air, measurements of the content of substances can be made by rather simple methods of the analysis, and the easy sampling which is not demanding the special difficult equipment, does a method snow surveys to even more universal. Thus it is necessary to analyze separately a firm and liquid phase of snow since the number of information on an atmosphere condition thus considerably increases and there is a possibility of an assessment of forms of migration of elements. The use of the chemical analysis of snow cover allows not only to estimate total and relative impurity of air in the city, but also to estimate existence of sources of pollution and area of their influence. Integrated approach of researches allows considerably will expand possibilities of monitoring of a condition of the atmosphere.

** The research work is executed with financial support of the Ministry of Education and Science; the Project of Tyumen State University on implementation of the Resolution of the government of the Russian Federation No. 220.*

Cesium adsorption by synthesized zeolites prepared from coal fly ash

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Fly ash represents massing power waste with high content of reactive materials like aluminosilicates with high specific surface area that make from it an attractive material for zeolite synthesis. In this study, two types of synthesized zeolite (SZ1 and SZ3) were obtained by hydrothermal treatment of fly ash coming from power station Nováky - ENO (Slovak Republic). Prepared zeolites were investigated as a potential sorbents for the removal of Cs^+ ions from aqueous solutions using radiotracer technique. Batch experiments were applied to evaluate the influences of initial cesium concentration, initial pH value and contact time on the efficiency of cesium uptake. By application of fly ash and both types of zeolites we observed that Cs^+ sorption was 286 times higher in case of SZ1 and 333 times higher in case of SZ3 in comparison with non-modified coal fly ash (Fig. 1).

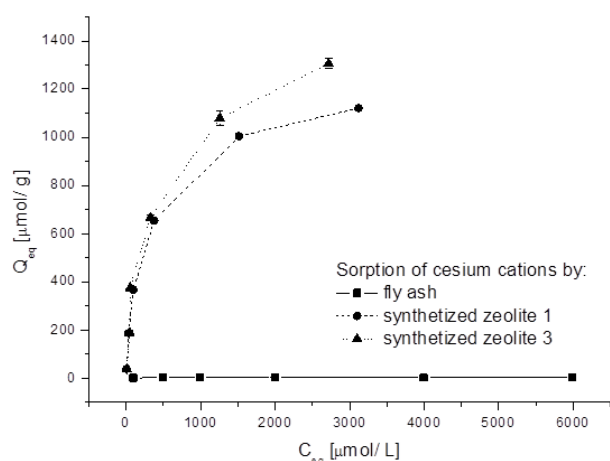


Fig. 1. The equilibrium sorption of Cs^+ cations by: (■) fly ash, (●) synthesized zeolite 1 and (▲) synthesized zeolite 3 (4 h, 22 °C and pH 6.0).

The sorption process was found to be rapid reaching equilibrium within 5 min at 22 °C with maximum at pH 5.0 - 6.0. Using of Akaike's information criteria we found that the sorption of Cs^+ ions by both types of zeolites obeys Langmuir adsorption isotherm model. The maximum sorption capacities Q_{max} at pH 6.0 calculated from Langmuir isotherm were $1177 \pm 49 \mu\text{mol Cs}^+/\text{g}$ of SZ1 and $1379 \pm 108 \mu\text{mol Cs}^+/\text{g}$ of SZ3.

Surface properties of studied sorbents and mechanism of sorption process were determined using different techniques and methods including X-ray diffraction (XRD), scanning electron microscopy coupled with energy dispersive X-ray analysis (SEM-EDX) and also determination of cation exchange capacity (CEC).

Chemical composition of grape stalks and coffee wastes. Role of the different compounds in Cr(VI) removal

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Grape stalks and exhausted coffee have shown to be effective in Cr(VI) reduction and sorption from aqueous solution [1,2]. Even though the optimum conditions for metal removal and reduction to Cr(III) are well known, compounds involved in both processes are not well established. In this work, a chemical characterization of grape stalks and coffee wastes was carried out to determine the role of the different compounds in chromium removal.

Chemical summative analysis of non-polar and polar extractives was carried out by using dichloromethane, ethanol, water and 1% NaOH solution. After each extraction the extracts were analyzed to determine their major components (fatty acids, aliphatic chains, total polyphenolic compounds and condensed tannins). Klason-lignin, soluble lignin and polysaccharides were analysed from the free-extractives materials. From the ashes of the materials, elemental composition was determined.

Results show that grape stalks chemical composition is 58.7% extractives, 14.4 % of lignin and 27.5% of polysaccharides. On the other hand, coffee waste contains 51.43% extractives, 26.51% of lignin and 22.0% of polysaccharides. Grape stalks and coffee wastes have an ash content of 4.45% and 0.52%, respectively.

To determine the role of the different compounds of grape stalks and coffee waste in chromium sorption and reduction, raw materials and the extracted solids after each extraction step were put into contact with Cr(VI) solutions at pH 2 and 3. Cr(VI) and Cr(III) concentration at equilibrium were determined to evaluate the extent of Cr(VI) reduction and sorption. Results showed that the removal of extractives from grape stalks and mainly condensed tannins are the responsible for the reduction and removal of Cr(VI). Conversely, Cr(VI) reduction and sorption by exhausted coffee seems not to be affected by the removal of extractives.

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Degradation of fluoroquinolones used in aquaculture

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The increasing demand for seafood and the depletion of wild fish stocks has led to a remarkable growth of aquaculture industry. This sector supplied about 46% of the world's fish food for human consumption in 2008¹. Aquaculture facilities often rely on the heavy input of formulated feeds, antibiotics, antifungals and/or agrochemicals² intended to increase the productivity of the aquatic organisms beyond the natural capacity of the environment¹. Since a significant fraction of the administrated antibiotics (up to 75%) end up in the surrounding environment, a special attention should be given to these chemicals. A close collaboration between research laboratories and fish/seafood producers might improve the sustainability of this industry by developing optimal environmental conditions, appropriate animal feeding and effective prevention of infectious diseases.

The current study is a part of the European INNOVAQUA³ project, which involves academic and private partners from Italy and Slovenia. The investigations focus on i) a better comprehending of the environmental fate of antibiotics used in aquaculture and, ii) the development of water treatment processes adapted to the needs of fish farming. Since they are commonly used in aquaculture, antibiotics belonging to the (fluoro)quinolone family have been chosen as model compounds in this study. The preliminary results deal with ciprofloxacin (CPF) and flumequine (FMQ) aqueous solutions (20 mg L⁻¹). The natural degradation of the antibiotics was monitored in a Suntest XLS+ apparatus simulating the sunlight. The photolysis under UV-A and UV-C light was performed in a circular photoreactor previously developed in the laboratory. In order to evaluate the efficiency of the TiO₂ photocatalysts on the removal of the antibiotics, a suspension of TiO₂ nanoparticles was added to the solutions. The analysis of the samples was carried out on a spectrophotometer and HPLC equipped with DAD and FLD detectors. A kinetic constant of $1.85 \times 10^{-3} \text{ min}^{-1}$, corresponding to a half-life of about 6 h, was found for the natural degradation of FMQ (250 W m⁻²). The presence of TiO₂ suspension in solution resulted in 11-fold enhancement of the degradation of FMQ. A similar behaviour was observed for CPF. The results regarding TiO₂ photocatalyst are encouraging and give promise for the complete elimination of the degradation products (non-identified yet). Further studies will focus on the toxicity of the samples as well as on the degradation of the antibiotics adsorbed on sediment.

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Physicochemical characterisation of surfactant modified activated carbon

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Adsorption techniques employing solid sorbents are widely used to remove chemical pollutants from waters. In the present work a commercially available activated carbon F400 (AC) was chemically modified. Anionic surfactant sodium dodecylsulphate (SDS) and cationic surfactant hexadecyltrimethylammonium (HDTMA) were used to modify surface of activated carbon.[1] Three sorbents were prepared, namely AC, SDS-AC and HDTMA-AC, respectively. Physicochemical characterisation was carried out for raw and modified samples by several techniques such as thermogravimetric analysis, N₂ adsorption-desorption isotherms obtained at 77K (BET surface area, pore volume distribution) and batch experiments for the adsorptive removal of lead and methylene blue. The later served to obtain kinetic and equilibrium data for the prepared sorbents. Besides, in order to elucidate the pores available for each solute, raw and modified AC samples with the maximum solute loading amount over the tested concentration ranges were prepared for N₂ adsorption measurement. TGA results indicate that the applied modification procedure ensured that about 0.20 and 0.22 mg of HDTMA and SDS, respectively, were effectively attached per milligram activated carbon. Both raw AC and SDS-AC samples adsorbed about 90 µmol MB/g AC, whereas HDTMA tailored sample had a slight reduction of 17% on its equilibrium uptake capacity (75 µmol MB/g AC). Regarding Pb adsorption performance, the monolayer adsorption capacity of the AC was increased from 123 µmolPb/g for the unmodified AC to 274 µmolPb/g for the SDS modified AC, what represents a 122% increase in adsorption capacity. This uptake capacity can be deemed high compared with others reported in the literature.[2] Also, preliminary nitrogen isotherms data of exhausted sorbents revealed that micropore volume of three prepared adsorbents was attenuated markedly after adsorption of MB and Pb what indicates that surfactant impregnation did not block utilization of microspores. Further analyses are in progress. The obtained data will allow identification of any exclusion effect among utilized surfactants and pollutants (MB and Pb) and the effective usage of the pore distribution.

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Electrochemical disinfection of water by using stand-alone photovoltaic power system

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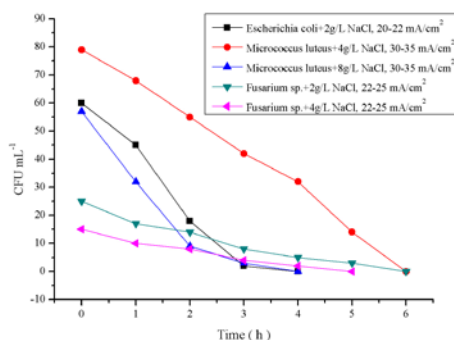
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Electrochemical disinfection has gained increasing attention as an alternative for conventional water treatment due to its high effectiveness and environmental compatibility. The most common method of electrochemical disinfection is the use of electro-generated oxidants, such as active chlorine and reactive oxygen species, as disinfectants.

