ABSTRACT BOOK

The 36th ISEAC International Symposium on Environmental Analytical Chemistry

Rome
October 5th-9th, 2010

Edited by Maria Luisa Grilli, Florinda Artuso

IAEAC

ENEA
Italian National Agency for New Technologies,
Energy and Sustainable Economic Development

ISEAC 36: BOOK OF ABSTRACTS

Edited by Maria Luisa Grilli, Florinda Artuso

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Italian National Agency for New Technologies, Energy and Sustainable Economic Development

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AWARD
Roland W. Frei Award
The best poster presentation at the conference will be honoured with the Roland.W. Frei Award

CONTENTS

MESSAGE OF GREETING

The 36th International Symposium on Environmental Analytical Chemistry (ISEAC 35), held in Rome from October 5th to 9th 2010, is the result of a trustful collaboration of ENEA and the IAEAC already experimented in 2004 in occasion of the successful 6th IAEAC Workshop on Biosensors.

The International Association of Environmental Analytical Chemistry (IAEAC) is a world-wide operating organization that aims at promoting and maintaining scientific excellence in analytical science as applied to different environmentally relevant research areas. Not only the traditional compartments soil, water, and air are included in its activities, but likewise fields such as process analysis, human health, or quality of food. In these efforts the IAEAC strongly interacts with relevant disciplines other than chemistry. I enthusiastically approached the leading spirit of the association when I participated to several IAEAC workshops and finally when elected in the IAEAC Extended Executive Committee in 2006. In these last years, due to my increasing involvement in the association, I greatly appreciated its idealistic aims thanks to our President, Prof. Dieter Klockow.

ENEA is the Italian National Agency for New Technologies, Energy and Sustainable Economic Development. The Agency's activities are targeted to research, innovation technology and advanced services in the fields of energy. ENEA performs research activities and provides agency services in support to public administrations, public and private enterprises and citizens. Environmental aspects of these activities are studied in several departments involving engineers, biologists and analytical chemists.

This is the 36th event of a series of successful IAEAC symposia. It started in 1971 in Halifax/Nova Scotia, Canada, marking the birth of our Association, and had its last edition in 2008 in Gdansk, Poland. The symposium now being held in Rome, Italy, once again underlines the IAEAC's idealistic goals, namely to provide platforms for scientists to exchange "cutting-edge" results relevant to our environment, at locations throughout the world to maximize the opportunities for researchers in the respective fields to participate.

I am extremely thankful to the ENEA staff and to Mrs. Marianne Frei (IAEAC) for accompanying me in the organization of the symposium. Through their engagement I hope a good frame has been established for an international event comprising a quite promising scientific and social program in the Eternal City.

It is now up to us, organizers and participants, to fill this program with a breath of life, to exchange know-how and brand-new results, and by these means building **bridges** between our respective research institutions or countries, contributing for a little to pull down the existing **walls** at least during our symposium and maybe in our future research activities.

On behalf of the ISEAC 36 scientific and organizing committees and the IAEAC executive committee, I wish all of you a successful and scientifically stimulating symposium in the highly impressive City of Rome.

R. Pilloton

Chair, ISEAC 36

PROGRAM

OCTOBER 5TH

5.00 PM **GET TOGETHER PARTY AT AUDITORIUM VIA VITTORIO VENETO 89**

OCTOBER 6TH

8.30 AM	**OPENING**

SESSION 1	**CHAIR**	**P. MASSANISSO**	
9.00 AM	**IL 1**	**P. GARRIGUES**	**REACH: REGULATION AND ANALYTICAL CHEMISTRY**
9.30 AM	O1	M. ABU-DAABES AND H. ABU QDAIS	EFFECT OF LANDFILL AGING AND CONTROL ON MUNICIPAL LEACHATE CHARACTERISTICS IN JORDAN
9.50 AM	O2	H. ARDAĞ AKDOĞAN, N. PAZARLIOĞLU	FLUORENE BIODEGRADATION IN BATCH CULTURES OF SELECTED SUB-TROPICAL WHITE ROT FUNGI
10.10 AM	O3	K. HIROTA, D. PARAJULI AND N. SEKO	BIOMASS FOR THE SEPARATION OF FISSION PLATINOIDS
10.30 AM	O4	M.R. RAHIMIBASHAR, V. ALIPOOR, M.GIAHI	THE DETERMINATION OF LC50 AND BIOCONCENTRATION OF MERCURY CHLORIDE ($HgCl_2$) IN (*ESOX LUCIUS)*

10.50 AM	**COFFEE BREAK**

SESSION 2	**CHAIR**	**R. NIESSNER**	
11.10 AM	O5	C. BELPAIRE, S. FRASELLE, C. GEERAERTS, H. KAYIREBE, D. LAZA, T. REYNS, J. VAN LOCO	DYE RESIDUES IN FERAL EUROPEAN EEL IN BELGIUM: AN EMERGING RISK?
11.30 AM	O6	M. T. S.R. GOMES AND M. I. S. VERÍSSIMO	THE USE OF BIODISEL WITH COLD WEATHER: POUR POINT DETERMINATION USING AN ACOUSTIC WAVE SENSOR
11.50 AM	O7	T. KOSAKA AND K. SATO	NOVEL DENSIFICATION MECHANISM OF GADOLINIUM-DOPED CERIA AS ENERGY AND ENVIRONMENTAL MATERIAL
12.10 PM	O8	G. ARANA, A. DE DIEGO, S. FDEZ-ORTIZ DE VALLEJUELO, A. GREDILLA, J. M. MADARIAGA	COMBINATION OF REGULAR MONITORING, SEDIMENT QUALITY GUIDES, CHEMOMETRIC TOOLS AND EXTENSIVE SAMPLING TO INVESTIGATE THE QUALITY OF SEDIMENTS. A CASE STUDY: THE ESTUARY OF THE NERBIOI-IBAIZABAL RIVER (BILBAO, BASQUE COUNTRY)
12.30 PM	O9	A. GROSS AND M. MAGES	TRACE METAL ANALYSIS OF BIOINDICATORS BY TXRF
12.50 PM	O10	M. HAMZEH, B. OUDDANE, G. BILLON	TRACE METALS MOBILIZATION FROM SURFICIAL SEDIMENTS OF THE RIVER SEINE ESTUARY
1.10 PM	O11	A. MOHAMAD, R. KREUZIG, M. BAHADIR	FATE MONITORING OF ^{14}C-DICLOFENAC IN LABORATORY WATER/SEDIMENT SYSTEMS

1.30 PM	**LUNCH**

2.15 PM	**POSTER SESSION A**

SESSION 3	**CHAIR**	**P. GARRIGUES**	
3.00 PM	**IL 2**	**R. NIESSNER**	**MICROARRAY TECHNOLOGY: A WAY TO EXONERATE CLASSICAL ANALYSIS**
3.30 PM	O12	I. JURANOVIĆ CINDRIĆ, I. KRIZMAN, G. STINGEDERAND M. ZEINER	DETERMINATION OF SELECTED TOXIC ELEMENTS IN APPLES FROM ORGANIC FARMING
3.50 PM	O13	M. KRÖPPL, C. LANZERSTORFER, M. ZEINER	BIOMASS ASHES – USEFUL OR HARMFUL FOR PLANTS?
4.10 PM	O14	F. CERECEDA-BALIC, J. L. GUEVARA, X. FADIC, C. MIRO, M. R. PALOMO, E. PINILLA, F. RUEDA, V. VIDAL	MAJOR AND TRACE ELEMENTS COMPOSITION OF TOTAL (WET AND DRY) DEPOSITION IN THE INDUSTRIAL AREA OF PUCHUNCAVÍ, CHILE

4.30 PM	**COFFE BREAK**

SESSION 4	**CHAIR**	**M. KHANMOHAMMADI**	
4.50 PM	O15	P. CORVINI, G. H. FLOOR, M. IGLESIAS, M. LENZ, G. ROMAN-ROSS	SELENIUM TRACE SPECIATION IN ACIDIC ENVIRONMENTAL SAMPLES BY HPLC-ICP-MS
5.10 PM	O16	T. KIMURA, M. MAGARA, Y. MIYAMOTO, AND K. YASUDA	SEQUENTIAL SEPARATION FOR ULTRA-TRACE ANALYSIS OF U, Th, Pb, AND LANTHANIDES IN ENVIRONMENTAL SAMPLES
5.30 PM	O17	K. A. HUNTER, M. NUMATA, M. R. REID AND C. H. STIRLING	ISOTOPIC TRACING OF LEAD POLLUTION IN NEW ZEALAND
5.50 PM	O18	A. ESMAILI SARI, A. MASHINCHIAN, M. POURKAZEMI, F. SHARIATI	EFFECTS OF SUBLETHAL EXPOSURE TO WATERBORNE Cd IN PERSIAN STURGEON: TISSUE SPECIFIC METAL ACCUMULATION

6.10 PM	**IAEAC MEMBERS: GENERAL ASSEMBLY**

OCTOBER 7TH

SESSION 1	**CHAIR**	**F. ARTUSO**	
8.30 AM	**IL 3**	**C. ZHANG**	**SAMPLING AND SAMPLING STRATEGIES FOR ENVIRONMENTAL ANALYSIS**
9.00 AM	O19	A. AL-RASHDAN, M.I.H. HELALEH, A. NISAR, A. IBTISAM	FAST ANALYSIS OF POLYCYCLIC AROMATIC HYDROCARBONS, ORGANO-CHLORINATED PESTICIDES AND POLYCHLORINATED BIPHENYLS IN ENVIRONMENTAL MARINE SAMPLES BY AUTOMATED PLE AND POWER ^{PREP} CLEAN-UP SYSTEM
9.20 AM	O20	M. KHANMOHAMMADI, S. ARMENTA, S. GARRIGUES, M. DE LA GUARDIA	STOPPED FLOW-FTIR SPECTROMETRIC DETERMINATION OF METRIBUZIN IN PESTICIDE FORMULATIONS
9.40 AM	O21	B. M.R. APPENZELLER, O. BRIAND, M. MILLET, L. TUDURI, C. SCHUMMER	SIMULTANEOUS PASSIVE SAMPLING OF POLYCYCLIC AROMATIC HYDROCARBONS (PAHs) AND CURRENT-USE PESTICIDES AND THEIR SPATIAL AND TEMPORAL VARIATIONS IN THE ATMOSPHERE OF LUXEMBOURG
10.00 AM	O22	M. N ABBAS, A. L. A. RADWAN	SOLID-CONTACT SULFIDE-SELECTIVE SENSOR FOR ITS FLOW INJECTION DETERMINATION IN ENVIRONMENTAL WATER
10.20 AM	O23	A. AKDOĞAN, Ü. DIVRIKLI, L. ELÇI	DETERMINATION OF PESTICIDE RESIDUES IN WATER SAMPLES BY DISPERSIVE LIQUID-LIQUID MICROEXTRCTION WITH CHEMOMETRIC APPROACH COUPLED WITH GC-MS
10.40 AM	O24	A. ARSLAN KARTAL, L. ELÇI	DETERMINATION OF CHLOROPHENOLS IN WATER SAMPLES USING DISPERSIVE LIQUID-LIQUID MICROEXTRACTION COMBINED WITH GC-MS

11.20 AM	**COFFEE BREAK**

SESSION 2	**CHAIR**	**C. ZHANG**	
11.40 AM	O25	M. KHANMOHAMMADI, N. DALLALI, F. KARAMI, A. BAGHERI GARMARUDI	MULTIVARIATE CURVE RESOLUTION ALTERNATING LEAST SQUARES ASSISTED DETERMINATION OF FORMALDEHYDE IN INDUSTRIAL WASTE WATER BY SPECTROPHOTOMETRY
12.00 PM	O26	R. BAUDOT, A. BULETE, C. CREN-OLIVE, J. GARRIC, M. GUST, L. WIEST	NANO-LIQUID CHROMATOGRAPHY-NANOSPRAY-MASS SPECTROMETRY FOR THE DETECTION AND QUANTIFICATION OF TRACES OF ENDOCRINE DISRUPTORS IN BENTHIC INVERTEBRATES
12.20 PM	O27	B. A. DINEEN, M. G. CAHILL, J. O'HALLORN, F. VAN PELT AND K. J. JAMES	SEMI-AUTOMATED LIQUID CHROMATOGRAPHY - MASS SPECTROMETRY (LC-MS/MS) METHOD FOR MICROCYSTINS IN LAKEWATERS
12.40 PM	O28	H. A. KADIR AND N. A. FAKHRE	FLOW-INJECTION SPECTROPHOTOMETRIC DETERMINATION OF NITRATE IN WASTE WATER SAMPLES USING DIAZOTIZATION COUPLING REACTION
1.00 PM	O29	G. C. GHOSH, H. TANAKA, N. YAMASHITA, N. NAKADA, T. AZUMA	UPLC-ESI-MS/MS METHOD FOR THE DETERMINATION OF FDA APPROVED ANTI-INFLUENZA PHARMACEUTICALS IN WATER ENVIRONMENT
1.20 PM	O30	M. GIAHI, M. R. RAHIMIBASHAR	NOVEL ZrO^{2+} ION-SELECTIVE ELECTRODE BASED ON A HEXA COSINE COMPOUND AS NEUTRAL CARRIER IN PVC MATRIX

1.40 PM **LUNCH**

2.25 PM **POSTER SESSION B**

SESSION 3	**CHAIR**	**R. DURST**	
3.10 PM	O31	M. GREGUSOVA AND B. DOCEKAL	MODIFIED DIFFUSIVE GRADIENT IN THIN FILMS TECHNIQUE IN DETERMINATION OF URANIUM IN SEDIMENTS
3.30 PM	O32	A. HÖL, L. ELÇI	OPTIMIZATION OF DISPERSIVE LIQUID-LIQUID MICROEXTRACTION OF NICKEL (II) BY ATOMIC ABSORPTION SPECTROMETRY
3.50 PM	O33	G. ANSANELLI, S. CANNARSA, S. CHIAVARINI, C. CREMISINI, G. DI LANDA, M. FANTINI, P. MASSANISSO, M. PEZZA, C. UBALDI	ASSESSMENT OF ANTIFOULING BIOCIDES CONTAMINATION IN DIFFERENT COASTAL AREAS OF ITALY
4.10 PM	O34	L. ACHENE, V. MELINI, M. OTTAVIANI, M. L. RICCI, E. VESCHETTI	AN ON-LINE ANALYTICAL EQUIPMENT TO DETECT H_2O_2 RESIDUES IN WARM-WATER DISTRIBUTION SYSTEMS DISINFECTED WITH H_2O_2 – Ag^+ AGAINST LEGIONELLA

4.30 PM **COFFEE BREAK**

SESSION 4	**CHAIR**	**C. BRUNORI**	
4.50 PM	O35	N. PARTHASARATHY, M. PELLETIER AND J. BUFFLE	DETERMINATION OF LIPOSOLUBLE NEUTRAL Cu(II) COMPLEXES IN NATURAL WATERS USING A PERMEATION LIQUID MEMBRANE PRECONCENTRATION PROBE
5.10 PM	O36	Z. A. ZHAKOVSKAYA, V. A. NIKIFOROV, V. N. PETROVA	PAHs IN ARCTIC SNOW
5.30 PM	O37	A. DOMBI, K. GAJDA-SCHRANTZ, E. ILLÉS, L. NOVÁKOVÁ, M. SEIFRTOVÁ, P. SOLICH	DEGRADATION OF FLUOROQUINOLONE ANTIBIOTIC PEFLOXACIN BY UV PHOTOLYSIS, OZONATION AND THEIR COMBINATION
5.50 PM	O38	S. ALI, S. A. S. CHATHA , A. I. HUSSAIN AND A. SHOUKAT	OPTIMIZATION OF FENTON'S PROCESS FOR THE DECOLORIZATION OF AZO DYES
6.10 PM	O39	K. CHOJNACKA, I. MICHALAK, A. ZIELIŃSKA	THE EFFECT OF HAIR CHARACTERISTICS AND TREATMENTS ON MINERAL COMPOSITION OF SCALP HAIR
6.30 PM	O40	R. BAUDOT, C. CREN-OLIVE, E. VULLIET, L. WIEST	LARGE SCREENING OF EMERGING POLLUTANTS IN SURFACE AND DEEP WATERS BASED ON ANALYSES BY LC/MS-MS