Stand-alone photovoltaic systems are designed to operate independent of the electric utility grid; it is without battery to store electrical energy system. Energy is used immediately, and combined with electrochemical disinfection it enables pre-treatment or treatment of water in remote places such as for swimming pools, water reservoirs, basins, tanks, dam etc.

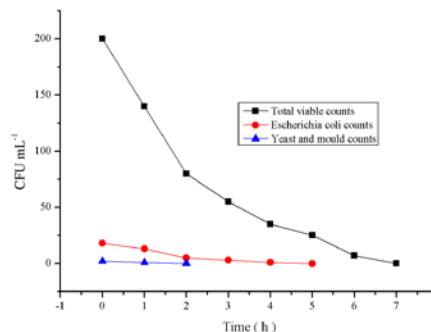
Laboratory experiments were carried out to investigate the disinfection effect of stand-alone photovoltaic system (RICH SOLAR, RS-M20, 12 V, 20 Wp) conjoined with electrochemical processing (2 x 11,017 cm² carbon electrodes) on 5 L artificial water contaminated by monocultures of microorganisms *Escherichia coli*, *Micrococcus luteus*, *Fusarium sp.* (A) or microorganisms in natural surface water from the dam (B). In examined water was disinfection effect monitored during electrochemical processing by using the classical plate method with counting of the number of colonies formed units (CFU).

The results of these experiments conclude that electrochemical disinfection with stand-alone photovoltaic power system can be effective to water treatment.



A

Counts of CFU during electrochemical disinfection of pure water with the addition of chlorides contaminated by monocultures of microorganisms



B

Counts of CFU during electrochemical disinfection natural surface water from the dam without the addition of chlorides, current density 6-8 mA/cm²

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Assessment of synthetic musk compounds in waste waters

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The synthetic aromatic substances are present in the products of daily use, in personal hygiene, cosmetics, soaps, detergents, cleansing articles, etc. After the application these compounds are drained away into the waste water. The technological process used in waste water treatment plants is not able to eliminate these substances completely and their residuals influence the environment. So-called musk compounds create significant group of synthetic fragrances which are distinguished by specific fragrance reminiscent of musk. Recently great attention is devoted to musk compounds because they were found in different environmental compartments [1,2,3].

The aim of this study is the determination of four selected linear musk compounds (2-cyclohexylethanol, Fresco Menthe, Citronellol and Isobornyl acetate) in the waste water. The real samples were taken on the place of influent of the sewage discharge and on the place of the effluent from the sewage plant in the University of Veterinary and Pharmaceutical Sciences Brno. Another group of linear musk compounds (Arocet, Aroflorone, Linalool 925, Lilial, Isoamyl salicylate) was analyzed in real samples of waste water in the influent and effluent from the waste water treatment plant Brno-Modřice. Set of musk compounds produced in AROMA joint stock company, Židovice, Czech Republic, were selected as target compounds. On the basis of measurements and subsequent evaluation of obtained data it was possible to express the efficiency of the elimination of linear musks from waste water.

At first it was necessary to adapt the selected analytical method to the physical and chemical qualities of the selected analytes. The optimization of selected method was performed and then this method was used for analysis of real samples. The analytes were extracted from the samples by the method of the Solid Phase Microextraction (SPME). Comprehensive two-dimensional gas chromatography with mass spectrometric detection makes the identification and quantification possible. Therefore, we can claim that linear musk compounds will continue to replace more problematic nitromusk and polycyclic musk compounds significantly.

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Cr(VI) removal by exhausted coffee from binary mixtures (Cr(VI)-Cu(II))

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Exhausted coffee has been proved to be effective to reduce Cr(VI) and remove the metal ion from single metal solutions [1]. Nevertheless, in real situations more than one metal ion are present in solution and interactions between them occur. In this work Cr(VI) removal from single and binary mixtures Cr(VI)-Cu(II) has been investigated to assess the interactions between copper and chromium and their effect on chromium reduction and removal.

Experiments have been carried out in a stirred batch reactor. For all experiments a mass of 27 g of exhausted coffee (particle size 0.50-1.0 mm) were added to a volume of 4 L of Cr(VI) single metal ion or binary mixtures Cr(VI)-Cu(II) solutions at pH 2.0 and 3.0 into a reactor under constant agitation (125 rpm). In binary mixtures, metal ions concentration was varied within the range 0.2-0.8 mM in order to get a total metal ion concentration of 0.8 mM.

Sampling was performed at predetermined intervals of time to determine Cr(VI), Cr(III) and Cu(II) concentration in order to get the metal ions sorption kinetics profile in each of the studied single and binary mixtures.

Results put into evidence that total chromium removal was not affected by the presence of Cu(II) in any of the binary mixtures tested. Nevertheless, the presence of copper resulted in faster Cr(VI) reduction and removal. This catalytic effect becomes more evident at pH 3.0 for the binary mixture 0.6 mM Cu(II)-0.2 mM Cr(VI). It must be remarked that in the range of Cr(VI) initial concentrations tested the residual chromium was in its trivalent form. Furthermore, it was found a linear regression between Cr(VI) initial concentration and metal adsorbed at equilibrium.

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Recovery of selenium-containing wastes and middling products of the gas-cleaning system in copper-nickel production

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It is known that both the wastes and middling products of the gas-cleaning system of the copper-nickel production contain numerous impurities, including toxic ones. Ineffective recovery results in losses of valuable materials and environment pollution. Recently become the considerable volumes of unconditioned solutions are directed to neutralization and dumping, and solid-phase middling products are stored or buried.

At the same time, selenium-containing products may become an alternative source of marketable selenium, in addition to electrolysis slime.

The experiments were performed on scrubbing sulphuric acid solutions, flue duct condensates and selenium cakes of the Kola MMC gas-cleaning system. By the developed flow-sheets, primary concentrates and marketable products can be obtained; purified solutions can be used in the mainstream manufacturing technology.

There has been developed a method providing the extraction of selenium from scrubbing sulphuric acid solutions and flue duct condensates and involving cementation on a copper-containing reagent. By this method, the selenium content in solutions is diminished to almost 0.1-0.2 mg/L, which allows to return the solutions to the mainstream technology and obtain selenium-enriched concentrates. Introducing the cementation purification at Severonikel combine has resulted in diminishing of the volumes of dumped scrubbing sulphuric acid and eliminating the discharge of highly-acidic condensates from the process cycle.

The possibility of in-depth processing of selenium cakes was studied on the gas-cleaning systems of Severonikel and Pechenganikel combines. We proposed some regimes of hydrochemical concentration to increase the selenium contents and separate the selenium base from the bulk of impurities, as the result of which it becomes economical to jointly process the cakes differing in chemical composition. The selenium obtained by sulphite processing of the concentrate met the “technical-grade” (GOST) requirements. There have been optimized conditions for selective leaching and sorptional concentrating of silver on a Purolite S920 chelate-forming cationite. By using mass-spectrometry, the noble metal distribution was analyzed. Noble metals were found to concentrate in the sulphite leaching residue yielding a nickel-containing concentrate.

To summarize, our studies have allowed to propose methods for recovery of selenium-containing solutions and solid-phase middling products for further processing within enterprises, and by that to prevent their removal from production cycle and environment pollution.

Application of the interpolmer complexation method for wastewater treatment

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The problem of the influence of pulp and paper industry (PPI) on the status of aquatic ecosystems is multidimensional. To solve it requires on the one hand, the improvement of technological processes, and on the other - the development of effective water treatment systems, taking into account environmental requirements. Mills producing sulphite (bisulfite) pulp characterized of wastewater that contain a significant amount of lignin impurities, which complicates the biological wastewater treatment. And since the latter decomposes almost lignosulfonates (LS) is a large part of them dumped in the water. Exacerbate the severity of the volume wastewater containing these pollutants - 60 - 800 m³ per ton of pulp. Currently, many mills reduced selection of liquors on evaporation, or they are not concentrated. Discharge of black liquor in natural waters greatly increases the chemical oxygen demand (COD) in them and violates the ecological balance.

Study of removal of lignin-containing compounds by complexation of the main pollutants of PPI wastewater in order to convert them into insoluble complexes will increase the efficiency of wastewater treatment and reduce water pollution. The resulting sediment - complexes are organic materials that can be used: to obtain sorbents for heavy metals; as a component of artificial soil for reclamation of lands disturbed anthropogenic impact; as a fuel with high calorific value.

We have shown that the anionic polyelectrolyte (PE) LS-Na capable of intermolecular interactions with oppositely charged cationic PE polyethylenepolyamine (PEPA) with the formation of polyelectrolyte complexes, stabilized by electrostatic, hydrogen bonding and by Van-der-Waals forces. Model experiments on the deposition of LS with PEPA were carried out on aqueous solutions of LS-Na with a concentration of 1-10 g/l and the addition of the polyamine in various mass ratios $Z = \text{PEPA} : \text{LS-Na}$ from 0,001 to 1. In this case $Z = 0,1$ closest to equimolar in terms of the content of ionogenic groups of PE involved in coordinating the formation of the complex-precipitate. In all the studied concentrations of LS-Na and the ratio Z the degree of removal of LS-Na by dint of polyamine is 60 - 95%.

The developed method was applied to wastewater treatment and tested on real LS - containing wastewater of branch of the "Ilim Group" in Koryazhma. Samples of wastewater were taken at three points. For each sample of wastewater treatment was carried out by complexation. In the initial and treated wastewater by standard methods determined the qualitative characteristics: color, COD, the content of LS-Na. The experimental results obtained in the process of wastewater treatment, in general, correlate with the data of model experiments and although the degree of precipitation of LS from model aqueous solutions increases from $Z = 0,1$ to 1, but the qualitative characteristics of the treated wastewater for $Z > 0,1$ worsen. Thus, the optimal addition of polyamine should recognize the relationship $Z = 0,1$.