8.30 PM **SOCIAL DINNER**

OCTOBER 8TH

SESSION 1	**CHAIR**	**D. KLOCKOW**	
8.30 AM	**IL 4**	**M. ÁLVAREZ-PRIETO, J. JIMÉNEZ-CHACÓN**	**A FITNESS FOR PURPOSE APPROACH TO VALIDATION OF ANALYTICAL PROCEDURES**
9.00 AM	O41	J. WU, Z. YANG, L. ZHANG	ARTIFICIAL SWEETENERS AND FLUORESCENCE WHITENING AGENT IN SURFACE WATERS: DETERMINATION AND APPLICATION AS CHEMICAL TRACERS
9.20 AM	O42	X. QIAN, R. HU, Z. YANG AND L. ZHANG	OFF-FLAVOR ODOROUS COMPOUNDS IN WATER AND THEIR DETERMINATION
9.40 AM	O43	M. P. B. ESPINO	COMBINED CHROMATOPROBE AND GC-MS ANALYSIS OF POLYBROMINATED DIPHENYL ETHERS IN INDOOR DUST IN THE PHILIPPINES
10.00 AM	O44	F. GUEGUEN, M. MILLET, P. STILLE	FIELD CALIBRATION OF PASSIVE BASED-XAD 2 AIR SAMPLERS FOR PCB ANALYSIS: INVESTIGATION IN GAS/PARTICLE DISTRIBUTION
10.20 AM	O45	A. KOWALSKI, I. KURZYCA, J. SIEPAK AND B. WALNA	MERCURY CONCENTRATION IN DIFFERENT ATMOSPHERIC PRECIPITATION SPECIES

10.40 AM	O46	A. LIMBECK AND A. MUKHTAR	SLURRY SAMPLING ICP-AES PROCEDURE FOR FAST AND ACCURATE DETERMINATION OF CRUSTAL AND TRACE ELEMENTS IN AIRBORNE PARTICULATE MATTER
11.00 AM	O47	F. CERECEDA-BALIC, J. CHRISTIE, X. FADIC, J. L. GUEVARA, A. L. LLANOS, C. MIRO, M. R. PALOMO, E. PINILLA, V. VIDAL	MONITORING THE FINGERPRINT OF SANTIAGO DE CHILE URBAN ATMOSPHERIC AEROSOL ON TRACE ELEMENTAL PROFILES OF SNOW PRECIPITATION IN THE ANDES

11.20 AM	**COFFEE BREAK**		

SESSION 2	**CHAIR**	**A. PICCOLO**	
11.40 AM	**IL 5**	**A. BAEUMNER**	**MICROFLUIDIC AND NANOFIBER APPROACHES FOR DIAGNOSTICS IN RESOURCE-LIMITED SETTINGS**
12.10 PM	O48	K. HARTONEN, E. M. KYRÖ, J. PARSHINTSEV, T. PETÄJÄ, M. L. RIEKKOLA, J. RUIZ-JIMENEZ, A. VIRKKULA AND M. KULMALA	ELUDICATION OF ORGANIC VOLATILE COMPOUNDS IN ANTARCTIC AEROSOL PARTICLES
12.30 PM	O49	C. L. W. ARCINIEGAS, V. P. CAMPOS, L. P. DOS SANTOS, A. M. C. SILVA, S. T. OLIVA, T. M TAVARES	ACTIVE AND PASSIVE SAMPLING TECHNIQUES AND STRATEGIES FOR AIR MEASUREMENTS OF INORGANIC NITROGEN SPECIES TO MEET THE NEW DEMANDS IN TROPICAL AREAS
12.50 PM	O50	H. T ZHANG, G. Q. ZHOU, J. YANG, M. LI, L. X. ZHANG	DEVELOPMENT OF GAS CHROMATOGRAPHY-INDUCTIVELY COUPLED PLASMA ISOTOPE DILUTION MASS SPECTROMETRY FOR ACCURATE DETERMINATION OF KRYPTON AND XENON
1.10 PM	O51	J. BEČANOVÁ, Z. FRIEDL, Z. ŠIMEK AND I. UNGRÁDOVÁ	DETERMINATION OF EXPLOSIVES AND THEIR DEGRADATION PRODUCTS IN CONTAMINATED SOIL AREA

1.30 PM	**LUNCH**		

2.15 PM	**POSTER SESSION C**		

SESSION 3	**CHAIR**	**A. BAEUMNER**	
3.00 PM		**J. BROEKAERT AND K. JANSSENS**	**ANNOUNCEMENT: ISEAC 37 (2012)**
3.10PM	**IL 6**	**A. PICCOLO**	**NATURAL ORGANIC MATTER IN THE ENVIRONMENT: FROM SUPRAMOLECULAR STRUCTURE TO HUMEOMIC**
3.40 PM	O52	M. G. CAHILL, G. CAPRIOLI, K. J. JAMES AND S. VITTORI	ELUCIDATION OF THE MASS FRAGMENTATION PATHWAYS OF POTATO GLYCOALKALOIDS AND AGLYCONS USING ORBITRAP MASS SPECTROMETRY
4.00 PM	O53	B. CAREY, K. J. JAMES, J. O'HALLORAN AND F. VAN PELT	COMPARISON OF HYBRID LINEAR ION-TRAP ORBITRAP MASS SPECTROMETRY AND TRIPLE QUADRUPOLE MASS SPECTROMETRY FOR THE DETERMINATION OF POLYETHER PHYCOTOXINS CONTAMINANTS IN SHELLFISH
4.20 PM	O54	M. I. H. HELALEH, A. AL-RASHDAN, A. NISAR, A. IBTISAM, Z. AL-BALLAM	DETERMINATION OF THE LEVELS OF POLYCYCLIC AROMATIC HYDROCARBONS (PAHs) IN TOASTED BREAD BAKED FROM BARLEY, BRAN, CORN, RICE, SOYA AND FLACKS MIXED WITH SUN FLOWER SEEDS FLOURS USING GAS CHROMATOGRAPHY MASS SPECTROMETRY

4.40 PM	**COFFEE BREAK**		

SESSION 4	**CHAIR**	**M. ALVAREZ PRIETO**	
5.00 PM	O55	S. A. S. CHATHA, A. I. HUSSAIN, AND Z. NAWAZ	PROXIMATE ANALYSIS, MINERAL COMPOSITION AND ANTIOXIDANT POTENTIAL OF SOME LOCALLY GROWN VARIETIES OF TOMATO (*LYCOPERSION ESCULANTUM*)
5.20 PM	O56	A. DOMBI, K. GAJDA-SCHRANTZ, E. ILLÉS, E. SZABÓ	ECOTOXICITY OF KETOPROFEN DEGRADATION PRODUCTS
5.40 PM	O57	A. DOMBI, K. GAJDA-SCHRANTZ, T. OPPENLÄNDER AND E. SZAKÁCS	INTRINSIC PRODUCTION OF HYDROGEN PEROXIDE BY 172 nm PHOTOLYSIS OF WATER AND DURING THE PHOTOMINERALIZATION OF IBU- OR KETOPROFEN BY 172 nm AND/OR BY 185/254 nm LIGHT

6.00 PM	O58	A. C. DUARTE AND R. DUARTE	OPTIMIZATION OF A SIZE-EXCLUSION METHOD FOR THE CHARACTERIZATION OF NATURAL ORGANIC MATTER USING EXPERIMENTAL DESIGN TOOLS
6.20 PM	O59	K. SATO, K. FUJIMOTO, M. NAKATA, AND N. SHIKAZONOS	ELEMENTAL MIGRATION THROUGH NANO- AND SUBNANO-SCALE PORES IN GEOLOGICAL ENVIRONMENT

6.40 PM **ROLAND FREI AWARD: D. KLOCKOW, M. FREI, R. PILLOTON**

POSTER SESSIONS

OCTOBER 6TH, POSTER SESSION A P1-P50

P1	M. H. BANITABA, A. MEHDINIA, S. SEYEDHOSSEINIDAVARANI	APPLICATION OF A DNA-IL-CPE MODIFIED ELECTRODE AS AN ELECTROCHEMICAL BIOSENSOR FOR DETERMINATION OF TRACE AMOUNTS OF AFLATOXIN B1
P2	O. BAUSHEVA AND A. L. RANTALAINEN	MONITORING OF HYDROPHOBIC ORGANIC POLLUTANTS IN URBAN RUNOFF AND SEDIMENTS WITH PASSIVE AND ACTIVE SAMPLING
P3	Y. BENMALEK	STUDY ON HEAVY METAL RESISTANT BACTERIA IN OUED EL- HARRACH
P4	R. BAUDOT, J. CAMILLERI, C. CREN-OLIVE, E. VULLIET, L. WIEST	TRACE ANALYSIS OF 29 ENDOCRINE DISRUPTORS COMPOUNDS IN ENVIRONMENTAL SAMPLES BY LIQUID CHROMATOGRAPHY TANDEM MASS SPECTROMETRY
P5	I. G. DAKOVA, V. A. DAKOV, I. B. KARADJOVA AND M. G. KARADJOV	TRACE METAL SPECIATION IN BLACK SEA WATERS EVALUATED BY CHITOSAN MEMBRANES AND DGT
P6	F. AFLAKI, G. DANESHVAR, M. SALAHINEJAD	OPTIMIZATION AND DETERMINATION OF CADMIUM IN DIFFERENT ENVIRONMENTAL WATER SAMPLES WITH DISPERSIVE LIQUID–LIQUID MICROEXTRACTION PRECONCENTRATION COMBINED WITH INDUCTIVELY COUPLED PLASMA OPTICAL EMISSION SPECTROMETRY
P7	D. ALBANESE, M. DI MATTEO AND R. PILLOTON	SCREENING AND RESOLUTION OF CARBAMIC AND ORGANOPOSPHATE PESTICIDES MIXTURE IN EXTRA VIRGIN OLIVE OIL WITH A BI-ENZYMATIC AMPEROMETRIC SENSOR
P8	P. DIVIŠ AND J. MACHÁT	THE USE OF AQUATIC MOSSES FOR MONITORING OF METAL POLLUTION IN MORAVA RIVER
P9	Ü. DIVRIKLI , A. AKDOĞAN, A. HOL, M. SOYLAK, L. ELÇI	DETERMINATION OF CHROMIUM (VI) IN ENVIROMENTAL SAMPLES BY ELECTROTHERMAL ATOMIC ABSORPTION SPECTROMETRY AFTER LEACHING WITH SODIUM CARBONATE
P10	R. DJINGOVA AND V. V. LYUBOMIROVA	ENVIRONMENTAL FATE OF TRAFFIC RELEASED RARE EARTH ELEMENTS
P11	V. DREVENKAR, G. MENDAŠ, AND M. VULETIĆ	ANALYSIS OF METABOLITES IN URINE AS BIOCHEMICAL INDICATORS OF HUMAN EXPOSURE TO ATRAZINE
P12	M. R. DRISS, W. BEN AMEUR	PERSISTENT ORGANOCHLORINE PESTICIDES, POLYCHLORINATED BIPHENYLS, POLYBROMINATED DIPHENYL ETHERS IN FISH FROM BIZERTE LAGOON, TUNISIA
P13	N. RÉ-POPPI, S. S. GEBARA	BTEX DETERMINATION IN UNDERGROUND WATER AT GAS STATIONS USING HS-SPME/GC – MS/MS IN CAMPO GRANDE, MS BRAZIL
P14	M. DEDUCH, S. R. G. BARRETO AND W. J. BARRETO	A STUDY ON THE PARTITION COEFFICIENTS OF METALS IN TROPICAL SURFACE WATER
P15	M. G GIGIMOL, K. R DHANYA, M BEENA.	HAZARDOUS DYE REMOVAL BY POLYMERIC HYDROGEL
P16	K. HIROTA AND D. PARAJULI	PROSPECTIVE OF EFFECTIVE SEPARATION OF FISSION PALLADIUM USING BIOMASS SORBENT
P17	Z. HOLUBOVA, M. MOOS, L. SOMMER	SIMULTANEOUS DETERMINATION OF METALS BY ICP-MS IN ENVIRONMENTAL WATERS USING SPE PRECONCENTRATION ON DIFFERENT SORBENTS
P18	G. GŁOSIŃSKA, A. IBRAGIMOW, M. SIEPAK AND B. WALNA	HEAVY METALS IN FLOODPLAINS SEDIMENTS – THE ROLE OF SAMPLING AND EXTRACTION PROCEDURES
P19	M. IDOUHAR, A. TAZEROUTI	SPECTROFLUORIMETRIC DETERMINATION OF ANIONIC SURFACTANTS USING RHODAMINE 6G
P20	K. KARIMZADEH, A. ZAHMATKESH	DETERMINATION OF OIL POLLUTION IN SEDIMENT USING FT- IR IN MAHSHAHR REGION, PERSIAN GULF
P21	M. R. DRISS, J. EPISSARD, A. GUENNE, I. LIMAM AND L. MAZEAS	PHENOL AND PENTACHLOROPHENOL BIODEGRADATION DURING MESOPHILIC AND THERMOPHILIC MUNICIPAL SOLID WASTE ANAEROBIC DIGESTION: TEMPERATURE EFFECT AND METABOLITES IDENTIFICATION USING A STABLE ISOTOPIC APPROACH

P22	A. M. CARRO, R. CELA, D. GARCÍA-RODRÍGUEZ, R. A. LORENZO	OPTIMIZATION OF A MATRIX SOLID-PHASE EXTRACTION METHOD FOR THE DETERMINATION OF PYRETHROID, ORGANOPHOSPHORUS AND CARBAMATE PESTICIDES IN EDDIBLE SEAWEED SAMPLES.
P23	SY CHENG, TF KANG, LP LU, LH XU	SULFATE (PFOS) ON ZrO_2 / DDAB ACTIVE NANO-ORDER FILM
P24	A. CRAVADOR, M. C. MATEUS, D. NEVES, O. WÓJCIK	NEW TRENDS IN CHEMICAL CHARACTERIZATION OF *PHLOMIS PURPUREA*ROOT EXTRACTS BY ION TRAP HPLC-PDA-ESI/MS/MS
P25	M. DJOGO, A. DVORNIĆ, D. MILOVANOVIĆ, J. RADONIĆ, M. TURK SEKULIĆ, M. VOJINOVIĆ MILORADOV, G. VUJIĆ	DETERMINATION OF HEAVY METALS IN LEACHATES FROM MUNICIPAL LANDFILL IN NOVI SAD
P26	I. G. DAKOVA, I. B. KARADJOVA AND E. K. MLADENOVA	TRACE MERCURY IN THE ENVIRONMENT
P27	T. PARYJCZAK, D. RYLSKA, J. SOKOŁOWSKI, K. SOKOŁOWSKI, M. I. SZYNKOWSKA	ASSESSMENT OF CORROSION RESISTANCE OF MILLED RESTORATIVE MATERIALS
P28	A. KINDNESS AND L. PILLAY	BEHAVIOR OF A NUMBER OF METAL SPECIES IN A CONTAMINATED ESTUARINE SYSTEM
P29	B. M. R. APPENZELLER, O. BRIAND, M. MILLET, C. RAEPPEL, L. TUDURI	EVALUATION OF AIR CONTAMINATION GENERATED BY NON-AGRICULTURAL PESTICIDES: A FIELD CALIBRATION OF TENAX PASSIVE SAMPLERS
P30	S. RAHMANPOUR, H. REZAIE, M. S. HASHTROUDI	POLLUTION ASSESSMENT AND SOURCE IDENTIFICATIONS OF POLYCYCLIC AROMATIC HYDROCARBONS IN THE COASTAL SEDIMENTS OF KISH ISLAND
P31	A. Z. RAZYAPOV, S. S. VORONICH, A. P. SKIBARKO, A. G. YUDIN, L. A. SHULTS	ENVIRONMENTAL PROBLEMS OF THERMAL PROCESSING OF WASTE AND ANALYTICAL MAINTENANCE OF THE CONTROL POLLUTION
P32	A. R. RIBEIRO , P. M.L CASTRO AND M. E.TIRITAN	DEVELOPMENT OF CHIRAL HPLC METHOD FOR MONITORING ENANTIOSELECTIVE BIODEGRADATION STUDIES OF PROPRANOLOL AND ATENOLOL
P33	I. RIBALCHENKO, I. RODIN , O. SHPIGUN , R. SMIRNOV	METABOLITES OF NERVE AGENTS DETERMINATION BY CAPILLARY ELECTROPHORESIS
P34	I. BEŠLIĆ, V. DREVENKAR, R. GODEC, M. SAMBOLEC, K. ŠEGA, AND Ž. VASILIĆ	ORGANOCHLORINE PESTICIDES AND POLYCHLORINATED BIPHENYLS IN ATMOSPHERIC FINE PARTICLES COLLECTED IN ZAGREB OVER TEN YEARS
P35	L. SANG AND Z. ZHANG	PHOTOELECTROCHEMICAL PROPERTIES OF NANOSTRUCTURED ELECTRODE WITH TITANIA NANOTUBE ARRAYS
P36	J. SOKOŁOWSKI, K. SOKOŁOWSKI, M. I. SZYNKOWSKA	THE INFLUENCE OF NANOSILVER ADDITION ON METAL IONS RELEASE FORM LIGHT-CURED COMPOSITE AND COMPOMER RESTORATIVE MATERIALS INTO 0,9% NaCl
P37	M. F.ALPENDURADA, E. CUNHA, C. GONÇALVES AND M. A. SOUSA	ENVIRONMENTAL “LIFE COURSE” OF A REPRESENTATIVE LIST OF PHARMACEUTICAL POLLUTANTS AND RESULTING TRANSFORMATION PRODUCTS: A PORTUGUESE CASE STUDY
P38	P. DIVIŠ, H. DOČEKALOVÁ, M. KADLECOVÁ, R. SZKANDERA AND J. TRÁVNÍČKOVÁ	USE OF TiO_2 IN DIFFUSIVE GRADIENTS IN THIN FILMS TECHNIQUE (DGT) FOR MERCURY DETERMINATION IN AQUATIC ENVIRONMENT
P39	E. LEŚNIEWSKA, T. PARYJCZAK, A. PAWLACZYK, J. SOKOŁOWSKI, K. SOKOŁOWSKI, M. I. SZYNKOWSKA	THE RELEASE STUDY OF THE METAL IONS FROM RESTORATIVE MATERIALS INTO 0,9 % NaCl SOLUTION
P40	G. A. KEENAN, L. M. MELTON, E. A. SHARP, M. J. TAYLOR AND J. E. WATSON	USING LIQUID CHROMATOGRAPHY-TANDEM MASS SPECTROMETRY TO MONITOR ACCIDENTAL OR DELIBERATE PESTICIDE POSIONING OF VERTEBRATE WILDLIFE AND DOMESTIC ANIMALS IN SCOTLAND
P41	C. MARANHÃO, M. T. SOARES, A. R. RIBEIRO, V. GONÇALVES, A. MAIA, M. F. CARVALHO, P. M.L CASTRO, AND M. E.TIRITAN	MICROBIAL DEGRADATION OF SEVERAL PHARMACEUTICAL MONITORING BY VALIDATED HPLC-DAD METHOD
P42	L. CAMPANELLA, E. MARTINI, M. TOMASSETTI	NEW IMMUNOSENSORS FOR 2,4-D AND 2,3,5-T PESTICIDES DETERMINATION
P43	B. DOČEKAL, H. DOČEKALOVÁ, J. TRÁVNÍČKOVÁ	APPLICATION OF DGT TECHNIQUE IN ASSESMENT OF AVAILABILITY OF COPPER TO *RAPHANUS SATIVUS*
P44	E. G. AMVRAZI, M. A. MARTINI AND N. G. TSIROPOULOS	HEADSPACE SINGLE-DROP MICROEXTRACTION OF COMMON PESTICIDE CONTAMINANTS IN HONEY