The resulting wastewater treatment by complexation quality changed as follows: the content of LS-Na decreased an average of 20 times, color has decreased in 10 times, and COD decreased by 30%. The proposed method of wastewater treatment with PEPA can be used as the stage of local treatment of LS - containing wastewater to reduce the load on the biological treatment plant.

Ecological and economic evaluation of metallurgical dust emitted from the Kola MMC

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Pyrometallurgical processing of sulphide copper-nickel minerals is accompanied by discharge of different kinds of metallurgical dust. The finest dust fractions may differ from the feed to a great degree due to concentrated volatile impurities. Most frequently, the ferrous and non-ferrous metallurgical dusts contain much zinc and lead, which creates problems with the dust processing and contaminates the environment. Besides, some of the non-ferrous dust may contain rare metals.

To determine the chemical composition of the Kola MMC dusts, we selected samples from electric filters of the Pechenganikel smelter and the Severonikel metallurgical shop (Kola MMC) for analysis of non-ferrous, rare and noble metal contents. The elements were identified after microwave pressure digestion (MWS 3+ and SW4, BERGHOF) using the methods of mass-spectrometry, atomic absorption and atomic emission spectrometry at ELAN 9000 DRC-e, AAnalyst 400 (Perkin Elmer), ICPE 9000 (SHIMADZU) devices.

It has been shown that the dusts most differing in composition from the furnace feed come from the smelter. They contain little copper and nickel but much lead (3-5 %), arsenic (2-5%) and zinc (1-3%), and also a series of rare elements with the following contents, g/t: Se – 1700; Te- 2900; Cd- 1200; Tl- 286; Re – 57; Mo – 78; Ge – 160. It is clear that the dusts contain considerable amounts of valuable rare elements. Calculations have shown that the value of rare elements in the dusts exceeds that of non-ferrous metals in the feed. However, the dusts still remain unprocessed but returned to the process or dumped to the stockpile with the purpose of removing Zn and Pb. The Severonikel dust, though enriched in nickel and copper, contains fewer rare elements. Moreover, the nickel process dust contains silver in contents of up to 1 kg/t in some of the samples. The dusts resulting from the nickel concentrate sintering were ruthenium-enriched (up to 60 g/t).

Since some of the pyrometallurgical dust remains unpurified, its emissions continue polluting the environment with heavy metals. What is needed is both capturing the dust by introducing more efficient technologies and processing it with extraction of rare and noble metals to target products.

At the moment, we have developed and tested on a pilot scale several processes to extract silver and rhenium as concentrates and compounds. Evidently, introducing these technologies and developing new ones for extraction of such elements as thallium, arsenic and cadmium, would both increase the cost of the entire commercial output of a plant and prevent the environment pollution with highly toxic elements.

Recycling of spent sulfuric acid of sulfuric acid alkylation isoalkanes with alkenes obtain commercial products

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Oil refineries and petrochemical industry are the sources of large-waste, a large share of which is sulfur-containing waste, including spent sulfuric acid alkylation process isoalkanes with alkenes.

Methods for recovering and recycling waste sulfur thermal, physico-chemical, chemical methods are associated with the complexity of design process, the formation of by-products and waste, large economic costs of these processes.

It is an urgent task today to develop new methods for recycling and disposal of waste sulfur oil, and optimize existing ones, and also involving them as raw material sources in the processes of production of commodity products.

Thereupon, the possibility of H_2SO_4 involvement in the preparation of sodium sulfate and ammonium sulfate, with the release of the organic component was researched.

The experiment was carried out by varying the basic parameters of the ratio of " H_2SO_4 : Base" as a base to use 10% of the masses NaOH solution and 25% by weight NH_4OH , temperature and pH of the reaction mixture.

Extraction of organic contaminants was carried out by polar solvents containing functional hydroxyl and ketone groups. The reaction was spontaneously separated into two layers: the bottom - a saturated aqueous solution of salt (or crystalline precipitate, or a saturated aqueous salt solution with precipitation of crystalline salt) and the upper - a mixture of the organic component of waste sulfuric acid and extractant. The top-layer extractant removed at a certain temperature and recycled. From a saturated aqueous solution of lower layer salt precipitate separated.

Found that the yield of salt, and also the shape of its output (crystals or a saturated aqueous solution) are dependent on the solvent and the mass concentration in the reaction mixture.

It was demonstrated here the possibility of using the organic component in formulations for oil displacement, industrial cleaning agents and as additives to increase aggregate stability in fuel compositions, as it is composed of up to 23% by weight sulfonic acids having surface-active properties.

Stability and toxicity of selected sun protective compounds in disinfection processes

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The usage of different solar blocking personal care products to prevent the risk of skin cancer development is increasing constantly. These products contain various protective compounds, which are relatively stable when exposed to UV radiation. However, if they are used under certain special conditions, they might decompose by light or may react with the disinfection agents, such as those commonly present in pools.

In the present research, selected benzophenones (BP-3, BP-4, DHHB) were applied as model compounds for the stability and toxicity studies of UV filters in presence of chlorine-based disinfectants such as NaOCl or trichloroisocyanuric acid (TCCA). The results showed that BP-3 and BP-4 react with NaOCl and TCCA, in both cases mainly two chlorinated products, 5-chloro and 3,5-dichloro derivative, were identified. In the chlorination experiments of DHHB treated with the same reagents, we observed very fast reaction, leading to the formation of 3-chloro derivate of DHHB, as well as other at the moment unidentified products. Chlorinated products were determined by HPLC and compared with independently prepared standards. For identification of chlorinated products GC-MS and LC-MS were applied.

Toxicity testing with luminescent bacteria *V. fischeri* was performed. Results revealed that DHHB caused 20% of inhibition in the luminescence of bacteria within 30 minutes of exposure and 30 min EC₂₀ value was 0.96 mg L⁻¹.

In addition to *V. fischeri* toxicity testing, aqueous solutions of DHHB (as analytical standard or 'in-house' synthesized product) and its possible chlorinated derivatives (3-chloro and 5-chloro DHHB) were tested for possible adverse effects on microalgae *Selenastrum capricornutum* (*Pseudokirchneriella subcapitata*) and microcrustacean (*Daphnia magna*). Obtained data demonstrated that algae were more sensitive to DHHB than to its chlorinated products with an EC₅₀ (72 h) for DHHB of 0.011 ppm (analytical standard) and 0.068 ppm (for 'in-house' synthesized). On contrary, *D. magna* was affected more by DHHB's chlorinated products, especially 3-chloro DHHB with a EC₅₀ for 24 and 48 h of 0.89 and 0.38 ppm, respectively. In general, algae resulted more sensitive to DHHB-mediated action compared to tested microcrustacean.

Potential estrogenicity and toxicity of BP3, BP4 and chlorinated BP3 product (5-chloro BP3) to different aquatic species from different taxonomic groups were studied. Toxic effects of UV filters were studied on bacteria *Vibrio fischeri*, algae *Desmodesmus subspicatus*, water fleas *Daphnia magna* and zebrafish *Danio rerio*. We found that UV filter BP3 was more toxic than BP4; the highest sensitivity was observed when water fleas *Daphnia magna* and algae *Desmodesmus subspicatus* were used as test organisms. BP4 revealed adverse effects on aquatic organisms only at concentrations of some tens milligrams per liter. The acute toxicity of chlorinated product (5-chloro BP3) did not increase significantly in comparison to BP3; increased toxicity was found only in a case of algae. The results of YES assay showed no estrogenic activity of both tested UV filters and chlorinated product.

Determination of concentrations of estrone and estradiol in *Rana/Pelophylaxperezii* males, by RIA

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In last years, has been increased the concern about health of aquatic fauna living in waters containing dynamic levels of estrogenic compounds, in part responsible for disruption of reproduction and development in some wildlife populations, altering blood hormone levels, reducing fertility and fecundity, masculinisation of females and feminization of males [1,2]. Low-level exposures also cause similar effects in human beings. However, the information of impacts of estrogenicity on wildlife populations is limited to a few species of animals, including some vertebrate and invertebrate. So, is fundamental more knowledge of the impact of estrogens in different wildlife, like the amphibians population in rivers [2,3].

The aim of this study was, therefore, to investigate the concentrations of estrone and 17 β -estradiol in *Rana/Pelophylaxperezii* on four rivers downstream output's waste water treatment plants, located in Portugal central region, comparing to two control groups living in a non-contaminated water environment. Concentrations between 53-101 pg/ml were founded for estrone, and 37-149 pg/ml for estradiol, using the radioimmunoassay method in blood/serum fraction of the amphibians.

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Ecotoxicological evaluation of selected foam extinguishing agents

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Present time is characterized by intensive development in all spheres of life. A whole range of new materials bring positives to mankind, but on the other hand, they can be highly flammable and can negatively affect the environment. Similarly, the extensive use of the products of the oil industry increased the risk of fires and water fire fighting wasn't effective in such cases. That is the reason of increasing use of foam extinguishing agents. Thus fires have a negative impact on the environment not only through the production of many toxic products like PAHs, PCDDs, PCDFs, CO etc. but also through application of modern fire extinguishing agents, especially foams based on surfactants. In Europe the EU regulation REACH (Registration, Evaluation, Authorisation and Restriction of Chemical substances) entered into force on 1st June 2007. Following this Regulation till 2020 it should be ensured that within the territory of the European Community only chemical substances and preparations with known hazardous properties will be produced and imported and that their production, use and elimination will be safe. In fact information about hazard to the environment (ecotoxicity) which should be part of safety data sheet of the modern foam extinguishing agent is rare or is completely absent.