P45	M. TANGUY, C. VIALLE, C. SABLAYROLLES, M. MONTREJAUD-VIGNOLES	DETERMINATION OF PESTICIDES BY SPE AND HPTLC: APPLICATION IN REUSE RAINWATER
P46	DR. C. D. GEDDES, S. A. YOUNG	METAL-ENHANCED FLUORESCENCE BASED DETECTION OF BISPHENOL A
P47	G. A. ZACHARIADIS, E. TRIKAS	SPECIATION METHOD FOR Cr^{3+}, Cr^{6+}, As^{3+} / As^{5+} DETERMINATION BY SOLID PHASE EXTRACTION AND INDUCTIVELY COUPLED PLASMA ATOMIC EMISSION SPECTROMETRY
P48	D. ALBANESE, M. DI MATTEO AND A. CRESCITELLI	SCREEN PRINTED BIOSENSORS BASED ON NITRATE REDUCTASE FROM ASPERGILLUS NIGER AND ESCHERICHIA COLI
P49	S. A. A. ALMEIDA, A. M. HEITOR, M. C. B. S. M. MONTENEGRO, M. G. F. SALES	MONITORING SULFAMETHOXAZOLE IN AQUACULTURE WATER
P50	S. ARPADJAN, J. KNUTSSON, P. PETROVA, K. TSEKOVA	FIELD SAMPLING, SPECIATION AND DETERMINATION OF DISSOLVED IRON(II) AND IRON(III) IN WATERS

OCTOBER 7TH, POSTER SESSION B P51-P100

P51	M. ASIABI, A. JABBARI AND A. MEHDINIA	ELECTROCHEMICAL PREPARATION OF NANO-STRUCTURED COPOLYMER OF ANILINE AND m-AMINO BENZOIC ACID COATING AND ITS APPLICATION IN THE HEADSPACE SOLID-PHASE MICROEXTRACTION OF FATTY ACIDS IN ZOOPLANKTONS
P52	J. AUFARTOVÁ ,L. NOVÁKOVÁ, J. J. SANTANA-RODRÍGUEZ, P. SOLICH, Z. SOSA-FERRERA, M. E. TORRES-PADRÓN	COMPARISON OF DIFFERENT CAPILLARY COMLUMNS IN THE OPTIMIZATION OF IN-TUBE SPME EXTRACTION OF ENDOCRINE DISRUPTORS IN ENVIRONMENTAL LIQUID SAMPLES
P53	R. ZAKERIAN, S. BAHAR	DISPERSIVE LIQUID PHASE MICROEXTRACTION COMBINED WITH FLAME ATOMIC ABSORPTION SPECTROMETRY FOR DETERMINATION OF Fe IN ENVIRONMENTAL WATER SAMPLES
P54	N. D. BERNARDINO, R. AFONSO, S. R. G. BARRETO, S. M. OBARA DOI AND W. J. BARRETO	A KINETIC STUDY ON THE BIODEGRADATION OF TEXTILE EFFLUENT USING UV-VIS SPECTROSCOPY AND PLS
P55	A. M. FREITAS, D. N. ISHIKAWA, E. M. DEDUCH, K. P. S. ZANONI, M. C. SOLCI, M. DO C. S. RIBEIRO, S. R. G. BARRETO AND W. J. BARRETO	UV-VIS SPECTROSCOPY AND CHEMICAL PROPRIETIES APPLIED TO CHARACTERIZE WATERS OF A TROPICAL RESERVOIR
P56	A. N. BAUTISTA FLORES, J. DE GYVES M., J. Å. JÖNSSON, E. R. DE SAN MIGUEL G.	PASSIVE SAMPLING OF Ni(II) USING A KELEX 100-CONTAINED HOLLOW FIBER SUPPORTED LIQUID MEMBRANE DEVICE
P57	E. BECERRIL-BRAVO, J. P. LAMAS, L. SANCHEZ-PRADO, M. LORES, C. GARCIA-JARES, B. JIMENEZ, AND M. LLOMPART	ALLERGEN FRAGRANCES IN WATER FOR ULTRASOUND-ASSISTED EMULSIFICATION–MICROEXTRACTION
P58	A. BOUDINA, R. BAUDOT, J.M. CHOVELON	TRACE LEVEL ANALYSIS OF TRIFLOXYXTROBIN AND ITS TRANSFORMATION PRODUCTS IN WATER BY HPLC/MS
P59	X. BOUTSIADOU AND D. HUNKELER	IN SITU SYSTEM DEVELOPMENT FOR MEASURING CHLORINATED HYDROCARBONS IN GROUNDWATER
P60	A. BAHLMANN, V. CALISTO, V. I. ESTEVES, R. J. SCHNEIDER	DETERMINATION OF THE PSYCHIATRIC DRUG CARBAMAZEPINE IN WASTE WATERS BY ELISA
P61	C. CREMISINI, L. DELLA SETA, M. R. MONTEREALI, W. VASTARELLA	AMPEROMETRIC DETERMINATION OF ARSENIC(III) USING PLATINUM -MODIFIED SCREEN-PRINTED CARBON-BASED ELECTRODES
P62	L. DIDAOUI AND A. TOUABET	HIGH-PERFORMANCE LIQUID CHROMATOGRAPHY WATER ANALYSIS USING COMBINED UV-ELECTROCHEMICAL DETECTION OF SOME EXPLOSIVES, BY-PRODUCTS AND METABOLITES
P63	M. DJOGO, A. DVORNIĆ, D. MILOVANOVIĆ, J. RADONIĆ, M. TURK SEKULIĆ, M. VOJINOVIĆ MILORADOV, G. VUJIĆ	DETERMINATION OF POLLUTANT PARAMETERS USING AAS IN LANDFILL LEACHATE WATER OF VOJVODINA REGION
P64	H. EBRAHIMZADEH, M. M. AMINI, N. TAVASSOLI	SOLID PHASE EXTRACTION OF Ni(II) ON NOVEL PYRIDINE-FUNCTIONALIZED MCM-41 AND MCM-48 MESOPOROUS SILICAS AND ITS SUBSEQUENT DETERMINATION BY FAAS

P65	S.M. CARDOSO, I. V. ESTEVES, A. P. FONSECA	OPTIMIZATION OF AN SPE PROCEDURE FOR ANALYSIS OF HORMONES IN WATER SAMPLE BY HPLC-UV
P66	T. DAVIS, F. GAGNÉ, C. GAGNON AND P. TURCOTTE	SIZE DISTRIBUTION AND ENVIRONMENTAL FATE OF ENGINEERED NANOPARTICLES UNDER AQUATIC CONDITIONS
P67	R. CELA, I. GONZÁLEZ, J. B. QUINTANA AND I. RODRÍGUEZ	OCCURRENCE AND BIODEGRADATION OF PARABENS AND THEIR MOST COMMON HALOGENATED BY-PRODUCTS IN WASTEWATER
P68	M.-H. GUERMOUCHE	WASTE WATER POLYAROMATIC HYDROCARBONS POLLUTION CONTROL USING LIQUID CHROMATOGRAPHY WITH A NEW BONDED LIQUID CRYSTAL STATIONARY PHASE AND OFF-LINE SOLID PHASE EXTRACTION
P69	A. ASGHARINEZHA, H. EBRAHIMZADEH, F. KAMAREI, N. TAVASSOLI	SEPARATION AND SPECTROPHOTOMETRIC DETERMINATION OF VERY LOW LEVELS OF Cr(VI) IN WASTEWATER ON NOVEL PYRIDINE-FUNCTIONALIZED MESOPOROUS SILICAS
P70	A. KASHTIARAY AND H. R. SOBHI	TANDEM USE OF SOLID-PHASE EXTRACTION AND DISPERSIVE LIQUID-LIQUID MICROEXTRACTION FOR DETERMINATION OF SOME PHTHALATE ESTERS IN WATER SAMPLES
P71	M. KHANMOHAMMADI, A. BAGHERI GARMARUDI, H. ELMIZADEH	INVESTIGATING THE PHOTOCATALYTIC CAPABILITIES OF IRON OXIDE DOPED NANO TITANIUM OXIDE IN DEGRADATION OF FORMALDEHYDE
P72	S. HASSANPOOR, G. KHAYATIAN, F. NASIRI, A. ZOLALI	PREPARATION OF DIMETHYL(*E*)–2–(1-ACETYL)-2-OXO PROPYL-2-BUTENDIATE AS A NEW LIGAND FOR SOLID PHASE EXTRACTION AND SPECIATION OF Fe^{2+} AND Fe^{3+} IONS IN ENVIRONMENTAL WATER SAMPLES
P73	C. JANFELT, R. GRÆSBØLL AND F. R. LAURITSEN	PORTABLE ELECTROSPRAY IONIZATION MASS SPECTROMETRY (ESI-MS) FOR ANALYSIS OF CONTAMINANTS IN THE FIELD
P74	L. MACHÁČKOVÁ AND M. ŽEMBERYOVÁ	THE SELECTION OF AN UNIVERSAL CHEMICAL MODIFIER FOR VANADIUM DETERMINATION IN VARIOUS NATURAL WATERS BY ELECTROTHERMAL ATOMIC ABSORPTION SPECTROMETRY
P75	E. BEINROHR, R. HUDEC, A. MANOVA	DETERMINATION OF HYDRAZINE IN BOILER WATERS BY COULOMETRIC TITRATION
P76	C. CASAIS, R. CELA, C. MEJUTO, T. PENA, X. VECINO	DEVELOPMENT OF A IONIC LIQUID BASED DISPERSIVE LIQUID-LIQUID MICROEXTRACTION METHOD FOR BENZOTRIAZOLES AND BENZOTHIAZOLES DETERMINATION IN WATER SAMPLES
P77	M. MOOS, Z. HOLUBOVA, L. SOMMER	ECOTOXICOLOGY ASSESSMENT AND CHEMICAL CHARACTERISTICS OF WATER SAMPLES AFTER MINING AND PROCESSING OF URANIUM
P78	E. HERNÁNDEZ, F. MARTÍNEZ, B. E. OLIVA-HERNÁNDEZ, J. F. PÉREZ-SABINO, B. S. VALLADARES-JOVEL	CONTAMINATION OF LAKE ATITLÁN, GUATEMALA
P79	L. ACHENE, M. OTTAVIANI, P. PETTINE, E. VESCHETTI	FAST DETERMINATION OF ARSENIC INORGANIC SPECIES IN GROUNDWATER BY SPE-ETAAS
P80	R. BERNARDINO, J. P. NORONHA, Ž. PETROVSKI, M. I. PINTO	EXTRACTION OF AMITROLE FROM WATER SAMPLES BY SPME AND LPME PRIOR TO GC-MS ANALYSIS
P81	S. A.A. ALMEIDA, T. S. C. R. REBELO AND M. G.F. SALES	TRIMETHROPIM - IMPRINTED MATERIALS FOR POTENTIOMETRIC DETERMINATION IN AQUACULTURE WATER
P82	A. M. RODRIGUES, V. V. CARDOSO, E. FERREIRA, AND M. J. BENOLIEL	ANALYSIS OF ENDOCRINE DISRUPTORS IN WATER BY SOLID-PHASE EXTRACTION, LIQUID CHROMATOGRAPHY AND ELECTROSPRAY TANDEM MASS SPECTROMETRY – COMPARISON OF HPLC AND UPLC SYSTEM PERFORMANCE
P83	A. JABBARI, A. MEHDINIA AND F. ROOHI	DETERMINATION OF 1,4-DIOXANE IN WATER SAMPLES BY SELF-DOPED POLYANILINE BASED SOLID-PHASE MICROEXTRACTION FIBER
P84	M. SANGELY, C. SABLAYROLLES, P. STREHAIANO, L. THANNBERGER AND M. MONTREJAUD-VIGNOLES	FAITH OF POLYCHLOROBIPHENYLS' BEHAVIOUR DURING AN AQUEOUS BIOREMEDIATION ASSAY WITH PHANEROCHAETE CHRYSOSPORIUM. KINETICS OF DEGRADATION AND SORPTION ON MYCELIUM
P85	K. CHOJNACKA, I. MICHALAK AND A. ZIELIŃSKA	THE EFFECT OF LOCAL INDUSTRY IN WROCLAW CITY ON THE CONTENT OF HEAVY METALS IN HUMAN SCALP HAIR
P86	K. CHOJNACKA, I. MICHALAK, A. ZIELIŃSKA	THE CORRELATION BETWEEN MINERAL COMPOSITION OF HUMAN HAIR AND THE ILLNESSES

P87	I. RODIN, O. SHPIGUN, R. SMIRNOV, A. SMOLENKOV	UNSYMMETRICAL DIMETHYLHYDRAZINE AND GLYOXAL DETERMINATION BY HPLC-UV BASED ON THE REACTION OF ALKYLHYDRAZINES WITH GLYOXAL
P88	I. ÁBRAHÁM, A. DOMBI, M. MÁJER, K. MOGYORÓSI, E. SZABÓ, K. VAJDA, G. VERÉB	REMOVAL AND ANALYSIS OF ORGANIC POLLUTANTS IN INDUSTRIAL WASTE WATER AND THERMAL WATER
P89	I ÁBRAHÁM, A. DOMBI, M. MÁJER, K. MOGYORÓSI, K. GAJDA-SCHRANTZ, E. SZABÓ, K. VAJDA, G. VERÉB	REMOVAL OF ORGANIC POLLUTANTS FROM THERMAL WATER BY ADSORPTION-COAGULATION METHODS AND ADVANCED OXIDATION PROCESSES
P90	C. CASAIS, R. CELA, C. MEJUTO, T. PENA, X. VECINO	ANALYSIS OF POLYCYCLIC AROMATIC HYDROCARBONS IN SEWAGE SLUDGE SAMPLES BY HIGH PERFORMANCE LIQUID CHROMATOGRAPHY AND FLUORESCENCE DETECTION. COMPARISON OF DIFFERENT SAMPLE PREPARATION PROCEDURES
P91	R. CELA, I. GONZÁLEZ-MARIÑO, J. B. QUINTANA, R. RODIL, I. RODRÍGUEZ, E. VILLAVERDE-DE-SÁA	IN-SAMPLE ACETYLATION-NON-POROUS MEMBRANE-ASSISTED LIQUID-LIQUID EXTRATION FOR THE DETERMINATION OF PARABENS AND TRICLOSAN IN WATER SAMPLES
P92	H. AGAH, P. EGHTESADI ERAGHI, S. M. R. FATEMI, F. OWFI	ACCUMULATION OF MERCURY AND OTHER TRACE METALS IN LIVER AND MUSCLE OF MULLET AND KUTUM FISHES FROM THE CASPIAN SEA IN THE IRANIAN COASTLINE
P93	A. KASHTIARAY, N. ORUJI, AND H. R. SOBHI	APPLICATION OF ULTRASONIC PROBE-ASSISTED DISPERSIVE LIQUID-LIQUID MICROEXTRACTION FOR QUANTITATION OF SOME POLYCYCLIC AROMATIC HYDROCARBONS IN SOIL SAMPLES
P94	H. AGAH, S. M. R. FATEMI, A. MEHDINIA, A. SAVARI	COMPARISON OF DRY ASH AND WET EXTRACTION METHODS TO DETERMINE TOTAL MERCURY IN ENVIRONMENTAL SAMPLES (CASE STUDY: THE PERSIAN GULF AND THE CASPIAN SEA)
P95	C. ALVES, M. EVTYUGINA, C. GONÇALVES, C. MONTEIRO, A. VICENTE	ORGANIC COMPOSITION OF AEROSOLS EMITTED FROM A WILDFIRE IN CENTRAL PORTUGAL
P96	E. Y. ANDREEVA, S. G. DMITRIENKO, J. TANG	USE OF SOLID-PHASE EXTRACTION ON HYPERCROSSLINKED POLYSTYRENE FOR HPLC DETERMINATION OF METHYLXANTHINES
P97	V. V. APYARI, S. G. DMITRIENKO, P. A. VOLKOV, Y. A. ZOLOTOV	SILVER NANOPARTICLES IN POLYURETHANE FOAM: SYNTHESIS AND ANALYTICAL USING FOR DETERMINATION OF OXIDANTS AND REDUCTANTS
P98	F. ARTUSO, S. BECAGLI, C. BOMMARITO, D. CATALDI, M. MANSUETO, D. M. SFERLAZZO, P. SPEZZANO, R. UDISTI	CHARACTERIZATION OF PAHs IN ATMOSPHERIC PARTICULATE AT A REMOTE SITE IN THE MEDITERRANEAN
P99	P. I. AZEZ	EFFECT OF SOME POLLUTANTS ON THE ENVIRONMENTAL OF ERBIL CITY
P100	C. ARNAUDGUILHEM, A. BULETE, F. ROUVIERE	MULTIRESIDUE ANALYSIS OF ORGANOCHLORINES IN SOIL: A COMPARISON BETWEEN ASE AND QUECHERS EXTRACTION

OCTOBER 8TH POSTER SESSION C P101-P146

P101	H. DOČEKALOVÁ, V. KOVAŘÍKOVÁ, B. DOČEKAL	SOIL CHARACTERIZATION BY DIFFUSIVE GRADIENTS IN THIN FILMS TECHNIQUE
P102	A. C. DUARTE, L. I. B. SILVA, M. E. PEREIRA, M. FREITAS, T. A.P. ROCHA-SANTOS	MODELING THE ANALYTICAL RESPONSE OF CHEMICAL OPTICAL FIBER SENSORS
P103	J. FENOLL, M. D. HERNÁNDEZ, J. CAVA, M. MARTÍNEZ, M. V. MOLINA, P. HELLÍN AND P. FLORES	ORGANOCHLORINE CONTAMINANTS (PCBs AND OCPs) IN CAPTURED AND FARMED FISH FROM SPAIN
P104	V. DREVENKAR AND S. FINGLER	SORPTION BEHAVIOUR OF MUNITIONS CONSTITUENTS IN NATURAL SOILS
P105	N. BOUTARENE, Y. FOUDIL-CHERIF, B. Y. MEKLATI, N. YASSAA	ANALYSIS OF BIOGENIC VOLATILE ORGANIC COMPOUNDS EMITTED BY *JUNIPERUS COMMUNIS* USING HS-SPME/ GC/MS AND A COMPARISON WITH ITS ESSENTIAL OIL
P106	T. GARRIDO R. AND J. MENDOZA C.	PREPARATION AND VALIDATION OF DIFFUSIVE GRADIENTS IN THIN FILMS DEVICES (DGT) AND THEIR APPLICATION TO SOIL SOLUTIONS
P107	S. BOTTI, L. CANTARINI, M. FALCONIERI, G. GIUBILEO, A. PUIU, P. STACCHINI	OLIVE OIL ADULTERATION SENSING WITH LASER SPECTROSCOPY

P108	E. E. GOLIA, N. G. TSIROPOULOS, A. DIMIRKOU AND S. FLORAS	LEVELS OF HEAVY METALS IN SOIL EXTRACTS AND PLANT TISSUES AT AROUND OF A FACTORY LANDS
P109	F. GUEGUEN, J. J. SCHWARTZ, M. MILLET, C. SCHUMMER, P. STILLE	PASSIVE SAMPLING ON XAD-2 RESIN OF POLYCYCLIC AROMATIC HYDROCARBONS : FIELD CALIBRATION BY USING HIGH-VOLUME SAMPLING
P110	J. W. EINAX, T. HILDEBRANDT AND D. PICK	OPTIMIZING SAMPLING STRATEGIES IN TERRESTRIAL COMPARTMENTS FOR HOTSPOT DISTRIBUTIONS
P111	A. JABBARI, S. MAJDI	Fe_2O_3 CORE-$Co[Fe(CN)_6]$ SHELL NANOCATALYST FOR EFFICIENT ELECTROOXIDATION AND SENSITIVE DETECTION OF TRYPTOPHAN
P112	Y. KALEBAŞI AKTAŞ AND A. KOCABAŞ	DETERMINATION OF MANGANESE AT DIFFERENT DEPTHS OF ROADSIDE SOIL
P113	J. P. LAMAS, L. SANCHEZ-PRADO, E. BECERRIL-BRAVO, M. LORES, C- GARCIA-JARES, AND M. LLOMPART	ANALYSIS OF FRAGRANCE ALLERGENS IN INDOOR AIR BY SPE-SPME GC-MS
P114	S. HEIN, P. LEHNIK-HABRINK, I. NEHLS, T. WIN	MULTI-RESIDUE ANALYSIS OF PAH, PCB AND OCP OPTIMIZED FOR ORGANIC MATTER OF FOREST SOIL
P115	G. L. ERNY, V. I. ESTEVES, D. L. D. LIMA, C. P. SILVA	USING UV SPECTRAL DECONYOLUTION TO FOLLOW SORPTION EXPERIMENT IN SOIL AND COMPARISON WITH MEKC
P116	R. G. DJINGOVA AND V. V. LYUBOMIROVA	IDENTIFICATION OF PLATINUM-HUMIC ACID COMPLEXES IN SOILS AND STREET DUST SAMPLES BY MALDI-TOF-MS
P117	A. JABBARI, S. MAJDI	DETERMINATION AND ELECTROCATALYTIC OXIDATION OF METHIONINE BY NANOPARTICLES OF IRON(III) OXIDE CORE-COBALT HEXACYANOFERRATE SHELL-MODIFIED CARBON PASTE ELECTRODE
P118	J. MENDOZA, T. GARRIDO, V. BRIONES AND J. PARADA	DETECTION OF XANTHATES BY HPCL MS-MS AND QUANTIFICATION BY CAPILLARY ELECTROPHORESIS IN MINE TAILINGS AND SOILS
P119	M. FARAJI, M. HESABI , F. KEYHANIAN AND S. SHARIATI	APPLICATION OF SURFACTANT MODIFIED MAGNETIC NANOPARTICLES FOR REMOVAL OF METHYL VIOLET FROM AQUEOUS SOLUTIONS
P120	P. MIKUŠKA, M. VOJTĚŠEK, Z. VEČEŘA AND K. KŘŮMAL	SEMI-CONTINUOUS SYSTEM FOR ANALYSIS OF WATER-SOLUBLE FRACTION OF METALS IN ATMOSPHERIC AEROSOLS
P121	F. CERECEDA-BALIC, J. CHRISTIE, C. MIRO, E. PINILLA AND M. REIS	INDOOR MONITORING CAMPAIGN OF Rn-222 IN PUBLIC BUILDINGS OF THE CITIES OF VALPARAISO (CHILE) AND CACERES (SPAIN)
P122	M. HOSSEIN BANITABA, S. SEYEDHOSSEINIDAVARANI, A. MEHDINIA, A. A. MOHAMMADI	APPLICATION OF A POLYMERIC COATING ON GOLD WIRE FOR HS-SPME OF PAHs
P123	R. CELA, N. NEGREIRA. I. RODRIGUEZ, E. RUBÍ	SOLID-PHASE MICROEXTRACTION FOLLOWED BY GAS CHROMATOGRAPHY MASS SPECTROMETRY FOR THE DETERMINATION OF INK PHOTO-INITIATORS IN PACKED MILK
P124	J. NURMI	METHOD FOR SCREENING EMERGING CONTAMINANTS WITH LIQUID CHROMATOGRAPHY TIME-OF-FLIGHT MASS SPECTROMETRY
P125	O. MARTÍNEZ, B. E. OLIVA-HERNÁNDEZ, J. F. PÉREZ-SABINO, C. E. SILVA TORRES, J. P. TORRES	TOXIC METALS AND ORGANOCHLORINE PESTICIDES IN THE ENDEMIC WHITE FISH (*PETENIA SPLENDIDA*) AND CONTAMINATION OF THE LAKE PETÉN ITZÁ, GUATEMALA
P126	K. HARTONEN, M. KIVILOMPOLO, M. KULMALA, J. PARSHINTSEV, M. L. RIEKKOLA, J. RUIZ-JIMENEZ	PARTICLE-INTO-LIQUID SAMPLER ON-LINE COUPLED WITH LIQUID CHROMATOGRAPHY - MASS SPECTROMETRY FOR THE DETERMINATION OF ORGANIC ACIDS IN ATMOSPHERIC AEROSOLS
P127	J. BOJARSKA, E. LEŚNIEWSKA, T. PARYJCZAK, A. PAWLACZYK, S. SYPNIEWSKI, M. I. SZYNKOWSKA	CHARACTERIZATION OF TRACE ELEMENT PARTICLES DEPOSITED ON PLANT AND HUMAN HAIR SAMPLES COLLECTED FROM AREAS POLLUTED BY VARIOUS SOURCES
P128	A. M. CARRO, R. CELA, P. GONZÁLEZ, R. A. LORENZO, I. RACAMONDE	DETERMINATION OF CHLOROPROPANOLS IN FOOD SAMPLES BY PRESSURIZED LIQUID EXTRACTION (PLE) AND GAS CHROMATOGRAPHY-MASS SPECTROSCOPY (GC/MS)
P129	R. BAUDOT, C. CREN-OLIVE, M. V. SALVIA, E. VULLIET, L. WIEST	DEVELOPMENT OF AN ENVIRONMENTAL ANALYTICAL METHOD FOR THE DETERMINATION OF HORMONAL STEROIDS AND VETERINARY COMPOUNDS, AT TRACE LEVELS, IN SOIL

P130	M. FERNANDEZ-ALVAREZ, L. SANCHEZ-PRADO, J. P. LAMAS, M. LLOMPART, C. GARCIA-JARES, M. LORES	FIRST APPROACH TO THE STABILITY STUDY OF THE PRESERVATIVE BRONIDOX
P131	G. SEREN AND O.YORUK	INVESTIGATE OF ALUMINIUM CONCENTRATIONS IN SOIL AND SUNFLOWER (*HELIANTHUS ANNUUS L.*) BY ICP-OES IN ERGENE FIELD, TURKEY.
P132	M. H. BANITABA, S. SEYEDHOSSEINIDAVARANI, L. MASOOMI, H. R. LOTFI-ZADEH- ZHAD, O. SADEGHI	A NEW SPME FIBER FOR EXTRACTION OF 1,4-DIOXANE FROM ALKYL ETHER SULFATES AND COSMETICS USING HS-SPME AND GC ANALYSIS
P133	N. SHEIJOONI-FUMANI, R. YOUSEFI AND S. MIRZA	ANALYSIS OF AFLATOXIN B1 IN GRAINS BY HOMOGENEOUS LIQUID-LIQUID EXTRACTION METHOD
P134	J. AUGER AND V. SIMON	EVALUATION OF SEVERAL TECHNIQUES FOR DETERMINATION OF VOLATILE ORGANIC COMPOUNDS IN AIR SAMPLES
P135	I. JAKOVLJEVIĆ, G. PEHNEC, M. ŠILOVIĆ HUJIĆ, A. ŠIŠOVIĆ AND V. VAĐIĆ	SAMPLING AND ANALYSIS OF PAHs IN ZAGREB AIR
P136	V. DREVENKAR, M. ROŽIĆ, L. SEKOVANIĆ, S. STIPIČEVIĆ	POTENTIAL OF NATURAL AND MODIFIED MEDITERRANEAN SOIL TO PROTECT WATER SUPPLIES FROM TRIAZINE HERBICIDE RESIDUES
P137	N. TIGRINE-KORDJANI, F. CHEMAT, B. Y. MEKLATI	MICROWAVE ‘DRY’ DISTILLATION IN THE EXTRACTION OF *ROSMARINUS OFFICINALIS* L. ESSENTIAL OIL.
P138	V. VADJIĆ, S. ŽUŽUL	ARSENIC LEVELS IN FINE PARTICULATE MATTER IN ZAGREB AIR
P139	S. KHEDIDJI, R. LADJI, N. YASSAA	MEASUREMENTS OF *n*-ALKANES AND PAHs IN PM_{10} AND TOTAL SUSPENDED PARTICLES (TSP) IN URBAN AND INDUSTRIAL AREAS OF ALGIERS CITY
P140	D. CAMACHO-MUÑOZ, J. MARTÍN, J. L. SANTOS, I. APARICIO AND E. ALONSO	OCCURRENCE OF PHARMACEUTICALLY ACTIVE COMPOUNDS IN GUADIAMAR RIVER BASIN (SOUTH OF SPAIN)
P141	P. AVINO, G. CAPANNESI, M. MANIGRASSO AND A. ROSADA	DETERMINATION OF INTERSTING TOXICOLOGICALLY ELEMENTS IN PM2.5 BY NEUTRON AND PHOTON ACTIVATION ANALYSIS
P142	L. FOAN, C. SABLAYROLLES’ AND V. SIMON	OPTIMIZATION OF PRESSURIZED LIQUID EXTRACTION (PLE) OF POLYCYCLIC AROMATIC HYDROCARBONS FROM MOSSES ASSOCIATED WITH SOLID PHASE EXTRACTION (SPE) CLEAN-UP
P143	M. HUCULAK-MĄCZKA, K. HOFFMANN AND J. HOFFMANN	THE APPLICATION OF THE VOLTAMMETRIC METHOD TO DETERMINE THE DEGREE OF CHOSEN NUTRIENTS COMPLEXATION BY HUMIC SUBSTANCES
P144	V. V. APYARI, S. G. DMITRIENKO	POSSIBILITIES OF MINI-SPECTROPHOTOMETER EYE-ONE PRO AS AN ALTERNATIVE OF THE DIFFUSE REFLECTANCE SPECTROMETER FOR DETERMINATION OF ORGANIC SUBSTANCES USING DIAZOTIZED POLYURETHANE FOAM
P145	P. DIVIŠ, H. DOČEKALOVÁ, M. KADLECOVÁ, B. OUDDANE, R. SZKANDERA AND J. TRÁVNÍČKOVÁ	APPLICATION OF DIFFUSIVE GRADIENT IN THIN FILMS TECHNIQUE WITH DIFFERENT SPECIFIC RESINS IN CONTAMINATED AND UNCONTAMINATED RIVER SEDIMENTS AND ITS COMPARATION WITH OTHER COMMON TECHNIQUES
P146	C. SABLAYROLLES, C. VIALLE, J. SILVESTRE, M. TREILHOU, C. LHOUTELLIER, V. BROCHIER, M. MONTREJAUD-VIGNOLES	POLYCHLORINATED BIPHENYLES UPTAKE BY CARROTS AFTER SLUDGE COMPOSTS APPLICATION: WASTE-CASE AND OPERATIONAL PRACTICE IN GREENHOUSE CONDITIONS
P147	S. SCAGLIONE, I. DI SARCINA, D. FLORI, F. MENCHINI	MEASUREMENTS OF GLOBAL UV IRRADIANCE, BY A VERY STABLE HOME MADE NARROW BAND FILTER RADIOMETER

AUTHOR INDEX

ABSTRACTS

INVITED LECTURES

IL1- REACH: REGULATION AND ANALYTICAL CHEMISTRY

P. Garrigues

Institute or Molecular Sciences, UMR 5255
CNRS/Université de Bordeaux 1 (France)

Over the next decades thousands of chemicals manufactured in or imported into the European Union will have to be tested, assessed and registered under the REACH regulation. Information on health and safety of these chemicals must be provided by commercial companies to the European Chemicals Agency (ECHA) in Helsinki. In order to achieve a successful implementation of REACH, a comprehensive effort of fundamental research is imperative. This presentation will deal with the various aspects of the assessment of chemicals related to toxicology, ecotoxicogy, QSAR and with the role of advanced analytical chemistry. If analytical chemistry is not per se mentioned in REACH, it may be part of it at every stage of the Chemicals Policy.