The aim of our work was the ecotoxicological evaluation of selected foam extinguishing agents which are most often applied in case of fire in the Czech Republic: STAMEX F-15, EXPYROL F-15, MOUSOL APS F-15, FINIFLAM F-15 and PYROCOOL B. Since surfactants have a negative impact mainly on aquatic ecosystem predominantly the ecotoxicity on aquatic organisms was tested. Testing organisms were aquatic crustacean *Thamnocephalus platyurus* and *Daphnia magna*. For calculation the value of 24LC50 and 48LC50 alternative tests Thamnotoxkit FTM and Daphtoxkit FTM were used (purchased from MicroBioTests Inc., Gent, Belgium). The test procedure followed the Standard Operational Procedure manual of the both microbio test. The other aquatic organism was *Lemna minor* (dicotyledons plant). OECD Guidelines for the Testing of Chemicals, No. 221. *Lemna* sp. Growth Inhibition test was followed in this case. As the sole representative of terrestrial plant *Sinapis alba* (white mustard) was used. The *Sinapis alba* root growth inhibition test - test Guideline of the Ministry of Environment of the Czech Republic no. 11/2007 for the determination of the waste ecotoxicity was applied.

Based on the results of the ecotoxicological tests the values of LC50, EC50 and IC50 for the tested preparations were calculated and their ecotoxicities were compared. Ecotoxicological values for all foam extinguishing agent were from µL.L-1 (Pyrocool B) to mL.L-1 (Mousol APS F-15). These values indicate high ecotoxicity. Comparing sensitivity of testing organisms all water organisms were much more sensitive to all tested foam extinguishing agent than *Sinapis alba*.

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Study of bioaccumulation of selected pharmaceuticals in terrestrial organisms

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Pharmaceutical residues have become serious environmental contaminants in recent years due to their increasing concentration in various environmental compartments. Lots of consumed pharmaceuticals are released from human or animal organisms after administration and enter the sewer system [1]. In the wastewater treatment plants (WWTPs) these compounds are only partially removed during the cleaning processes [2]. Part of these substances is discharged with treated sewage water into surface streams and part is sorbed on the sewage sludge [3]. The sludge from WWTPs is quite often dispersed on fields as fertilizer [3]. This way these substances could get into the soil and influence soil organisms. Another source of soil contamination by foreign substances is the application of manure (excrements) from animals treated with antibiotics. Organisms present in the soil can accumulate these substances, but they can also be adversely affected.

This work is focused on the study of possible bioaccumulation of selected pharmaceuticals in soil organisms. For this purpose pharmaceuticals from the group of sulfonamide antibiotics were selected. These pharmaceuticals are characterized by their very frequent use in veterinary medicine. Earthworms were selected as the representative soil organisms, which are widely spread in almost all agricultural soils. In our study the testing organisms were exposed to the test substance during the uptake phase when the soil was spiked with test substances. The artificial soil described in the OECD Test Guideline 207 (Earthworm, acute toxicity test) was used in our experiments. Uptake phase (21 days) was followed by elimination phase, when the earthworms were transferred to a soil free of test substance. The elimination phase takes also 21 days. During the test the state of earthworms was observed. At the end of uptake and elimination phase, the analysis of soil and earthworms tissue was realized using HPLC/MS. For the extraction of target compounds from soils and tissues the pressurized solvent extraction (PSE) was used and extracts preconcentration and purification using solid phase extraction (SPE) was done. After analysis, the comparison of concentrations of selected compounds in soils and in the tissues of earthworms was performed. The obtained results should clarify the question whether the selected compounds could penetrate into the soil organisms, and if so, in what extent.

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Molecular electronic structure of persistent organic pollutants in their biological action mechanisms

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Earlier, our investigation of benzodiazepines (BDs) with the negative ion mass-spectrometry of the resonance electron capture by molecules, allowed finding a correlation between BD biological activity level and the resonance states (RSs) energies in the BD series [1]. This indicated a relationship between DB activity mechanism and the electronic structure of BD molecules. Later, during assignment of the RSs to so-called “*inter-shell resonances*” using UV absorption spectroscopy, this structure was identified as the energies of BD electronically-excited singlets (E_s). Then, these E_s values were noted to be nearly equal to Na and K atoms ionization energies (IE_{Na} and IE_K), and a hypothesis was put forward concerned with the working of the ion selectivity filter of the neuron membrane channel [2, 3]. It was proposed that Na^+ (or K^+) cation going through the filter forms a complex with the filter negatively charged CO groups, and an electron transits from them onto Na^+ (or K^+) cation. The energy nearly equal to IE_{Na} (or IE_K) is released which is absorbed by adjacent Phe (or Tyr) allowing by this way the process to occur. Phe (or Tyr) can do this because they have the singlet transitions of the same energy: $E_s^{Phe} \approx IE_{Na}$ (or $E_s^{Tyr} \approx IE_K$). If a closely placed foreign molecule like BD has the same transition, it can also absorb this energy, having interfered thereby with the process – either blocking the channel, or opening it, when it is wrong. The mechanism proposed allows explanation constancy of all Na- and K-channels traffic capacity (10^8 cations/sec), as well as the filter ability to push the cations against the electric field. Herein, some persistent organic pollutants (POPs) (endrin,

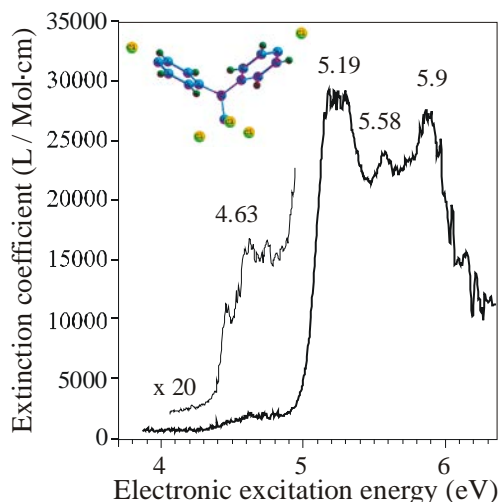


Fig. 1. DDT UV optical absorption spectrum.

aldrin, heptachlor, dieldrin, lindan, hexachlorobenzene, DDT, UU'DDD and UU'DDE) were studied with the photoelectron and UV absorption methods. It was found that UV band energies and extinction coefficients (ϵ) in the POPs investigated correspond to the mechanism proposed. In particular, it is well-known that toxicity of DDT is caused by its ability to keep the Na channels to be opened. Correspondingly, the intensive L_a band is registered in the UV spectrum of DDT at 5.19 eV that is equal to IE_{Na} (Fig. 1). Besides, the ϵ value of this L_a band is very large: it is nearly 4 times as large as that for chlorobenzene. The data obtained can be useful for searching for ways of the POPs neutralization by the action on their electronic structure.

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The distribution of chromium in the organs of aquatic macrophytes

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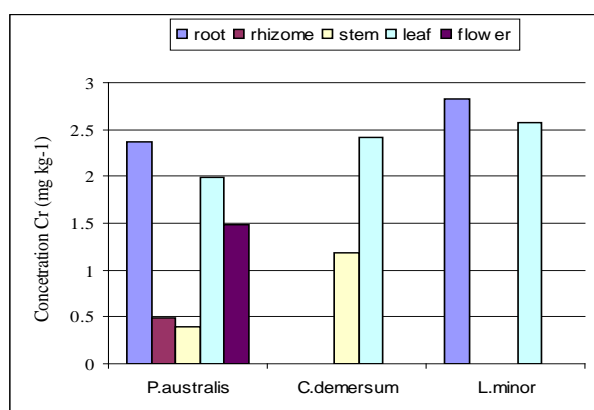
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Aquatic plants can accurately indicate the presence and intensity of certain pollutants into the aquatic environment, which makes them suitable for environmental monitoring of water quality. Emergent and free floating macrophytes plants adopt metals through the roots, while metals rootless submerged plants absorb metals shoots. Emergent plants remove metals from the sediment and the water while free floating and rootless submerged macrophytes only extracted metals from water [1].

In this study the ability of Cr bioaccumulation macrophytes plants: *Phragmites australis* (emergent), *Ceratophyllum demersum* (submerged) and *Lemna minor* (free floating). Plants were collected from four sites in the locality Crnojevića Rivers, tributaries of Skadar Lake, Montenegro, during October 2011. year.

Cr is toxic to plants and does not play any role in plant metabolism. Accumulation of Cr by plants can reduce growth, induce chlorosis in young leaves, reduce pigment content, alter enzymatic function, damage root cells and cause ultrastructural modifications of the chloroplast and cell membrane[2]. Normal range Cr in plants is 0.03-14 mg kg⁻¹ and critical concentration is 5-30 mg kg⁻¹ [3].

The mean Cr content in the sediment was 45.5 mg kg⁻¹ in water 0.002 mg L⁻¹. Bioaccumulation is the largest recorded in the root of *L. minor* (BCF = 1415) and the lowest in the stem *P. australis* (BCF=200). Cr is the aquatic macrophytes during the growing season accumulates in the root, which is probably a need to prevent pollution of the plant photosynthetic apparatus of traces of toxic metals. After completion of the growing season is



noticeable translocation of metals to aboveground plant parts. The ratio of root / leaf is 1.19 (*P. australis*) and 1.10 (*L. minor*). The rootless aquatic macrophytes (*C. demersum*) increased the concentration of Cr in the leaves rather than a stem. The leaves, which have a much larger surface area of absorbs the metal from water in addition to translocation from the stem. Concentration ratio of stem / leaf is 0.49.