Advances of analytical chemistry particulary in:

- better analytical specificities of analysed compounds including degraded and biotransformed compounds in various environmental compartments,
- low limits of detection linked to effects at low dose exposure,
- multi-component analyses to reduce human and environmental impacts and costs will be strongly involved into the implementation of REACH.

The research needs in conjunction with the REACH Regulation will be presented.

IL2- MICROARRAY TECHNOLOGY: A WAY TO EXONERATE CLASSICAL ANALYSIS

R. Niessner

Chair for Analytical Chemistry, Institute of Hydrochemistry, Technische Universität München,
Marchioninistrasse 17, D-81377 München (Germany)

A novel automated chemiluminescence (CL) read-out system for analytical flow-through microarrays based on multiplexed immunoassays has been developed. The microarray chip reader (MCR 3) is designed as a stand-alone platform, with the goal to quantify multiple analytes in complex matrices of food and liquid samples for field analysis or for routine analytical laboratories. The CL microarray platform is a self-contained system for the fully automated multiplexed immunoanalysis: the microarray chip, the fluidic system and the software module enable automated calibration and determination of analyte concentrations during a whole working day. The detection of antibiotics in milk was demonstrated to validate this device. There are few quantitative multi-residue detection methods for routine analysis although the EU has defined maximum residue limits (MRLs) for a number of antibacterial reagents. Therefore, an automated multianalyte detection instrument is needed quantifying simultaneously antibiotics within some minutes. Also regeneration is required to avoid replacing the assay surface. The MCR 3 uses a microarray chip, which consists of two channels for parallel measurement and regeneration. The microarray chip is designed for parallel analysis of up to 15 different antibiotics in milk applying an indirect competitive microarray immunoassay (MIA). Microspotted antibiotics are directly coupled to epoxylated PEG surfaces. The chip surface is regenerable for 50 measurement cycles per channel. Assay time, incl. Regeneration, is 6 min.

Fast, sensitive, and esp., multianalyte test systems are currently of high interest for the monitoring and quality control of drinking water, since traditional microbiol. methods are labor intensive and can take days until a response is achieved. The 1st flow-through chemiluminescence microarray was developed and characterized for the rapid and simultaneous detection of Escherichia coli O157:H7, Salmonella typhimurium, and Legionella pneumophila in water samples using a semiautomated readout system. Therefore, antibody microarrays were produced on poly(ethylene glycol)-modified glass substrates by a contact arrayer. For capturing bacteria, species-specific polyclonal antibodies were used. Cell recognition was carried out by binding of species-specific biotinylated antibodies. Chemiluminescence detection was accomplished by a streptavidin-horseradish peroxidase (HRP) catalyzed reaction of luminol and hydrogen peroxide. The chemiluminescence reaction that occurred was recorded by the MCR 3 platform. The overall assay time was 13 min, enabling a fast sample anal. In multianalyte expts., the detection limits were 3 × 106, 1 × 105, and 3 × 103 cells/mL for S. typhimurium, L. pneumophila, and E. coli O157:H7, resp. Quantification of samples was possible in a wide conc. range with good recoveries. The presented system is well suited for quick and automatic water analysis.

References

K. Kloth; R. Niessner Reinhard & M. Seidel (2009) Biosensors & Bioelectronics 24, 2106.
A. Wolter, R. Niessner & M. Seidel (2009) Analytical Chemistry 80, 5854.

IL3- SAMPLING AND SAMPLING STRATEGIES FOR ENVIRONMENTAL ANALYSIS

C. Zhang

School of Science and Computer Engineering, University of Houston-Clear Lake,
Houston, Texas 77058 (USA)

Introduction

The total error of environmental analysis is the sum of sampling error and analytical error. Sampling errors are generally believed to dominate the errors of analytical measurement. Under certain circumstances, the error ratio can reach up to 90% during the entire data acquisition process [1, 2], implying that further reduction in analytical uncertainty is probably of little importance [3, 4]. While analytical errors are frequently (yet improperly) reported to the third decimal point, sampling errors are hardly documented in environmental analysis. Such a discrepancy attributes to the difficulty in quantifying sampling errors due to various types of spatial and temporal heterogeneities. Traditional sampling theories, such as those developed for binary particulate systems, cannot be directly applied to complex environmental matrices.

The general strategies to reduce sampling errors, either through replicate samples or through increased sample size (volume or weight) [4, 5], are apparently not feasible. An optimal and practical sampling strategy should consider primarily sample representativeness while minimizing the total sampling and analytical cost. This presentation will address some important sampling strategies that are often overlooked in the analytical community who places more focuses on laboratory sample preparation and instrumental analysis. This talk will introduce several sampling approaches commonly employed in environmental sampling, as well as recent advance to formulate an optimal sampling strategy. Several key issues regarding, for example, the use of stratified random sampling, compositing, the effects of sample size and sampling frequency will be addressed with examples of sampling and sampling strategies applicable for chemical or biological analysis of air, water, soil, and hazardous waste sites.

Biased and Unbiased Sampling Approaches

Among a variety of sampling strategies, judgmental sampling and haphazard sampling are both non-probability based. While judgmental sampling can reduce sampling number using prior knowledge of sampling sites, it is biased and does not support any statistical interpretation. Haphazard sampling, mistakenly employed by many as a random approach, is also biased and legally not defensible since it encourages taking samples consciously at convenient locations or times [6]. Simple random sampling is applicable mostly for relatively homogeneous populations. It will result in more samples which is not cost-effective as other sampling designs [7]. This drawback can be overcome by systematic sampling design. Stratified random sampling is another common approach to reduce sample size and cost based on the variations and sampling cost in various strata. This sampling approach can significantly reduce standard deviation as compared to other approaches particularly if the strata are quite different from one another. The types of strata in environmental analysis vary depending on the differences in geographical, hydrological, meteorological, demographical, chemical, or biological features [e.g., 8, 9].

Reducing Sample Number and Sampling Frequency

Determining a minimally required sample number and sample frequency is often challenging for any environmental project. The minimal sample number to be representative of a population at a specified tolerable error limit can be determined: $n = \frac{s^2 t^2}{e^2}$, where s, t, and e are standard deviation, Student's t value, and allowable error, respectively. Since the t-value depends on sample number and confidence level, a prior knowledge regarding the spatial or temporal variations, albeit not always available, is needed to estimate n [6, 10]. In regulatory compliance monitoring, the "e" value can be substituted by RT- $\bar{x}$, where RT is regulatory threshold and $\bar{x}$ is the estimate of mean. This implies more samples are required when the estimated sample mean gets closer to the regulatory standard. In fact, a strategic oversampling (sampling out) occurred in some drinking water treatment systems where oversampling of drinking water was employed to avoid violation of the Total Coliform rule proscribed by the U.S. EPA [11].

In monitoring programs with a large number of monitoring stations and costly analysis, efforts have been made to reduce the cost by reducing the sampling frequency based on site-specific scenarios. Sampling frequency can be downgraded (e.g., annual to semiannual, or semiannual to quarterly) when contaminant concentration changes in groundwater wells become insignificant overt time [12]. However, problems arise when sampling become too infrequent. For example, the estimates of annual mean herbicide concentrations in Midwestern rivers due to "spring flush" were underestimated by quarterly sampling scheme as required by the U.S. EPA [13].

Compositing is another appealing sampling strategy to reduce sample numbers when sampling cost is low relative to analytical cost and the primary interest is to estimate the mean at the expense of variations [6, 14, 15]. Compositing can be achieved by physical grinding and mixing and flow-proportion for stormwater and wastewater sample collection.

Conclusions

It is of utmost importance for the environmental analytical chemists to be aware of the dominating sampling errors during the data acquisition process. One should recognize that all our careful lab work is wasted if a sample is not collected properly. In designing an optimal site-specific sampling strategy with regard to sampling location, time, frequency and sample number, one need to thoroughly examine the sources of temporal and spatial variations. In compliance monitoring, however, it is likely that the optimal strategy may not agree with what is required by the current regulatory agency.

References

[1] Crumbling D.M.; Groenjes C.; Lesnik, B.; Lynch, K.; Shockley, J.; Ee. J.V.; Howe, R.; Keith, L.; McKenna, J., Managing Uncertainty in Environmental Decisions, *Environ. Sci. Technol.,* 35:440A-409A (2001).

[2] Lame, F.P.J.; Defize, P.R., Sampling of Contaminated Soil: Sampling Error in Relation to Sample Size and Segregation, *Environ. Sci. Technol.,* 27:2035-2044 (1993).

[3] Kratochvil, B.; Wallace, D.; Taylor, J.K., Sampling for Chemical Analysis, *Anal. Chem*., 56, 113R-129R (1984).

[4] Kratochvil, B.; Taylor, J.K., Sampling for Chemical Analysis, *Anal. Chem*., 53, 924A-938A (1981).

[5] Ahmed, S.M.; Beasley, M.D.; Efromston, A.C.; Hites, R.A., Sampling Errors in the Quantitation of Petroleum in Boston Harbor Water, *Anal. Chem.,* 46:1858-1860 (1974).

[6] Zhang, C., Fundamentals of Environmental Sampling and Analysis, John Wiley & Sons, New York (2007).

[7] US EPA, Superfund Program Representative Sampling Guidance, volume 1-5 (1995).

[8] Short, J.W.; Maselko, J.M.; Lindeberg, M.R.; Harris, P.M.; Rice, S.D., Vertical Distribution and Probability of Encountering Intertidal Exxon Valdez Oil on Shorelines of Three Embayments within Prince William Sound, Alaska, *Environ. Sci. Technol*., 40:3723–3729 (2006).

[9] Friedman, W.; Brinkman, M.C.; Nishioka, M.G.; Cox, D.C., American Healthy Homes Survey: A National Study of Residential Pesticides Measured from Floor Wipes, *Environ. Sci. Technol.* 43:4294–4300 (2009).

[10] ACS Committee on Environmental Improvement, Guidelines for Data Acquisition and Data Quality Evaluation in Environmental Chemistry, *Anal. Chem*., 52:2242-2249 (1980).

[11] Bennear, L.S.; Jessoe, K.K.; Olmstead, S.M., Sampling Out: Regulatory Avoidance and the Total Coliform Rule, *Environ. Sci. Technol.,* 43:5176-5182 (2009).

[12] Johnson, V.M.; Tuckfield, R.C.; Ridley, M.N.; Anderson, R.A., Reducing the Sampling Frequency of Groundwater Monitoring Wells, *Environ. Sci. Technol.,* 30:355-358 (1996).

[13] Battaglin, W.; Hay, L.E., Effects of Sampling Strategies on Estimates of Annual Mean Herbicide Concentrations in Midwestern Rivers, *Environ. Sci. Technol.,* 30:889-896 (1996).

[14] Rohlf, F.J.; Akçakaya, H.R.; Ferraro, S.P., Optimizing Composite Sampling Protocols, *Environ. Sci. Technol*., 30:2899-2905 (1996).

[15] Whitman, R.L.; Nevers, M.B., *Escherichia coli* Sampling Reliability at a Frequently Closed Chicago Beach: Monitoring and Management Implications, *Environ. Sci. Technol.,* 38:4241-4246 (2004).

IL4- A FITNESS FOR PURPOSE APPROACH TO VALIDATION OF ANALYTICAL PROCEDURES

M. Álvarez-Prieto, J. Jiménez-Chacón

Institute of Science and Technology of Materials, University of Havana, Zapata y G,
s/n, Plaza, Ciudad de la Habana (Cuba)

Validation of analytical procedures is a fundamental requirement for reliability and applicability of results in environmental analytical chemistry. Several internationally agreed documents establish guidelines about performance characteristics of analytical procedures, experimental practices for validation and some other important issues [1]. These documents suggest a set of experimental tests that both assess any assumptions on which an analytical procedure is based and establish its performance characteristics, thereby demonstrating whether the procedure is fit for a particular purpose. However, instead of a set of diverse experimental tests, the validation process can be simplified taking everything into account by means of the fitness for purpose measurement uncertainty. If reliable estimates of uncertainty along a concentration range are available [2] and quantitative specifications of fitness for purpose are clearly defined in terms of required measurement uncertainty [3], it is possible to compare both magnitudes to determine if an analytical procedure is fitness for purpose. For such a goal, it is necessary to take into account the metrological meaning of different measurement uncertainty estimations [4].

Several performance characteristics of analytical procedures can be derived from or associated to the measurement uncertainty concept. This defines measurement uncertainty as a unifier concept for validation of analytical procedures. Precision, bias, trueness, detection capabilities [5], calibration, analytical range and some other important performance characteristics can be jointly estimated from a single validation experiment that represents standard analytical work routinely developed in the laboratory. This simplifies experimental labour and clarifies the validation process from a conceptual point of view. Conclusions on fitness for purpose results and analytical procedures have deep implications on conceptualization of quality of results and analytical procedures. This is especially important when specification limits or action levels are concerned for pollution studies. Some examples from environmental analytical chemistry are discussed.

[1] IUPAC Harmonized guidelines for single-laboratory validation of methods of analysis, Pure and Appl. Chem., 74, 835-855 (2002), and references therein.

[2] Jiménez-Chacón, J. and Alvarez-Prieto, M., Modelling uncertainty in a concentration range, Accred. Qual. Assur., 14, 15-27 (2009).

[3] Alvarez-Prieto, M. Jiménez-Chacón, J., Fitness for purpose in relation to specification limits, submitted for publication.

[4] Alvarez-Prieto M, Jiménez-Chacón J, Do we need to consider metrological meanings of different measurement uncertainty estimations? Accred. Qual. Assur., 14, 623-634 (2009).

[5] Jiménez-Chacón J., Alvarez-Prieto, M, An approach to detection capabilities estimation of analytical procedures based on measurement uncertainty, Accred. Qual. Assur., 15, 19-28 (2010).

IL5- MICROFLUIDIC AND NANOFIBER APPROACHES FOR DIAGNOSTICS IN RESOURCE-LIMITED SETTINGS

A. J. Baeumner

Cornell University, Ithaca, NY, 14853 (USA)

Microfluidic biosensors, labs-on-a-chip and lateral flow assays for the detection of viable organisms, toxins, and clinically relevant markers have been developed in our research group. Pathogenic organisms such as *B. anthracis, C. parvum*, dengue virus, *E. coli, S. pyogenes* have been identified using RNA target molecules and a DNA sandwich assay with liposome signal generation and amplification. By coupling the sandwich assay to nucleic acid sequence-based amplification, detection limits of 1 viable organisms have been determined in starting volumes of at least 1 ml. Cholera toxin has been detected using ganglioside receptors, CD4+ T-lymphocytes and myoglobin using immunological approaches, and thrombin with an aptamer. Liposomes enable visual, fluorescence, electrochemical or electrochemiluminescence detection and are optimized for each specific assay type and assay platform.

Microfluidic devices are made out of polymer substrates such as polymethyl methacrylate and polystyrene. Their surfaces are chemically modified in order to enable DNA probe immobilization, block non-specific binding and increase signal to noise ratios. Investigations of hot embossing fabrication technology led to rugged masters that enable rapid prototyping and long-term availability of patterns.