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Multistage *in situ* bioremediation of aquifer contaminated with petroleum pollutants

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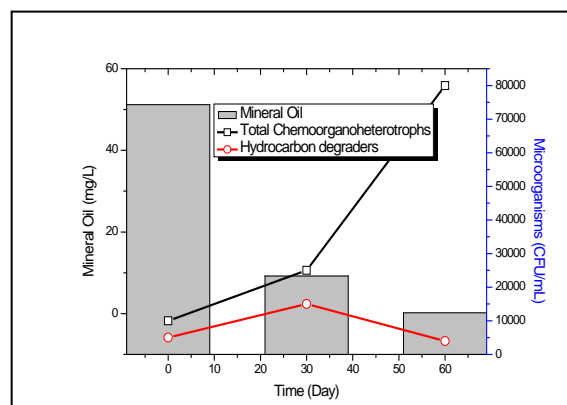
The locality of the company Niteks-Benetton in Niš (Serbia) was contaminated over several years with petroleum products due to the continuous pollution from leaking tanks. Ground waters (GW) which contained dissolved hydrocarbons and a floating layer of an oil pollutant (Light Non-Aqueous Phase Liquid - LNAPL) were treated with filtration-adsorption remediation technique, using the columns filled with natural inorganic hydrophobic adsorbents, and *in situ* bioremediation based on the principle of “bipolar” model, which was developed and tested by some of the authors of this research. *In situ* bio/remediation of GW and soil layers in contact with groundwater was accomplished by chemical and biological stimulation, augmentation and aeration in closed “bipolar” system (pumping out – pumping in), with adsorption in the “external unit”. This combination of methods is original and applied for the first time. Natural microbial processes in groundwater were additionally stimulated by chemical or physical increase in the aeration capacity. Bioaugmentation was achieved by injection of biomass of zymogenous microorganisms isolated from treated polluted GW [1,2].

Basic characteristics of treated GW are shown in the Table. The change in the content of the “mineral oil” – total petroleum hydrocarbons and the consortium of chemoorganoheterotrophic and hydrocarbon degrading microorganisms in the samples of water treated by bipolar system are shown in the picture.

Basic characteristics of the GW during the treatment

| Date [2012 Y] | t _{water} [°C] | pH | NTU | O ₂ [mg/L] | O ₂ [%] |
|---------------|-------------------------|-----|-----|-----------------------|--------------------|
| May, 1 | 15.4 | 6.9 | 80 | 3.4 | 34 |
| June, 1 | 16.1 | 6.9 | 22 | 8.5 | 86 |
| July, 1 | 16.9 | 7.0 | 5 | 8.8 | 91 |

After the *in situ* treatment, quality parameters of purified-waters complied with statutory criteria for groundwater which should not be treated.



Changes in concentrations of microorganisms from „mineral oil“.

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Monitoring of microbial protection of plants from the phytotoxic action of anthropogenic organic compounds by using of $^{13}\text{C}/^{12}\text{C}$ ratios as an indicator

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Global transport system and power generating industry are based on the extraction of fossil hydrocarbon fuels such as crude oil that may contribute to increased concentration of organic pollutants in the atmosphere, hydrosphere and geosphere. The pollution of soil poses the need for efficient monitoring and control of the fate of the anthropogenic hydrocarbons as they affect sustainability issues such as plant growth. The effect of naphthalene as a representative of polycyclic aromatic hydrocarbons (PAHs) on plants growing under sterile conditions and plants inoculated with microorganisms capable of naphthalene degradation and microorganisms incapable of this was studied using molecular and isotopic mass spectrometry.

Tobacco plants of the Samsun variety were grown in a closed gas-nutrient system and on a mineral medium with sucrose as a carbon source.

Naphthalene used as a toxicant at a concentration of $5.2 \cdot 10^{-4}$ % contained ^{13}C isotope whose amount was characterized by the value $\delta^{13}\text{C} = +285.4$ ‰ relative to the PDB standard and differed from that of sucrose, the main source of carbon ($\delta^{13}\text{C} = -12$ ‰). Degradation of naphthalene was determined by the inclusion of its carbon in metabolic CO_2 and plant tissues (the root, stem, leaves). The effect of naphthalene on plants was indicated by the rates of O_2 consumption and CO_2 uptake during the light period as compared with the dark period of exposure. A decrease of the toxic effect of naphthalene on plants was observed only at the inoculation of plants with *Pseudomonas aureofaciens* BS1393 rhizosphere bacteria bearing plasmid pBS216, which controls the naphthalene biodegradation ability. The occurrence of other heterotrophic microorganisms incapable of naphthalene degradation had no protective effect like this.

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Monitoring degradation of biocompatible copolymers using high performance liquid chromatography and gel permeation chromatography

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This study is focused on the degradation of biocompatible copolymers. Copolymers were studied based on poly(lactic-co-glycolic) acid and poly(ethylene glycol) PLGA-PEG-PLGA and further these copolymers were modified with itaconic acid ITA-PLGA-PEG-PLGA-ITA. Applications of PLGA-PEG-PLGA based polymers in delivery of therapeutics and tissue engineering. This group of copolymers is considered the stimuli-responsive polymers. Stimuli-responsive polymers or “smart” polymers react on a small change in external environmental conditions by dramatic changing their physical and chemical properties. They can be classified according to the stimuli they respond to as: temperature-, pH-, ionic-strength-, light-, electric and magnetic field-sensitive. Copolymers based on PLGA-PEG-PLGA are sorted into groups of temperature-sensitive polymers [1]. With increasing temperature of the sol copolymer becomes hydrogel copolymer and vice versa. First each copolymer was tested by inverting the test-tubes in order to determine whether it shows sol-gel phase transition. If the copolymer was soluble in water and formed a gel in the temperature range of 36-42 °C then it meets the conditions chosen for degradation. The effect of pH was monitored on degradation selected copolymers. Degradation of polymers occurred at 37 °C in phosphate solution with pH 4.2, 7.4 and 9.2. High performance liquid chromatography with UV-VIS detection of diode-array type was used for quantitative determination of lactic acid and glycolic acid as the final degradation products. Gel permeation chromatography with refractive index detector was used to determine the molecular weight decrease polymer chain after the degradation.

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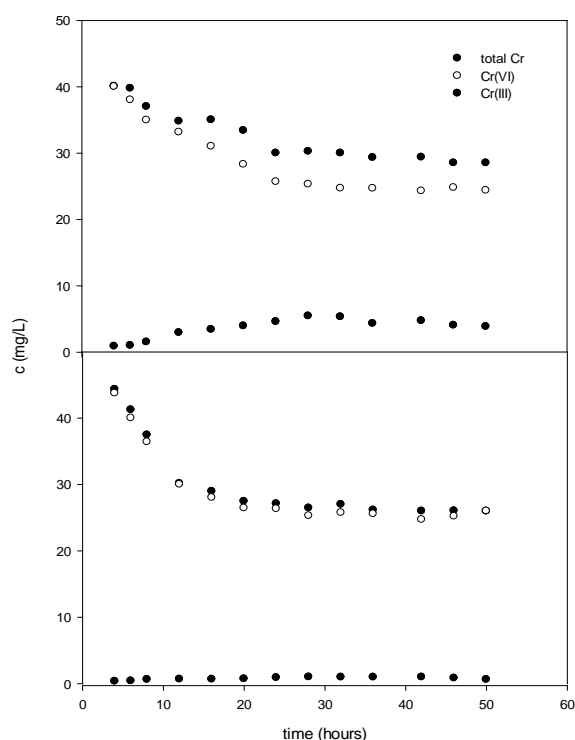
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Cr(VI) sorption onto biomaterials – ion exchange and isotopic study of sorption mechanisms

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The use of agricultural byproducts and industrial biowaste materials has been shown to be an attractive technique for removing Cr(VI) from contaminated waste waters. The knowledge of Cr(VI) reduction to Cr(III) by the biomaterials is essential to understand their sorption properties. In this study, the reduction potential and mechanism of brewers draff and grape stalks and husks on Cr(VI) was investigated. The materials were tested in two different modifications. The materials were dried, cut and sieved and portion of it was subjected to acid (2 M H₂SO₄) and alkali (0.5 M NaOH) pre-treatments [1]. Fourier transform infrared rays analysis on solid phase (FTIR-ATR) was used to determine the main functional groups that possibly control the metal uptake. Batch experiments were performed at different pH 3 and at initial concentration of Cr(VI) 250 mg L⁻¹.



The reduction of Cr(VI) was studied in both aqueous and solid phase after the sorption process. Reduction reactions tend to enrich products in lighter isotopes because they preferentially react and the residual reactants become progressively enriched in the heavier isotopes [2]. Elis et al. [3] showed that the Cr isotope fractionation changes during the Cr(VI) reduction. The ⁵³Cr/⁵²Cr ratio was measured in each biomaterial by MC-ICP-MS (Thermo, Germany). In order to identify extent the of Cr(VI) reduction in the aqueous phase, ion exchange separation on the AG1-X8 resin was used to separate the anionic Cr(VI) and the reduced cationic Cr(III) and subsequently the concentration of both forms was determined by ICP-OES (Agilent Technologies, USA).

As expected, Cr(VI) reduction occurred during the biosorption process. Cr(III) was determined both in the solid and aqueous phase (Fig. 1 - Cr_{tot}, Cr(VI) and Cr(III) concentration profiles during Cr sorption by untreated and

pre-treated brewers draff at initial pH 3). There was a variation in the ⁵³Cr/⁵²Cr ratio. The reduction capacity was different for untreated and pre-treated material.

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Searching of ways for synthethis of biodegradable polymers based on polyethylene

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Disposal and recycling, currently used to utilize plastic waste, does not improve the ecological environment. Radical solution of the "polymer waste" problem of, according to experts, is creation and development of a wide range of polymers biodegradable under appropriate conditions into harmless substances.

This study deals with the synthesis of biodegradable polymers based on polyethylene (PE). To promote its biodegradation were used polylactic acid, bone powder, and wood powder.

In order to improve a distribution of additives in polymer matrix as well as physical and mechanical properties of mixture we have made 10% - and 20% concentrates of bone and wood powder based on sevilen brands 11306-075 and 11104-030. The CA-100 - cetylstearyl alcohol and polyethylene wax were used as plasticizers. Furthermore using the obtained concentrates new compositions were produced: based on grade LDPE 15313-003 with 2% additives, and based on the grade LDPE 10803-020 with 2, 6 or 8% additives. Polylactic acid was introduced at all stages in its purest form.

To assess the effectiveness of modifying additives in photodegradation process these polymer compositions were subjected to photooxidative aging. The study of plates (thickness 1 mm) of the compositions obtained with laboratory press, shows that with increasing content of bone and wood powder in the compositions both strength and elasticity decrease, compared to the base polymers. For compositions with polylactic acid this decrease is slightly reducing. Test results after photooxidative aging show that all compositions are losing fluidity. For compositions with polylactic acid, that characterized by decreasing of strength and elongation, as well as for compositions with increasing of degree of filling of bone or wood powder additives, a gradual we fix an increase of strength characteristics accompanied by sharp loss of elastic properties. The analysis of film physical and mechanical tests after photooxidative aging were carried out. The maximum decrease in strength characteristics is inherent to compositions with additions of polylactic acid. Given working properties of the samples, together with their tendency to photodegradation and biodegradation we determined most optimal compositions.

Fate of the herbicide sulcotrione in a black vertisol

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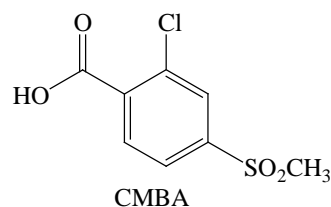
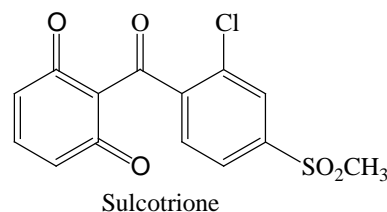
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One of the main processes governing the dissemination and fate of pesticides in agricultural soils is adsorption/desorption with solid particles and microorganisms. These interactions between soil particles and pesticide play a key role not only in their transport but also in their biodegradation, by acting on their bioavailability and also on the microbial metabolic activity. In order to better understand the mechanisms involved in the transfer/transformation processes of pesticides, we developed a study to identify the role of each soil component (coarse and fine fractions, organic matter and clay minerals) on their fate.

An agricultural soil from an experimental field located in the Limagne plane (France) was chosen and fully characterized. Due to its high amount of swelling clays (42%) that retains water and its high proportion in organic matter (2.3%) mainly linked strongly to clay minerals, this soil was classified as a black vertisol with pH buffered at 8.2 by carbonates.

The first pesticide studied was a triketone herbicide, sulcotrione, used as a selective herbicide in maize. This new generation herbicide was derived from a natural phytotoxin produced by the bottlebrush plant *Callistemon citrinus*.



The soil samples were separated into three fractions: $50\ \mu\text{m} < F1 < 500\ \mu\text{m}$; $2\ \mu\text{m} < F2 < 50\ \mu\text{m}$; $F3 < 2\ \mu\text{m}$. Adsorption kinetics and isotherms of sulcotrione and one of its metabolites, 2-chloro-4-methylsulfonylbenzoic acid (CMBA), with the various soil fractions were determined to quantify the soil response to pesticide contamination. The effect of organic matter on sulcotrione immobilization was studied by comparing hydrogen peroxide treated and bulk soils.

Biodegradation is an important process controlling the fate of pesticides. The dissipation of sulcotrione ($16\ \mu\text{g/g}$ dry soil) was monitored in field soil microcosms at different humidity content. Its half-life was 30 days for 35% humidity in this soil. Using a mineral medium containing the herbicide, sulcotrione-degrading microorganisms were then isolated from this soil. Among twenty bacterial colonies isolated, one strain showed biotransformation capabilities and a metabolite (CMBA) was found to accumulate in the medium.

Historical water contamination in an urban area: a geochemical study of middle age aqueduct deposits in Paris, France

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This work is part of the Hydro-Histeau project which objective is to characterize interactions between near surface groundwater and historical (XV-XXI centuries) urbanization of the northern part of Paris. This communication focuses on carbonate deposits in a Middle Age underground aqueduct devoted to drinking water supply on the right bank of the Seine River.

Carbonate deposits (CaCO_3) developed on the walls and the floor of the aqueduct, from lateral flowing and vertical dripping water. They are laminated, similar to caves' stalagmitic deposits.

We develop a methodology to reconstruct temporal variation of trace elements in sub-surface groundwater by studying their content within carbonates layers. Subsamples were drilled at different level in the deposits.

The first step consists in obtaining precise ages of different levels of these objects. We compare radiometric ages (U/Th ages that include correction for detrital contamination) with relative dating methods in order to validate a robust chronology. The studied samples represent a period of growth of more than 300 years.

Trace elements were then determined by ICPMS in the different layers of the deposit. The measured changes reflect their variation in the water that fed the deposits and then paleo-environmental modifications.

Two periods with high lead contamination are identified: one in the oldest part of the samples and a recent one. They are associated with high vanadium, aluminum and manganese contents. Ongoing work on lead isotopes will allow characterizing the origin of these contaminations.

A recent and high contamination in rare earth elements (REE) can be related to REE use in new technologies. The variations of alkali and alkaline earth observed along the growth axis of the deposits could reflect environmental changes (climate and urbanization).

Comparison between several samples allows discussing water circulation and contamination at local to city scale.

Self-cleaning materials on architectural heritage: photo– induced hydrophilicity of TiO₂ coatings on historic materials

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Despite numerous investigations concerning the protection of historic materials, there are only a few scientific studies that deal with the complexity related to the interactions among the protecting coating surface of the historic products and microorganisms. The material resistance toward these actions is a very complicated process due to complex relationships among raw materials characteristics, production parameters and properties of the final products. Porosity and pore size distributions are the most important parameters of historic materials for obtaining appropriate properties resistible to frost action and organic acid exudation by lichens, fungi and bacteria. The paper analysis the aspects of bricks and mortars durability, as construction materials of the Petrovaradin fortress tunnel walls, as the ability to withstand external climatic conditions as well as the weathering processes due to microorganisms attacks(1). The second part of the paper describes the appropriate surface protection using photo-catalytic and super-hydrophilic effects of a TiO₂ coating(2) . This part identifies several problems that need to be addressed within a wider scope of functional surface layers development in order to obtain multifunctional roles: (a) to protect and clean the tile substrates from microorganism attacks and (b) to preserve the functionality and the aesthetic look of tiles through long periods of time, Fig 1.

The subject of this paper presents a useful tool to those who are in charge of the production of materials as well as to those who are taking specific measures regarding the conservation and restoration procedures of the materials.

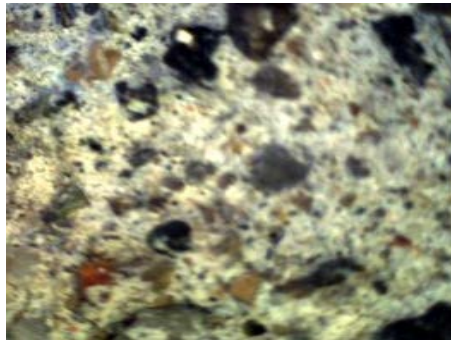
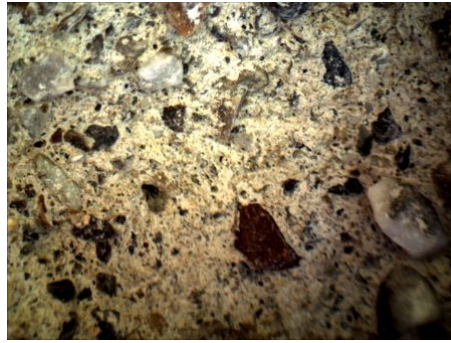


Fig 1. Optical microscopy of the old mortar: a) Before application of the protecting coating;
b) 4 weeks after application of the protecting coating

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Absorption spectra as the indicator of black ink aging during the sheet-fed offset press

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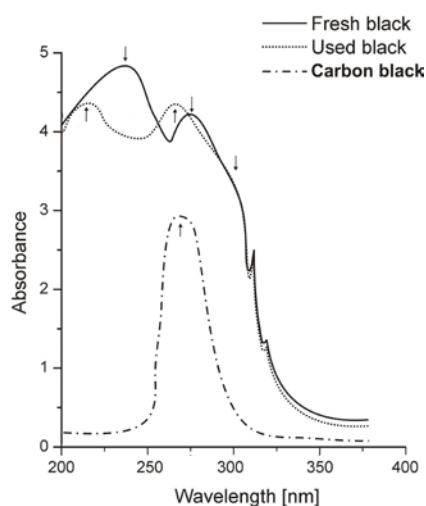
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In sheet-fed offset printing process a high color strength along with high pigment loadings, smooth flow, and a viscosity that is fairly working are needed from the application of carbon black (CB). CB is one of the most useful carbon materials used in printing inks [1]. There is some chances of hazards resulting from CB exposure: Group 2B (possibly carcinogenic to humans).

The paper considers the application of UV/VIS spectra of fresh and used black sheet-fed offset printing ink, as indicator of ink aging. Therefore the aim of investigation was to determine the course of ink aging during the sheet-fed offset press.

The optical properties of CB particles and especially the UV/VIS absorption behavior depend on the structure of the material, which has to be characterized on different relevant length scales. The UV absorption behavior of carbon materials is caused by electronic transitions between the bonding and antibonding π orbital. The $(\sigma-\sigma^*)$ transitions are expected in the far UV between 60 and 100 nm, whereas the $(\pi-\pi^*)$ transitions are located in the range between 180 and 290 nm. The position of the UV feature is extremely sensitive to



small changes in the internal electronic structure of the CB particles. A granular black pigment contains cobalt, which appears in used ink much more than in fresh sample due to the form of CoO or Co₃O₄ residual phases. Also the content of black pigment particles was decrease during the printing process. The position of the UV maximum of CB is strongly influenced by the internal electronic structure whereas the width of the maximum also depends on the state of agglomeration [2]. The obtained UV/VIS spectra showed the typical absorption profile of CB as a main structure of black ink. The characteristic band of $(\pi-\pi^*)$ transitions, with absorption maximum at 290 nm, splits into two bands with maxima at ~240 and 280 nm, which confirmed the presence of Co(II) ion with absorption maximum at 240 nm and CB at 280 nm, as shown in Fig. 1. The intensities of absorption maxima are smaller after 20,000 printed sheets, and the phenomena could be the indicator of ink aging process starting. With increasing the printing process the absorption maximum is shifted to higher wavelengths.