Recent research has focused on the development of a new class of lateral flow devices that combine the advantages of microfluidic devices and membrane-based lateral flow assays. Nanofibers are electrospun into microfluidic channels made out of polymers such as polymethyl methacrylate and polystyrene. Bearing various surface chemistries, these nanofibers can be spun into distinct locations within the fibers. The resulting fiber mats can be of varying density and size and hence generate a 3D-structure within the microfluidic channel. Nanofibers are being investigated as sample preparation and detection materials, as guiding lines, and as smart separators and concentrators.

IL6- NATURAL ORGANIC MATTER IN THE ENVIRONMENT: FROM SUPRAMOLECULAR STRUCTURE TO HUMEOMIC

A. Piccolo

Università di Napoli Federico II, Via Università 100, 80055 Portici (Italy)

Natural Organic Matter (NOM) or Humic Matter (HM) is an essential component of water and soil environments. NOM or HM control the biogeochemical cycle of carbon and nitrogen, the fate and transport of organic and inorganic xenobiotics, the availability of nutrients, and the rhyzospheric stimulation of plant growth. While the traditional knowledge indicates that these natural material, produced by the biotic and abiotic degradation of plant and animal molecular constituents, to have a macropolymeric structure, recent findings have proved experimentally that it is a supramolecular association of relatively small (<1000 Da) heterogeneous molecules held together in apparently large molecular dimensions by weak forces, mainly dispersive and hydrogen bonds[1]. Evidence of this new understanding of HM structure will be reported.

The recognized supramolecular nature of this natural matter opens up new opportunities to chemists for an overall molecular characterization and for developing new methods of controlling its environmental reactivity. For example, an extraction fractionation has been devised to sequentially isolate single molecules from the supramolecular assemblies in order to characterize their structure by MS and NMR. The sequential fractionation has been called Humeomic since, while preserving C-C bonds, it enables a progressive complete mapping of NOM molecular components[2].

Moreover, since the supramolecular structure of humified natural materials comprises hydrophobic and hydrophilic domains which are contiguous to or contained in each other, it provides the capacity to trap biogenic biolabile materials and exclude them from water and biodegradation, thereby reducing greenhouse gases (GHG) emissions to the atmosphere[3]. Similarly, cross-coupled catalyzed polymerization reactions may be devised to increase the overall humic chemical energy, prevent common degradation by microbial activity, and further decrease GHG emissions from agricultural soils[4, 5]. The principles and results of Humeomic and technologies of GHG control will be illustrated here.

Literature

[1] Piccolo A, *Adv. Agron.* **2002**, *75*, 57.
[2] Nebbioso A, Piccolo A. *Environ.Sci. Technol. 2010*, submitted.
[3] Piccolo A, Spaccini R, Nieder R, Richter J. *Clim. Change* **2004**, *67*, 329.
[4] Piccolo A, Conte P, Tagliatesta P, *Biomacromol.* **2005**, *6*, 351.
[5] Smejkalova D, Piccolo A, *Biomacromol.* **2005**, *6*, 2120.

ORAL PRESENTATIONS

O1- EFFECT OF LANDFILL AGING AND CONTROL ON MUNICIPAL LEACHATE CHARACTERISTICS IN JORDAN

M. Abu-Daabes[1] and H. Abu Qdais[2]

[1]Pharmaceutical-Chemical Engineering Department, School of Applied Medical Sciences,
German-Jordanian University, P.O. Box: 35247 Amman 11180 (Jordan)
[2]Department of Civil Engineering, Faculty of Engineering, Jordan University of Science and Technology, Irbid 22110 (Jordan)

Landfilling remains the predominant management method for the disposal of Municipal Solid Waste (MSW). Solid wastes deposited in landfill sites decompose by a combination of chemical, physical, and biological processes. Leachate emissions from landfill represent the major threat to groundwater resources among various forms of emissions. The chemical composition of MSW leachates is dependent on the types and amounts of waste landfilled, landfill age, and environmental conditions. MSW leachate may introduce heavy metals to groundwater resources which generates a serious environmental concern. To date there is no comprehensive study on leachate characteristics from the Jordanian landfills, counting about 21 operating sites [1]. These landfills do not contain gas and leachate treatment systems leading to several potential adverse environmental impacts. In this research, a survey was performed to study the characteristics of three major landfill sites in Jordan with different ages and controlling systems (lined vs. unlined landfills). The heavy metals and organic contents of leachate from each site were measured. The sites are: 1) Russiefeh-Zarqa (old-closed uncontrolled), 2) Akaider-Irbid (old-active uncontrolled site), and 3) Al Gabawi-Amman (new-active controlled site).

Preliminary results showed that the leachates from all sites are basic (pH range 7 – 9) and have high salt ion concentration, as indicated by leachate conductivity. Organic content analyzed by COD have values between 5,400 – 254,000 mg/L which is inversely proportional to the age of landfill. Several heavy metals were detected, mainly Ni, Cr, Pb, and As. The controlled sites exhibited higher heavy metal content than the uncontrolled sites. In all sites, the concentrations of heavy metals exceed the maximum allowable wastewater industrial limits which call for an urgent attention for setting a proper waste management system in these landfills. Leachate radioactivity was also measured based on quantification of gamma emitting nuclides and the results showed no significant concern. The leachates characteristics results obtained from this study will be the starting step to determine leachate treatment processes appropriate for each corresponding site. The goal of leachate treatment is to reduce the concentration of pollutants or stabilize them in order to comply with regulations and standards of discharge into the environment, or to pre-treat the leachate to acceptable level that allows the treatment at municipal wastewater treatment facilities.

[1] Abu Qdais, H.A., Waste Management 27, 1666-1672 (2007).

O2- FLUORENE BIODEGRADATION IN BATCH CULTURES OF SELECTED SUB-TROPICAL WHITE ROT FUNGI

H. Ardağ Akdoğan[1], N. Pazarlioğlu[2]

[1]Pamukkale University, Faculty of Science and Arts, Department of Chemistry 20070
Kinikli-Denizli (Turkey)
[2]Ege University, Faculty of Science, Department of Biochemistry 35100 Bornova-Izmir (Turkey)

Fluorene is a polycyclic aromatic hydrocarbon (PAH) that presents a high pollution potential and health risk and has been used as a model for degradation studies on PAHs because of its relative toxicity. In this study aimed to evaluate fluorene degradation by White rot fungi and *Trametes versicolor*, *Trametes trogii, Ganoderma carnasum* and *Pleuratus osteratus* were investigated for the biodegradation of fluorene. While *T.versicolor*, *T.trogii* and *G.carnasum* degraded fluorene about 30%, the *P.osteratus* strain metabolized approximately 85% of 30.0 mg L^{-1} fluorene within just six weeks. The maximum substrate concentration that could be completely degraded was 50.0 mg L^{-1}, thus it was selected as a fluorene degrading fungus for further studies. A study of the reduction of different concentrations of fluorene in the growth medium showed that toxicity to cell growth increased with increasing fluorene levels in growth media. *Pleuratus osteratus* reduced 92.9% of 5.0 mg L^{-1} fluorene. Laccase and MnP enzyme activities were also monitored. There was an attempt to identify metabolites with GC-MS and FT-IR. These results indicate that the samples did not contain any detectable metabolite.

O3- BIOMASS FOR THE SEPARATION OF FISSION PLATINOIDS

K. Hirota, D. Parajuli and N. Seko

Environmental and Industrial Materials Research Division, Japan Atomic Energy Agency,
1233-Watanuki, Takasaki, 370-1292 (Japan)

Low natural abundance and complex aqueous chemistry have made the platinum group metals (PGM) extremely scarce. Their increasing demand for several industrial purposes has prompted the need of recovery and recycling. Under such circumstances, it is worth to give attention to a rich source of such metals, high level radioactive liquid waste (HLW) generated during the reprocessing of spent nuclear fuel. It contains substantial quantity of platinum group metals like Palladium (0.018 M), Rhodium (0.008 M), and Ru (0.038 M) [1]. Among these, Palladium is of great interest for its high concentration with majority of stable isotopes. In addition, the radioactive isotope is also considered safe for several industrial applications as its intrinsic radioactivity is poor [2].

Two most common means of metal separation are solvent extraction and ion exchange. However, such extractants are seldom useful in highly radioactive mixtures like HLW. Instead, biomass sorbents, as described in our previous results, exhibit stable performance like in normal condition [3]. Because the biomasses in natural form are not directly applicable on separating the metals, some sort of functional modification is necessary. The merit of such modification is that by varying the moiety, variation in the selectivity pattern for different metals present in the mixture can be created. Hence, targeting the platinum group metals present in the case of HLW, modification of the biomass matrix with ion-exchange or chelating groups like amine, amide, thaiamide, iminodiacetic acid, polyamines, and so on, is preferred. In addition, use of least amount of chemicals during the functionalization process is also crucial from economic as well as environmental aspects.

[1] Inoue, T., Sakata, M., Miyashiro, H., Matsumura, T., Sasahara, A., and Yoshiki, N., Nucl. Technol. 93, 206-220 (1991).
[2] Kolarik, Z., Renard, E.V., Platinum Metals Rev. 49, 79-90 (2003).
[3] Parajuli, D., Hirota, K., J. Coll. Inter. Sci. 338, 371-375 (2009).

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O4- THE DETERMINATION OF LC50 AND BIOCONCENTRATION OF MERCURY (II) CHLORIDE IN *ESOX LUCIUS*

M. R. Rahimibashar*, V.Alipoor, M.Giahi

Department of Fishery, Islamic Azad University, Lahijan Branch, P.O.Box: 1616, Lahijan (Iran)
*rahimibashar@yahoo.com

Pike *(Esox lucius)* is one of the freshwater fish and it is a predator and carnivores. The fish is one of the commercial fishes and it is the people‘s diet who live near the Caspian Sea. The fish is at the top level of food chain and it feeds the other fishes, and crustaceans.

There are a lot of sources around the Caspian Sea that dump their waste in the rivers flowing in the Sea. Mercury chloride is one of the water pollutants which also exist in the waste of these sources, without being controlled are dumped in the rivers. Bio accumulation in the higher levels of food chains is more effective than the lower levels and the fish in the Caspian Sea is in the highest level.

The impact of mercury chloride on the fingerlings of pike was studied in 2008. The determination of the acute toxicity and bioaccumulation of mercuric chloride in pikeperch Juveniles weighting 20±5 grams. The fish were exposed to various chemical concentrations in water.

The tests were done in 20 liter tanks each containing 20 fish. We carried out six treatments with three replications and a control for each of the chemicals using the static O.E.C.D. method, and investigate four days, through which the lethal concentration (LC5096h) were studied.

During the test physiochemical parameters of water such as, pH, dissolved oxygen, total hardness and temperature were measured. The average pH was recorded as 8, total hardness 250 mg/lit, average water temperature was 25±1 degree centigrade and dissolved oxygen was 7.5±0.5 mg/lit.

The result showed that LC5096h and LC5024h of mercury chloride ($HgCl_2$) on pikeperch were 0.078 and 0.092 mg Hg/lit respectively.

The bioaccumulation values during 24h in muscle tissue, kidney and gill were 1.93, 18.6 and 28.2 mg Hg/lit respectively. The exposure of the values during 96h were 3.8, 19.5 and 30.6 mg Hg/lit in tissue, kidney and gill respectively. The bioconcentration values for muscle tissue, kidney and gill were higher than the ones in water.

O5- DYE RESIDUES IN FERAL EUROPEAN EEL IN BELGIUM: AN EMERGING RISK?

C. Belpaire[2], S. Fraselle[1], C. Geeraerts[3], H. Kayirebe[1], D. Laza[1], T. Reyns[1], J. Van Loco[1]

[1] Food, Medicines and Consumer Safety, Scientific Institute of Public Health,
Juliette Wytsmanstraat 14, 1050 Brussels (Belgium)
[2] Research Institute of Nature and Forest, Duboislaan 14, 1560 Groenendaal - Hoeilaart (Belgium)
[3] Research Institute of Nature and Forest, Gaverstraat 4, 9500 Geraardsbergen (Belgium)

Muscle tissue of yellow-phased European eel (*Anguilla anguilla*) is frequently used as a biological indicator to trace hazardous chemicals in aquatic ecosystems and potential human dietary exposure. A study was set up to investigate the possible presence of dye residues in yellow eel muscle. About hundred eels, captured in Flanders (Belgium) between 2000 and 2009 were analysed for 14 dyes, i.e. triarylmethanes, xanthenes, phenothiazines and phenoxazines. Sample pre-treatment involved an extraction with acetonitrile and McIlvain buffer followed by an oxidation step with 2,3-dichloro-5,6-dicyanobenzoquinone to include all leuco-forms of each dye. Extracts were further purified by a combined SPE extraction on a weak and strong cation exchanger and analyzed by UPLC-MS/MS. Results indicate that contamination of eels was present for malachite green, crystal violet and their respective leuco-metabolites. Preliminary results showed the presence of dyes in approximately 35 % of the eels. Concentrations ranged typically between 0.25 and 9.51 ng/g ww.

None of the dyes are registered for use as veterinary drugs. Nevertheless, some of them are widely illegally used in fish farming industry against protozoan, fungal and bacterial infections. Thus, residues are found during the food monitoring program of aquaculture products in the European Union. These dyes could be of concern due to possible toxicological properties. On the other hand, these multiple-use compounds have also numerous legal applications like hair dye, paper tissues, paints, printing inks, and the presence of residues of malachite green and leuco-malachite green has been reported in samples of soil and river sediment near to a dye manufacturing plant in the USA [1]. Recently, Schuetze *et al.* reported the presence of crystal violet and malachite green in a lesser extent in eels caught downstream from municipal sewage plants [2, 3].

These preliminary findings warrant further investigation on the presence of these chemicals in our environment, their potential effects on aquatic organisms and the dietary exposure by humans.

[1] Nelson C.R. and Hites R.A., Environ. Sci. Technol. 14, 1147-1149 (1985).
[2] Schuetze A., Heberer T. and Juergensen S., Chemosphere 72, 1664-1670 (2008).
[3] Schuetze A., Heberer T. and Juergensen S., Environ. Chem. 5, 194-199 (2008).

O6- THE USE OF BIODIESEL WITH COLD WEATHER: POUR POINT DETERMINATION USING AN ACOUSTIC WAVE SENSOR

M. T. S.R. Gomes and M. I. S. Veríssimo

CESAM/Chemistry Department, University of Aveiro, 3810-193 Aveiro (Portugal)

With the winter arrival the problems with the sluggish of the diesel fuel and the necessity to use anti-gel additives begins. This problem turns to be more relevant when using biodiesel that tends to gel at a higher temperature than diesel. However, biodiesel is an environmentally friendly fuel [1] that can be used in any diesel engine without modification. It is biodegradable, non-toxic, show low emission during combustion, and offer the same performance and engine durability as petroleum diesel fuel. Besides, biodiesel fuel helps stimulate rural economies. Crystallization of the saturated fatty acid methyl ester components of biodiesel during cold seasons causes fuel starvation and operability problems, as solidified material clog fuel lines and filters. With the temperature falling more solids form and biodiesel approaches the pour point, the lowest temperature at which it will cease to flow. Usually, the pour point is determined with a rheometer. This work aims to propose an alternative low cost and easy to use method based on an acoustic wave sensor, for monitoring the pour point, i.e. the minimum temperature at which biodiesel can be safely used, without clogging. Several types of homemade biodiesel, with and without the addition of additives [2] to decrease the pour point temperature, were analyzed. Frequencies of oscillation and the equivalent circuit parameters of the piezoelectric quartz crystal were monitored while temperature was decreasing, until biodiesel gelling point.

[1] Bozbas, K, Renew Sustain. Energ. Rev. 12, 542–552 (2008).
[2] Bhale, P. V., Deshpande, N.V. and Thombre, S.B., Renew. Energy 34, 794-800 (2009).

O7- NOVEL DENSIFICATION MECHANISM OF GADOLINIUM-DOPED CERIA AS ENERGY AND ENVIRONMENTAL MATERIALS

T. Kosaka[1] and K. Sato[2]

[1]Department of Chemistry, Tokyo Gakugei University, Nukuikita 4-1-1,
Koganei 184-8501 Tokyo (Japan)
[2]Department of Environmental Sciences, Tokyo Gakugei University,
Nukuikita 4-1-1, Koganei 184-8501 Tokyo (Japan)

Gadolinium-doped ceria (GDC) is considered to be most promising as an electrolyte for solid oxide fuel cells (SOFC) operating over 773-973K. Generally, GDC is desired to have a density greater than 95% of theoretical for SOFC application. The characteristics of GDC powders greatly affect to the density of sintered body and their local structure such as grain boundary. Recently, we have found by positron lifetime spectroscopy [1-2] that local atomic structures in the vicinity of grain boundary are closely correlated with densification mechanism upon sintering [3]. In this study, the local atomic structures were further studied by a series of positron annihilation spectroscopy together with high resolution dilatometry. The Ce-Gd oxalate precipitates were prepared by dropping Ce-Gd nitrate mixed solution into oxalic acid solution . The concentration of Ce, Gd nitrate, oxalic acid in the solution were 0.16, 0.04, OAM, respectively. The oxalate precipitates were decomposed to GDC powder by calcining at 873K for 1h in air and the GDC pellets were prepared. Density measurements through Archimedes principle, x-ray diffraction measurements, high-resolution dilatometry, and a series of positron annihilation spectroscopy were conducted for GDC. Based on these results, novel mechanism of densification upon sintering will be presented on an atomic scale.