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The influence of some pyrazole derivatives and its newly synthesised transitional metal complexes on the inhibition of *Phomopsis viticola* Sacc. (Sacc.) under laboratory conditions

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***Phomopsis viticola* Sacc.**

Based on data found in literature [1-3] about synthesis and characterisation of some pyrazole derivatives and some significant transitional metal complexes which have practical application in pharmacy, agriculture and environmental protection, this research paper analyses influence of pyrazole derivatives 3,5 dimethyl – 1- thiocarboxamid pyrazole,(L1); 4-acetyl-3(5)-amino-5(3)-methylpyrazole,(L2); 3(5)-amino-5(3)-hydroxy pyrazole,(L3) and the newly synthesised Cu(II) and Zn(II) complex on the inhibition of pathogenic fungal mycelium *Phomopsis viticola* Sacc.(Sacc) that causes phomopsis cane and leaf spot disease, a very significant grapevine disease that is common in Montenegrin vineyards [4.5]. The results of the newly synthesised complexes are compared to the results of commercial fungicide Cabrio Top whose active substance pyraclostrobin belongs to pyrazole derivatives [6].

Chemical inhibition of phomopsis cane and leaf spot disease of grapevine has important practical significance, and it is mainly focused on winter season treatment of grapevine which purpose is to reduce infectious effects of fungi and prevent primary infections at the beginning of the vegetation process.

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Analysis of tar formed by gasification of biomass

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This work is focused on the analysis of the tar formed during combustion of biomass. Samples of the tar were provided by Energy Institute, Faculty of Mechanical Engineering. Gasification is a complex thermal and chemical conversion of organic matter in conditions of oxygen deficiency into a low heating value (LHV) gas (4 MJ/m³_n to 15 MJ/m³_n) consisting of a series of simple reactions. The process occurs at higher temperatures, typically between 750°C and 1000 °C. Heat for endothermic reactions is most frequently obtained from partial oxidation of the material under gasification (gasification by means of air or oxygen) or is supplied from external sources [1,2].

The product of the process of gasification is gas, the main constituents of which are CO, CO₂, H₂, CH₄, higher hydrocarbons, N₂, and impurities. The main focus in the gas is on its quality (heating value, composition) and quantity generated during gasification - plus amount and composition of impurities. Impurities include dust (airborne solids), alkalic compounds, nitrogen compounds, sulphur compounds, compounds containing chlorine and fluorine, and tar (i.e. all organic compounds with boiling point above that of benzene, i.e. 80.1°C). Tar and dust are the main factors limiting the use of fuel gas [3].

BTEX compounds (benzene, toluene, ethylbenzene and xylenes), polycyclic aromatic hydrocarbons (PAHs) and n-alkanes were chosen as groups of target compounds. Samples (tar solutions in acetone) were refined before the final analysis. In the case of BTEX and n-alkanes, only filtration and dilution were used. In the case of polycyclic aromatic hydrocarbons, samples were filtered and then cleaned-up by column chromatography on silica using stepwise elution. Gas chromatography with flame ionization detector (GC-FID) was chosen as an appropriate analytical method for the determination of BTEX and n-alkanes. Target compounds from the group of polycyclic aromatic hydrocarbons were analysed by gas chromatography with mass spectrometric detection (GC-MS).

Acknowledgment

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Low temperature preparation of a platinum catalyst

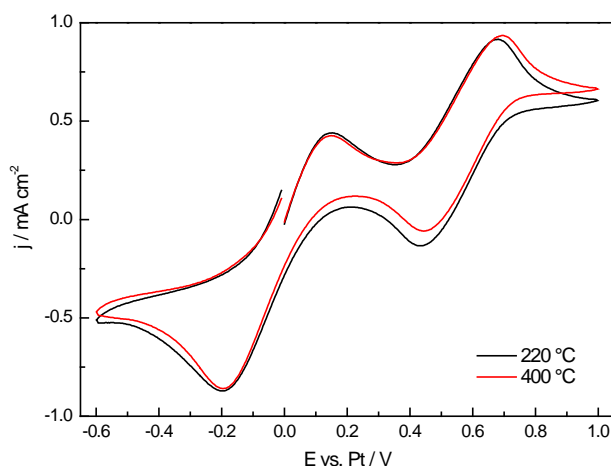
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Dye-sensitized nanocrystalline solar cells (DSSCs) have been widely studied in the last few years since even though their absolute efficiency is low, their high power production to cost ratio make them a valid alternative to conventional silicon based solar cells. Being based on TiO_2 and immune to the defects of the semiconductor also makes them cheap and easy to manufacture. The cell itself is composed of several layers: the first conductive substrate is covered with particles of TiO_2 sensitized with a dye, while the second conductive substrate is covered with a platinum catalyst and the space between them is filled with an electrolyte (usually iodide/iodine). By developing an easy way to deposit the semiconductor and catalyst at low temperatures and fabricating flexible cells, the possible applications of DSSCs can be further extended.

The standard method for preparation of the Pt catalyst requires high temperature which damages most of the commonly used flexible foils. This work presents a two-step method for producing Pt nanoparticles with good adhesion to the substrate. The first step involves the synthesis of a matrix formed by the ester of citric acid and ethanol and the addition of H_2PtCl_6 to prepare solutions with several different concentrations of the Pt precursor. The precursor solutions were deposited on SnO_2/F coated glass using dip-coating. In the second step, the prepared layers were exposed to 175, 220 or 400 °C for 20 minutes to facilitate the reduction of Pt^{4+} and the thermal decomposition of the ester. X-ray photoelectron spectroscopy indicated that the prepared platinum was in metallic state. Cyclic voltammetry (CV) in an iodide electrolyte [2] was used to determine the catalytic activity of the prepared Pt nanoparticles.



The catalytic activity of the samples prepared at 175 °C is negligible indicating that reduction of Pt^{4+} to Pt did not occur, while the catalytic activity of samples prepared at 220 °C is comparable to those prepared at 400 °C. SEM images have shown that the surface of the samples prepared at 220 °C is covered by uniformly distributed nanoparticles of Pt about 10 nm in size. The catalytic activity of the Pt nanoparticles was tested in DSSCs using it as the counter electrode. There is no difference in cell efficiencies between the cells using catalysts prepared at 220 or 400 °C.

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Hydrogenation of phenylacetylene catalyzed by carbon coated metal nanoparticles: possibility of inherent catalytic activity of carbon shell

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Implementation of catalytic processes instead of stoichiometric is one of the principles of sustainable chemistry. Carbonaceous materials have received a great attention as possible catalysts [1, 2] and construction blocks for the design of new nanomaterials. In most cases the carbon materials have low catalytic activity in such important processes as Friedel-Crafts benzoylation, racemization and nucleophilic substitution [2] and no activity in hydrogenation. On the base of experimental investigations and first-principles calculations [3,4] we suggested that carbon shell of carbon coated Me nanoparticles could have inherent activity in H₂ dissociation due to changes of its electron structure as a result of space deformations and the presence of metal sublayer. In this work catalytic properties of Me-C nanocomposites containing Fe or Ni (Fe@C and Ni@C) were investigated. Nanocomposites were prepared as described in [3]. Fe@C and Ni@C particles were about 10 nm in diameter and consist of metallic core

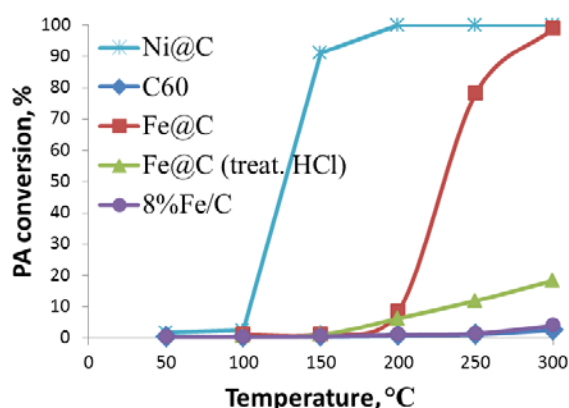


Figure 1. Conversion of PA on the Fe-C and Ni-C

and few layers of graphene shell (C content is about 30%). According to XPS, XAS, and Raman data, these systems have many structural defects due to high strains of graphene layer on nanosized metal particles. We used phenylacetylene (PA) hydrogenation as test reaction (fixed-bed reactor, 1 atm. H₂, 50-300°C). The substrate was injected with a syringe (three pulses of 0.228 mmol PA at each temperature) into a flow of H₂ (12 ml/min). Several systems were tested (Fig.1): pristine nanocomposites Ni@C and Fe@C; Fe@C treated by conc. HCl (210°C, 5 h.) to remove metal particles that don't contain carbon shell; fullerene (C60) as model carbon structure with the curvature of graphene surface similar to

those in Me@C particles; and 8%Fe/C as a common catalytic system having similar chemical composition with Fe@C. Fe/C and C60 provide negligible PA conversion at the temperatures below 250°C. In contrast, Ni@C, Fe@C and Fe@C (treat.HCl) provide significant PA conversion at the temperature above 100°C, 200°C and 200°C respectively. High activity of Ni@C and Fe@C could be explained by possible presence of metal nanoparticles that have broken or no carbon shell. However in Fe@C(treat.HCl) sample all such metal particles (including Fe, its oxides and carbides) have been removed, but the sample has evident catalytic activity. So we suggest that carbon shell has inherent catalytic activity. This suggestion was confirmed by H-D exchange experiment, which proves H₂ dissociation on Fe@C.

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Analysis of chemical composition brown algae of the White sea

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Arctic brown algae is the unique source of the wide range of biological active compounds (BAC). Main types of the brown algae in the White sea that forming the main stocks are *Laminaria saccharina*, *L. digitata*, *Fucus vesiculosus* and *ascophilum nodosum*. The listed samples of brown algae was the object of research.

Table 1 - hydrocarbon composition of the brown algae

| Raw material | Alginic acids, % | Mannitol, % | Cellulose, % | Easily hydrolyzed polysaccharides, % | Difficult hydrolyzed polysaccharides, % |
|----------------------|------------------|-------------|--------------|--------------------------------------|---|
| <i>l.saccharina</i> | 22,2 | 17,3 | 33,0 | 11,0 | 7,9 |
| <i>l.digitata</i> | 23,3 | 16,7 | 38,2 | 9,1 | 9,2 |
| <i>f.vesiculosus</i> | 31,1 | 13,2 | 64,0 | 15,5 | 4,4 |
| <i>a.nodosum</i> | 34,1 | 10,1 | 64,0 | 16,3 | 9,7 |

* the content of alginic acids, mannitol and cellulose is defined with a relative error no more 5%, the content of easily hydrolyzed polysaccharides and difficult hydrolyzed polysaccharides is defined with a relative error no more 10%

Results of the element analysis shows that the maintenance of basic elements, such as carbon, hydrogen, sulfur and nitrogen for different groups of seaweeds (*laminariales* and *fuciales*) considerably different from each other, but in one family we can see close values.

The total content of amino acids in samples of brown algae differs slightly and approximately equal 15%. In *fuciales* in difference from *laminariales* significant amount asparagine (4,1 % and 5,4 % for *f.vesiculosus* and *a.nodosum* respectively) was found. Samples of *laminariales* algae, in difference from *fuciales*, contains a proline and glutamine.

There are significant amounts of very necessary for people micro- and macro elements in brown algae, that does it very valuable raw material for pharmaceutical industry.

The analysis of a chemical composition of investigated algae shows the possibility of using a principle of green chemistry (a supercritical fluid extraction) for allocation of valuable BAC (polyunsaturated fatty acids, pigments) in the low-changed condition that is extremely important in medicine and pharmaceutical practice.

It was established that *laminariales* algae are richer source of mannitol (table 1) and macro- and microelements, then *fuciales*.

F.vesiculosus and *a.nodosum* could contain over 8,4% lipophylic compounds that's why it could be valuable source of this BAC, such as polyunsaturated fatty acids, pigments and other lipids.

Table 2 - containing of lipophylic substances

| Raw material | Lipophylic substances, % | Chlorophyll, % | carotenoids, mg/g |
|----------------------|--------------------------|----------------|-------------------|
| <i>l.saccharina</i> | 3,89 | 0,28 | 0,037 |
| <i>l.digitata</i> | 5,70 | 0,60 | 0,025 |
| <i>f.vesiculosus</i> | 8,23 | 0,41 | 0,079 |
| <i>a.nodosum</i> | 8,36 | 0,24 | 0,063 |

Binding of asymmetrical dimethylhydrazine by sphagnum peat: influence of certain factors upon the process

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There is a pollution of areas of falling of the empty fuel tanks of carrier rockets caused by toxic components of rocket fuels, including asymmetrical dimethylhydrazine (ADMH) as a result of the Russian Federation space-rocket activity. Introduction of technologies of a detoxication of soils in the areas of falling rocket tanks, and operative removal of pollution requires creation of the inexpensive, available and effective sorbents, capable to bind hydrazines. The peat possesses unique ability to adsorb various pollutants and this fact is also approved by the field studies in the area of influence of «Plesetsk» spaceport, showing limited distribution of ADMH in peat soils [1].

The purpose of the present work is identification of the major factors influencing sorption of ADMH by high-moor peat. Duration of contact of phases, solution concentration, temperature, pH, ionic strength of solution were chosen as major factors. Research of sorption of ADMH by peat was carried out under static conditions at a ratio of solid and liquid phases 1:625. Measurement of equilibrium concentration of ADMH was carried out by the method of ionic chromatography with amperometric detecting (HPLC system «Stayer», close corporation «Akvilon», Russia) [2]. Experimental results were expressed in the form of a sorption rate of ADMH by the formula (1)

$$C_E = ((C_0 - C_P) \cdot V) / g, \quad (1)$$

where C_E - quantity of binded ADMH, mmol/g; C_0 , C_P - initial and equilibrium concentration of ADMH in solution, respectively, mmol/g; V - solution volume, l; g - sorbent mass, g.

Studies on the time of achievement of sorption equilibrium were carried out. It is established that time of achievement of sorption balance in «sorbent-solution» system is 30 minutes.

The acidity plays important role in sorption process. It was shown that the maximum degree of ADMH sorption is observed at pH about 6. Acidity was created by means of universal buffers in an interval pH from 3 to 9.

As a result of research of influence of ionic force of solution on sorption of ADMH by peat it is established that depending on electrolyte structure, the sorption of ADMH proceeds most intensively in case of application of salts with smaller radius and a charge of ions.

When studying influence of temperature on sorption process of ADMH by high-moor peat S-shaped sorption isotherms that points to polymolecular sorption, were obtained. It is also shown increase in temperature causes an increase of sorption, that is typical for a chemisorption process.

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Selective production of chloroaniline, N-ethylaniline or quinoline derivatives from chloronitrobenzene on Ni, Ni-Au, Ni-Pd and Ni-Zn catalysts

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Amines, amides and other nitrogen-containing compounds are commonly used as intermediates in the production of pharmaceutical and agrochemical industry. Such aniline derivatives as chloroaniline (CAN), N-ethylaniline and substituted quinoline are of great importance. The reaction of *N*-alkylation of primary amine with alkyl halides is widely employed for synthesis of N-amines but simultaneously large amounts of inorganic salts are evolved as wastes. It's undesired for the "green" synthesis. An alternative environmentally-benign approach is the *N*-alkylation with alcohols in the presence of transition metal catalysts, because water is the only byproduct. When the selective hydrogenation of nitro-group in the presence of other active substituents is performed it's important to avoid the formation of azo- and azoxy- toxic derivatives. The better way of CAN, N-ethylaniline or substituted quinoline production in one process includes hydrogenation of chloronitrobenzene (CNB) in the presence of metal-containing catalysts.

The aim of the present study is to find the active catalyst for a selective production of chloroaniline (CAN), N-ethylaniline or quinoline derivatives by hydrogenation of chloronitrobenzene (CNB). Catalytic reaction was carried out in a tubular pulse-regime reactor in H₂ flow. Substrate was injected intermittently as 0.1 M ethanol solution. Ni/ZrO₂, Ni/Al₂O₃, Au/Ni/Al₂O₃, Pd-Ni/Al₂O₃, Zn-Ni/Al₂O₃ were tested as catalysts.

The nature of support influences on the products composition due to the changes in supports acidity and porous structure (average pore diameter of Al₂O₃ was 10 nm, for ZrO₂ – 3 nm). In the presence of 6%Ni/Al₂O₃ at 200°C two main products with 60% conversion were formed: CAN (selectivity higher than 60%) and chloromethylquinoline (selectivity about 30%). Substitution of Al₂O₃ with ZrO₂ leads to CAN formation with high selectivity (more than 80%) and a high conversion (about 90%) even at 100°C.

The second way to change the activity and selectivity of Ni catalyst is the addition of second metal (Pd, Zn or Au). It was found that addition of less than 0.5 wt. % of Au to 6%Ni/Al₂O₃ results in the change of reaction path. *N*-alkylation was followed by hydro-dechlorination and nitro-group hydrogenation. As a result N-ethylaniline was formed with the selectivity of about 40%. Addition of Pd (0.022 wt. %) leads to an excellent conversion (100%) of CNB, but the selectivity to all desired products is low. When significant amounts of Zn were introduced (20 wt. %), N,N-alkylated aniline was formed along with N-ethylaniline. Such differences in the products composition and selectivity of reaction could be explained in terms of different ability of modified metal active centre to hydrogen activation.

As a result, changing the nature of the support and the composition of active metal site gives possibility to produce CAN, N-ethylaniline or chloromethylquinoline from CNB in the reductive medium and using ethanol as a solvent.

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Coimparative analysis of composition of birch polypore and its nano-disperse form

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The composition of native birch polypore, its nano-disperse form, produced by as well as, its medicinal form "Befungin" has been studied by mass spectrometry with both electronic ionization and MALDI techniques.

The fraction of steroids of various structure was found in starting birch polypore. The structure of each steroid was defined. Main components of steroid fraction are shown to be ergosterol, lanosterol, inotodiol and etc. The steroid fraction extracted from starting birch polypore is 0,21 %.Traces of fatty acids i.e. palmitic, linoleic, olein and stearin are found along with the steroids.

As to the medicinal form of birch polypore "Befungin" absence no steroid fraction detected but there is a water-soluble polymeric humin-like substance, so-called «polypore acid». In fact a destruction of this substance lead to a number of acids such as oksibenzoyny, vanillin and lilac. Thus, polymeric polypore acid consists of fragments of aromatic oxyacids.

After separation of polypore acid the next step of extraction was made and the following fraction of humin-like substance was produced. It consists of so-called Gebbert's ketones. In addition to them this fraction includes сирингол, lilac and vanillin acids. The composition of this fraction and exact masses of M⁺ ions were defined.

Lack of the technology of production of the medicinal form is a large number of waste products, i.e. part of a mushroom that is insoluble in water. We developed a new technology of producing with the size of particles of 20-30 microns. This form is nontoxic and it appeared to be completely soluble both in water and in 40% ethanol solution. Its composition includes polymeric forms based on oxyacids, and on ketones. It is well known many antibiotics contain ketone fragments it means this form can be more biologically active then other ones.

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