[1] K. Sato et aI., Phys. Rev. Lett. 92, 127403 (2004).
[2] K. Sato et aI., Phys. Rev. Lett. 96, 228302 (2006).
[3] S. Ohta et aI., Journal of Physics: Conference Series, in press .

O8- COMBINATION OF REGULAR MONITORING, SEDIMENT QUALITY GUIDES, CHEMOMETRIC TOOLS AND EXTENSIVE SAMPLING TO INVESTIGATE THE QUALITY OF SEDIMENTS. A CASE STUDY: THE ESTUARY OF THE NERBIOI-IBAIZABAL RIVER (BILBAO, BASQUE COUNTRY)

G. Arana, A. De Diego, S. Fdez-Ortiz De Vallejuelo, A. Gredilla, J. M. Madariaga

Department of Analytical Chemistry, Faculty of Science and Technology,
University of the Basque Country, Sarriena auzoa, z/g, 48940 Leioa (Basque Country)

Sediments are good indicators of the general health of an estuary. A large variety of chemical pollutants, including persistent organic pollutants, metals and organometals, from both natural and anthropogenic activities originated in the surroundings of the river basin, accumulate in sediments. Regular monitoring of sediments may be useful, consequently, to study historical records of contamination in a given area. Contamination means the existence of pollutants over a given level of concern, e.g., background values estimated for the area, and pollution is related to real toxicological risk. In this framework, the use of sediment quality guides is a powerful tool in order to decide whether a given sediment is affected or not by chemical contamination/ pollution. In addition, mathematical models obtained by multivariate analysis methods may be used to classify sediments collected in extensive samplings. We have applied this approach to investigate the estuary of the Nerbioi-Ibaizabal River (Bilbao, Basque Country), using the metal content of sediments as chemical variable for discrimination. This estuary has been subjected to an important industrial and mining activity along the 20th century. Although appropriate remediation actions have been executed over the last 30 years within the framework of a general plan to regenerate the estuary, the footprint of past activities is still noticeable in its sediments. Sediments were collected every three months at eight selected points of the estuary from January 2005 to January 2008. The concentration of fourteen previously selected elements was simultaneously measured by ICP/MS in the acid leachates of the sediments. After a preliminary and basic statistical analysis of the data set, Principal Component Analysis (PCA) was applied to the whole set, revealing the existence of three different classes among samples. The k Nearest Neighbour (kNN) method confirmed that classes did not overlap significantly. Application of the supervised Linear Discriminant Analysis (LDA) allowed us to define a model which was used to classify sediments collected in two extensive sampling campaigns (49 sampling points all over the estuary) conducted in January 2009 and January 2010. Most of the sediments were classified into the "low contamination level" class, but some of them laid in the group characterised by high concentrations of toxic elements, and this calls for specific actions to be taken in those areas. Calculation of geo-accumulation indexes (based on background values estimated for the area) allowed us to determine the extent of anthropogenic input for each metal in each sampling point of the extensive campaign. Effect Range Medium quotients were also computed and used to estimate the toxicological risk associated to the sediments.

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O9- TRACE METAL ANALYSIS OF BIOINDICATORS BY TXRF

A. Gross[1] and M. Mages[2]

[1] Bruker Nano GmbH, Schwarzschildstr. 12, 12489 Berlin (Germany)
[2] Helmholtz Centre for Environmental Research, Dep. for River Ecology,
Brueckstr. 3a, 39114 Magdeburg (Germany)

In the last decades, total reflection X-ray fluorescence (TXRF) analysis was proven to be an easy and versatile method for the determination of trace elements [1]. TXRF can be applied to different sample types, like solids in form of micro fragments, powders, suspensions, thin films or liquids.

Bioindicators are biological species used to monitor the health and integrity of an environment or ecosystem [2-4]. Such organisms can be used as monitor for changes of metal pollutions in surface waters and sediments. TXRF is a micro-analytical method, which allows the analysis of individual organisms for internal contaminant concentrations. In addition, a portable TXRF spectrometer is suitable for in-field investigations and monitoring of pollutant dispersal.

This paper describes the suitability of different bioindicators and the in-field trace metal analysis of single organisms and biofilms by TXRF:

- Zooplankton is an important bioindicator for the characterisation of the water quality and gives first information on the bio-availability of metals and their bioaccumulation through the food chain as shown by in-field measurements of Cu and Zn in single daphnia.
- Fish eggs and embryos were exposed to metals via the water phase as well as via direct contact with contaminated sediment particles. TXRF analysis indicated individual embryos with dramatically enhanced exposure compared to other individuals despite uniform exposure conditions on a macro scale.
- Biofilms grown on natural stones in mining drains accumulate high amounts of heavy metals also at poor availability of nutrients. The accumulation factor of metals in biofilms has been investigated, showing an ascending order from Pb > Cu > Zn > other metals.

We conclude that TXRF is suitable for the in-field analysis of trace elements in bioindicators and supports an indication of water quality.

[1] Klockenkämper, R., *Total-Reflection X-Ray Fluorescence Analysis*, Wiley & Sons (1997).
[2] Mages, M., Woelfl, S., v. Tümpling, W., *Spectrochimica Acta*, Part B 56, 2209-2217 (2001).
[3] Mages, M., v. Tümpling, W., van der Veen, A., Baborowski, M., *Spectrochimica Acta*, Part B 61, 1146-1152 (2006).
[4] Mages, M., Bandow, N., Küster, E., v. Tümpling, W., *Spectrochimica Acta*, Part B 63, 1443-1449 (2008).

O10- TRACE METALS MOBILIZATION FROM SURFICIAL SEDIMENTS OF THE RIVER SEINE ESTUARY

M. Hamzeh*, B. Ouddane, G. Billon

FRE - CNRS 3298 Géosystèmes, Analytical and Marine Chemistry team C8,
University Lille1, 59655 Villeneuve d'Ascq, (France)
*mariam.hamzeh@ed.univ-lille1.fr

Environmental contamination by metals is a worldwide problem. Urban, industrial and agricultural activities have contributed to a widespread contamination of aquatic ecosystems. Most of the metals are introduced in the aquatic environment associated to fine grained particles that progressively accumulate in the surface of the sedimentary column. Scavenging of trace metals in the sediments can be reversible due to several perturbations so as sediments also act as a source of pollutants for the overlying water. For instance, daily or seasonal natural events (tide, flood, storm) and anthropogenic processes (water management actions) can cause a disturbance of sediments and a subsequent remobilization of pollutants to the overlying water, thereby posing a potential threat for aquatic organisms.

The estimation of the metal mobility was undertaken in this study on sediments sampled in the Seine estuary at the Pose dam, a site considered as one of the most polluted of the estuary. Sequential extractions of Fe, Cd, Mn, Cr, Ni, Cu, Pb and Zn were undertaken in surficial sediments for evaluating their distribution into four different fractions (exchange and carbonates, reducible, oxidizable and residual). The procedure used for these experiments is based on the BCR protocol (Rauret et al, 2007) with some modifications and has been validated by testing successfully the certified sediment material CRM 601. Some of our sediment samples were in anoxic conditions, and in order to limit the reoxidation of the reduced phases like iron sulphides, the two first steps of the sequential extraction were carried out under nitrogen environment.

Another approach consists on sediment resuspension experiments in laboratory under controlled conditions to get new insights on the metal mobility in the overlying water. For that purpose, wet sediment was introduced into oxic filtrated river water and the mixture was stirred in an open cell during several days. Metal releases from the particles have been observed within the first minutes after the mixing, followed by a fast adsorption process on the suspended particles.

Finally, these preliminary results obtained in the framework of the national program Seine-Aval (ToxSeine Project) will be confronted to toxicity tests carried out on the same sediments by the University of Bordeaux to get new information on the metal mobility towards the biota.

O11- FATE MONITORING OF ^{14}C-DICLOFENAC IN LABORATORY WATER/SEDIMENT SYSTEMS

A. Mohamad, R. Kreuzig, M. Bahadir

Institute of Ecological Chemistry and Waste Analysis, Faculty of Life Sciences, Technische Universität Braunschweig, Hagenring 30, D-38106 Braunschweig (Germany)

The non-steroidal anti-inflammatory drug diclofenac belongs to the group of human pharmaceuticals that were frequently found in waste and surface waters. For the environmental risk assessment, hence, its fate in water/sediment systems is of major relevance. In accordance to regulatory recommendations, therefore, the OECD 308 water/sediment simulation test was performed under aerobic conditions. Within the 100-day incubation period, ^{14}C-diclofenac continuously disappeared from the aqueous phase while the residues increased in the sediment. After a first increase, the ethyl acetate extractable residues dropped while the non-extractable residues continuously increased and finally reached 82 %. Mineralization increased up to 13 %.

Since diclofenac is known as a photosensitive substance and may thus undergo phototransformation in surface water, water/sediment tests have been also conducted in a special irradiation apparatus to advance the fate monitoring under laboratory conditions. In contrast to the incubation in the dark, up to 70 % of non-extractable residues were formed under irradiation within 3 days even though the formation of more polar phototransformation products with lower affinity to the sediment was expected.

In order to study why the formation of non-extractable ^{14}C-diclofenac residues was promoted by light, fortified water samples were additionally tested for the formation of phototransformation products. There, 8-chloro-9H-carbazole-1-acetic acid (PTP1), 8-hydroxy-9H-carbazole-1-acetic acid (PTP2) and 8-chloro-9H-carbazole-1-methanol (PTP3) could be identified by means of HPLC/UVD and LC/MS/MS. In contrast to this water test, only diclofenac and PTP1 could be detected in the water phase of a water/sediment test after 5 h of irradiation. PTP2 as well as PTP3 seem to contribute to the formation of non-extractable residues in the sediment.

The present study clearly showed that the fate of ^{14}C-diclofenac in aquatic ecosystems can be partly simulated by the standard water/sediment test. So far biotransformation is also accompanied by phototransformation, advanced laboratory-test systems have to be applied to complete environmental risk assessment of photosensitive substances.

O12- DETERMINATION OF SELECTED TOXIC ELEMENTS IN APPLES FROM ORGANIC FARMING

I. Juranović Cindrić[2], I. Krizman[2], G. Stingeder[1] and M. Zeiner[1]

[1]Division of Analytical Chemistry, Department of Chemistry, University of Natural Resources and Applied Life Sciences (BOKU), Muthgasse 18, 1190 Vienna (Austria)
[2]Laboratory of Analytical Chemistry, Faculty of Science, University of Zagreb,
Horvatovac 102a, 10000 Zagreb (Croatia)

Due to the elevated ecological awareness nowadays the consumption of products of organic agriculture is increasing. Organic farming means excluding the use of synthetic inputs, such as synthetic fertilizers and pesticides or genetically modified organisms, but there are only a few regulations regarding heavy metal concentrations in soils. Thus a not negligible uptake of metals from the soil where the apple trees are grown may occur. Furthermore inorganic copper compounds being traditional fertilizers for apple trees are not considered as synthetic fertilizers, thus they are still used in organic apple farming for soil or foliar application, although their application rate is decreasing.

Thus also apples produced by organic agriculture may contain toxic elements, such as cadmium, chromium, copper, and lead. The concentrations of these elements were determined in whole apples, as well as in the flesh and peel in order to estimate the possible risk for human health. After harvesting, the apples were either worked up immediately or dried before sample preparation. Prior to quantification by inductively coupled plasma – optical emission spectrometry (ICP-OES) all samples were digested by a microwave assisted digestion system using HNO_3 using either open or closed vessel mode. The results obtained for all methods were compared and the best method was chosen for further optimization. The final validated analytical procedure was then used for the analysis of twenty eight apple samples collected in Croatia.

O13- BIOMASS ASHES – USEFUL OR HARMFUL FOR PLANTS?

M. Kröppl[1], C. Lanzerstorfer[1], M. Zeiner[2]

[1]University of Applied Sciences Upper Austria, Campus Wels, Stelzhamerstr. 23,
A-4600, Wels (Austria)
[2]Hasenhutgasse 7/5/9, A-1120, Vienna (Austria)

During combustion of biomass (e.g. wood) the organic material is decomposed and the inorganic components remain as ashes. In a biomass incinerator usually two ash fractions are generated: the coarse ash which remains at the bottom of the furnace (bottom ash) whereas the fine ash is collected from the flue gas (fly ash) in a dedusting device. Both ash fractions contain valuable plant nutrients like N, P, K, Ca, Mg, S, and other trace elements. Therefore the aim is that these ashes can be returned to the soil as soil enhancers. On the other hand biomass ashes also contain heavy metals harmful to plants, causing for example minor growth or harm animals or men consuming these plants. As the plant availability of components depends on their solubility at the environmental conditions in the soil (the components are absorbed from the plants in form of ions) it is important to know under which conditions these components are bioavailable.

For this reason, plants (e.g. green salad) have been grown in laboratory experiments with ash application. In order to evaluate the leachability and mobility of nutritive components and heavy metals from biomass ashes, distilled water has been used as water source and fly ashes have been added to the plants (either spread on top of the plants or mixed in the earth). In every test line the amounts of ashes was varied and at the same time plants cultivated without using any ashes were analysed as control group.

After growing for a certain time, the plants were collected, dried and milled. A microwave assisted acidic digestion was then performed for bringing the elements into a measurable form. All solutions were then analyzed with inductively coupled plasma optical emission spectroscopy (ICP-OES). For the investigated elements the additional uptake of the plants form the biomass ash was calculated. Furthermore the influence of the application mode (on the plants or on the soil) of the ashes on the final concentrations was studied.

O14- MAJOR AND TRACE ELEMENTS COMPOSITION OF TOTAL (WET AND DRY) DEPOSITION IN THE INDUSTRIAL AREA OF PUCHUNCAVÍ, CHILE

F. Cereceda-Balic[1], J. L. Guevara[1], X. Fadic[1], C. Miro[2], M. R. Palomo[3],
E. Pinilla[3], F. Rueda[3], V. Vidal[1]

[1]Environmental Chemical Laboratory, Environmental Technology Centre (CETAM), Technical University Federico Santa María, Av. España 1680, Casilla 110-V, Valparaíso (Chile)
[2]Department of Applied Physics, University of Extremadura,
Av. de la Universidad sn, 10071- Cáceres (Spain)
[3]Department of Analytical Chemistry, Faculty of Science, University of Extremadura,
Av. de Elvas sn, 06071- Badajoz (Spain)

The Valley of Puchuncaví, located in the central region of Chile, is a zone where an important industrial complex is emplaced, which it include a Copper smelting and a thermoelectrical plant. In this valley the main observed emissions correspond to particulate matter, heavy metals, SO_2 and NOx, the last two are the major precursors of acid rain. During the past four years, our research group is conducting studies on chemical characterization (ions, metals, metalloids, pH, and conductivity) of atmospheric deposition and soil in Puchuncaví valley, in order to analyze the effects on the environment of emissions from anthropogenic sources and the magnitude of acid rain phenomenon. Monitoring campaigns are carried out in four network stations belonging to the AES-Gener-Codelco: "The Greda (LG)," The Maitenes "(LM)," Puchuncaví "(PU) and" Valle Alegre "(VA). In each there is one Total Deposition Passive Collector [1] and one Wet Only Collector [2].

This work shows the results of the elements profile of the total atmospheric deposition in the year 2008 obtained in quartz filters. The sampling period on the monitoring stations was 16 weeks (from April to August). The Analyses were performed in a Perkin Elmer ICP-MS ELAN 9000 equipment and quantification was carried out using the internal standard method. The results show that LG station, closer to the major emissions sources, has the highest average concentration of total elements (about 3,500 μg /month m^2), followed by PU and LM (1,400 μg /month m^2), and VA (780 μg /month m^2). A preliminary factor and cluster analysis shows that the elements of the total deposition can be divided into three groups, G1 (crustal): Ca, Ce, K, Mg, Mn, Sr, Ti; G2 (traffic/industrial): As, Ba, Cd, Co, Cu, Fe, Pb, Sb, V, Zn and G3 (undetermined): Al. Also, it was possible correlate the total deposition of elements, like Cu, with emissions of SO_2 and PM of an industrial source in the area.

[1] Aikawaa, M., Hirakia, T., Tamakia, M. and Shoga, M., Atmospheric Environment 37, 2597–2603(2003)
[2] Chantara, S. and Chunsuk, N., Atmospheric Environment 42, 5511– 5518 (2008).

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O15- SELENIUM TRACE SPECIATION IN ACIDIC ENVIRONMENTAL SAMPLES BY HPLC-ICP-MS

P. Corvini[2], G. H. Floor[1], M. Iglesias[1], M. Lenz[2], G. Roman-Ross[1]

[1] Department of Chemistry. University of Girona. Campus de Montilivi s/n. 17071 Girona (Spain)
[2] Institute of Ecopreneurship, University of Applied Science Northwestern Switzerland,
Gründenstrassse 40, CH-4132 Muttenz (Switzerland)

Selenium (Se) is a trace element of environmental relevance due to its narrow range between essential and toxic concentrations. Information on speciation is crucial for the understanding of Se cycling, since it determines its mobility, bioavailability, transport mechanisms and toxicity. Although the impact of the chemical form on the behaviour was already early recognized, it was not until the last decades that analytical advances have allowed the determination of Se speciation at sufficiently low concentrations to be of true interest to environmental studies.

An important issue in Se speciation analyses is to preserve the integrity of the samples. Pre-treatment of samples is sometimes needed, but might cause analyte lost and/or species interconversion. Acidic aqueous environmental samples are often rich in dissolved iron (Fe) and aluminium (Al), which represents a major concern, since the latter elements can precipitate when the samples are adjusted in e.g. pH. The precipitates form important adsorption sites for Se, decreasing the level of dissolved Se, and moreover Fe oxides trigger redox transformations. Previous work for Se speciation used buffers with pHs of 4.8 or higher, which is sufficient to induce precipitation of Al and Fe dissolved under environmental low sample pH.

In this work we developed a new protocol for Se speciation by HPLC-ICP-MS in acid solutions using a low-pH buffer. Since the buffer is matching the natural low pH of the samples, no adjustment is needed, therefore preventing Fe/Al precipitation. To illustrate the need and the performance of this new approach, we used as case study acid rain – soil interaction at Mount Etna volcano. Firstly, thermodynamic modelling (PHREEQC-2) was used to show that Fe and Al precipitation can occur at the mobile phase pH of the so far published protocols. Secondly, we evaluated the influence of the mobile phase composition on effective separation of selenite and selenate at low pH. Our results show that the optimum mobile phase is 20 mM of citrate ammonium at pH 3 with 2% methanol, in which both species can be separated within eight minutes (total run time ten minutes). Lastly, we applied this developed method to our sample set. Se species are baseline separated from the Br interference and allows the detection of both ^{78}Se and ^{80}Se at low levels (lower µg/kg range) can be detected. In conclusion, the obtained speciation information allows for the geochemical interpretation of Se mobility around Mount Etna.

O16- SEQUENTIAL SEPARATION FOR ULTRA-TRACE ANALYSIS OF U, Th, Pb, AND LANTHANIDES IN ENVIRONMENTAL SAMPLES

T. Kimura, M. Magara, Y. Miyamoto, and K. Yasuda

Research Group for Radiochemistry, Nuclear Science and Engineering Directorate,
Japan Atomic Energy Agency (JAEA), Tokai-mura, Ibaraki 319-1195 (Japan)

Abundance and isotopic ratios of trace uranium (U), thorium (Th), lead (Pb) and lanthanides in environmental samples play a key role to investigate features of the samples. The analytical data may give information on origin of the sample, dating of mineral formation, history on mineralization, and age determination of nuclear materials. High resolution inductively-coupled plasma mass spectrometers (HR-ICP-MS) are powerful analytical instrument for quantitative and isotopic analyses. The instrument generally can measure abundance and isotopic ratios of an element of interest without sample pre-treatment. In most environmental samples such as rocks, soils, and airborne dusts, trace U, Th, Pb, and lanthanides are contained with major elements such as Na, K and Fe. These major elements and the polyatomic ions which originated from the co-existing elements affect accuracy of analytical results measured by ICP-MS [1, 2]. The analytes, therefore, should be separated from the interfering elements. Chemical separations are good solution for accurate analyses, but the procedures are generally complicated and time-consuming. The authors developed the technique for sequential separation of U, Th, Pb, and the lanthanides using a single anion-exchange column and mixed media consisting of hydrochloric acid (HCl), nitric acid (HNO_3), acetic acid (CH_3COOH), and hydrofluoric acid (HF) [3]. With a single anion-exchange column, sequential separation of 50 ng each of U, Th, Pb, and the lanthanides in an ICP-MS calibration solution was successfully carried out. Using a mixture of CH_3COOH and other mineral acids (HCl and/or HNO_3) enabled complete separation of the analytes. The absorption of the elements of interest on the column was enhanced in the mixture of CH_3COOH compared with simple HCl and HNO_3 media. Alkali metals, alkali earth metals, and Fe which are representative interferences for isotopic analysis in geological samples were eliminated from U, Th, Pb, and the lanthanides. The recovery yields of the elements of interest were more than 95%. This separation technique is simple, and it can be applied for ultra-trace analysis with highly pure reagents. The authors will give a presentation on the overview of this sequential separation, and optimization of the column size and the grain size of resin for improving the peak resolution. To evaluate feasibility of this separation in environmental samples, the target elements in 500 μg of the basaltic sample, JB-1 issued from Advanced Industrial Science and Technology (AIST) were separated and determined. The analytical results also will be mentioned.

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[1] Magara, M., Sakakibara, T., Kurosawa, S., Takahashi, M., Sakurai, S., Hanzawa, Y., Esaka, F., Watanabe, K. and Usuda, S., J. Nucl. Sci. Technol. 39, 308-311 (2002).

[2] Magara, M., Sakakibara, T., Kurosawa, S., Takahashi, M., Sakurai, S., Hanzawa, Y., Esaka, F., Watanabe, K. and Usuda, S., J. Aanl. At. Spectrom. 17, 1157-1160 (2002).

[3] Miyamoto, Y., Yasuda, K., Magara, M., Kimura, T. and Usuda, S., J. Nucl. Radiochem. Sci. 10,7-12 (2009).

O17- ISOTOPIC TRACING OF LEAD POLLUTION IN NEW ZEALAND

K. A. Hunter, M. Numata, M. R. Reid and C. H. Stirling

Department of Chemistry, University of Otago, Union Place West,
PO Box 56, Dunedin 9054 (New Zealand)

Sources of heavy metal pollution are ubiquitous in urban and rural New Zealand. Lead is of particular concern given that New Zealand previously allowed the presence of lead additives in gasoline at the world's highest levels. One reliable way to trace different sources of metals is through the analysis of their isotope ratios. Our goal is to establish methods of high precision lead isotope analysis by utilizing multiple-collector (MC) ICP-MS and to apply isotopic tracing to New Zealand environments.

Our MC-ICP-MS instrument (Nu Plasma HR, Nu Instruments, UK) consists of a double-focusing mass analyser, novel ion zoom lens system and 12 fixed Faraday cups, enabling simultaneous detection of multiple isotopes. We correct for the sizable (per cent-level) instrumental mass fractionation of lead by using thallium, without assuming equal mass bias behavior between lead and thallium. This type of correction procedure relies on a well-defined mathematical relationship between measured ratios of an isotopic lead standard and a thallium spike [1] and, hence, requires a degree of spread in the data points to achieve a high level of accuracy and precision [2, 3]. We found that addition of an amount of barium as a secondary spike to the isotopic lead standard solution (NIST 981) ensures a sufficient spread of data each day. Sample lead is purified by double-pass anion exchange column chemistry and then spiked with thallium prior to mass spectrometry. Repeat analyses of a USGS reference material (BCR-2) demonstrate excellent resolution power for lead isotope ratio differences (e.g. ≈0.01% (2σ) for ^{206}Pb/^{207}Pb) and give rise to lead isotope ratios that are in perfect agreement with those reported previously, verifying the accuracy of our approach.

Using these protocols, we have analyzed a set of pit (to one-meter deep) soil samples collected from suburban Auckland, the largest metropolitan region of New Zealand, and have identified natural background lead isotope ratios in deep soils containing ≈10 mg/kg dry weight of lead. These ratios resemble those reported for basaltic rocks of the Auckland/South Auckland volcanic fields [4, 5] which lie nearby our study sites. Closer to the surface, as the soil lead concentration approximately doubles, the isotope ratios become significantly less radiogenic, presumably reflecting anthropogenic inputs dominated by the Broken Hill ore source in Australia. We are currently analyzing surface soils and sediments collected from a range of freshwater-estuarine waterways impacted by either stormwater runoff, industrial activities or farming, in order to elucidate contributing sources and their transport characteristics.

[1] Maréchal, C.N., Télouk, P. and Albarède, F., Chem. Geol. 156, 251–273 (1999).
[2] Woodhead, J., J. Anal. At. Spectrom. 17, 1381–1385 (2002).
[3] Archer, C. and Vance, D., J. Anal. At. Spectrom. 19, 656–665 (2004).
[4] Cook, C., Briggs, R.M., Smith, I.E.M. and Maas, R., J. Petrology 46, 473–503 (2005).
[5] Huang, Y., Hawkesworth, C., van Calsteren, P., Smith, I.and Black, P., Earth Planet. Sci. Lett. 149, 67-84 (1997).

O18- EFFECTS OF SUBLETHAL EXPOSURE TO WATERBORNE Cd IN PERSIAN STURGEON: TISSUE SPECIFIC METAL ACCUMULATION

A. Esmaili Sari[1], A. Mashinchian[2], M. Pourkazemi[3], F. Shariati[4*]

[1] Department of Environment, Natural Resources and Marine Science Faculty,
Tarbiat Modarres University, Noor (Iran)
[2] Department of Marine Biology, Faculty of Marine Science and Technology, Science and Reseach Branch, Islamic Azad University, Tehran (Iran)
[3]International Sturgeon Research Institute, Guilan (Iran)
[4] Department of environment, Natural Resources Faculty, Islamic Azad University,
Lahijan Branch, Lahijan, PO Box: 1616 (Iran)
[*]shariat_20@yahoo.com

Cd in one of non essential metals which enters to the environment through industrial activities. Tissue specific metal accumulations (gills, liver, kidney and muscle) in Persian sturgeon (*Acipenser persicus*) were compared during exposure during 1, 2, 4 and 14 days to sublethal levels of waterborne Cd (50, 400 and 1000 $\mu g \cdot L^{-1}$).

Cadmium was determined in samples after digestion with 3 fold concentrated nitric acid using a graphite furnace atomic absorption spectrometry. The results obtained indicate that at the end of 4 and 14 days of exposure, the total tissue organ cadmium concentration followed the pattern: liver> gill> kidney> muscle for each of the exposure concentrations.

Also, sequestration of Cd to both the soluble cytosolic and insoluble particulate cell fractions determined. The contribution of each cell fraction to Cd sequestration differed between the three organs in different concentrations and exposure durations; in the liver, a larger portion of Cd was associated with the soluble fraction, while in the gill and kidney, the difference between soluble and insoluble fractions was lower.

The total protein of cytosol in each tissue was determined through Bradford method using a Cary 300 spectrophotometer. The results show that in high concentrations in 4 and 14 days exposure, total protein was decreased significantly. But in 50 $\mu g \cdot L^{-1}$ Cd exposure, no significant change was observed.

[1] Vlatka Filipović Marijić, Biserka RASPOR, Age- and tissue-dependent metallothionein and cytosolic metal distribution in a native Mediterranean fish, *Mullus barbatus*, from the Eastern Adriatic Sea, Comp Biochem Physiol, Part C 143, 382–387(2006).
[2] Jerry M. Neff, Bioaccumulation in Marine Organisms, Elsevier, First Edition, pp.89-102 (2002).

O-19 FAST ANALYSIS OF POLYCYCLIC AROMATIC HYDROCARBONS, ORGANO-CHLORINATED PESTICIDES AND POLYCHLORINATED BIPHENYLS IN ENVIRONMENTAL MARINE SAMPLES BY AUTOMATED PLE AND POWER ^{PREP} CLEAN-UP SYSTEM

A. Al-Rashdan, M.I.H. Helaleh, A. Nisar, A. Ibtisam

Kuwait Institute for Scientific Research (KISR), Central Analytical Chromatography (CAL),
Chromatographic Section, 13109 Safat, P.O. Box 24885 (Kuwait)

A fast and selective automated PLE extraction followed by power ^{prep} clean-up system were used for the simultaneous extraction and clean up of polycyclic aromatic hydrocarbons (PAHs), organo-chlorinated pesticides (OCPs) and polychlorinated biphenyls (PCBs) in various environmental marine samples such as fish, shrimp, bivalves shell and squid. OCPs and PCBs were determined using negative chemical ionization gas chromatography-mass spectrometry (GC-MS-NCI) whereas PAHs were determined using electron impact gas chromatography-mass spectrometry (GC-MS-EI). About 5 g of fish marine samples were mixed with anhydrous sodium sulphate. The samples were filled into the extraction cell. The PLE system is controlled by means of a PC using software (DMS 6000). Purification of the extract was accomplished by automated power ^{prep} clean-up system. Hexane extracts were loaded and pumped through silica column. All PAHs, OCPs and PCBs were eluted from the silica column with hexane and dichloromethane. Concentrations of the PAHs, OCPs and PCBs were measured in fish, shrimp, bivalves shell and squid. Concentrations of PAHs were in the range of 1.64-194.72 ng/g, 6.07-139.26 ng/g, 0.8-43.43 ng/g and 0.07-79.33 ng/g for fish, shrimp, bivalves shell and squid, respectively. Concentrations of PCBs were in the range of 0.02-0.57 ng/g, 0.01-1.37 ng/g, 0.01-0.05 ng/g and 0.01-0.08 ng/g for fish, shrimp, bivalves shell and squid, respectively. Concentrations of OCPs were in the range of 0.29-2.21 ng/g, 0.14-2.62 ng/g, 0.13-1.38 ng/g and 0.01-0.75 ng/g for fish, shrimp, bivalves shell and squid, respectively. Lipids were removed with gel permeation chromatography. Analytical criteria such as recovery, reproducibility and repeatability were evaluated through the range of the biological matrices. The feasibility of the proposed PLE/ power ^{prep} method was evaluated by analyzing certified reference materials and spiked samples with satisfactory results. The internal standards were satisfactorily recovered with averages ranging from 86% to 113%.

O20- STOPPED FLOW-FTIR SPECTROMETRIC DETERMINATION OF METRIBUZIN IN PESTICIDE FORMULATIONS

M. Khanmohammadi[1*], S. Armenta[2], S. Garrigues[2], M. de la Guardia[2]

[1] Chemistry Department, faculty of science, IKIU, Qazvin (Iran)
[2] Department of Analytical Chemistry, University of Valencia, Valencia (Spain)
*mrkhanmohammadi@gmail.com

Metribuzin [4-amino-3-methylthio-6-tert-butyl-1,1,2,4-triazin -5(4H)-one] is a herbicide applied to soil for the control of annual grasses and broadleaf weeds in potatoes, tomatoes , asparagus, soybeans and sugarcane. Metribuzin (MT) is manufactured in several commercially available pesticide formulations as powder in a concentration of 70 %w/w. MT determination can be carried out in different types of samples by microwave –assisted water extraction followed by liquid chromatography, pressurized liquid extraction and liquid chromatography –tandem mass spectrometry. An analytical procedure has been developed for quantitative determination of metribuzin (MT) in pesticide formulations. The method was based on the transmittance measurement of data obtained by stopped flow Fourier transform infrared (SF-FTIR) spectrometric method in the peak area measurement between 1198-1185 cm^{-1} with an baseline fixed between 1212 and 1169 cm^{-1} in acetonitrile solutions of MT and 1688-1667 $cm^{-1}$with a single point defined at 1877 cm^{-1} in chloroform solutions respectively. The repeatability, as relative standard deviation of three independent analyses of 20.3 mgg^{-1} and 10.2 mgg^{-1} MT standard were 0.524% and 0.084% and limit of detection 0.018 mgg^{-1} and 0.007 mgg^{-1} in acetonitrile and chloroform respectively. Absorbance spectra were employed for measurement using a set of five standard solutions of MT for every solvent. The method is simple, rapid, low cost and environmentally friendly alternative to the HPLC procedures usually employed in quality control process of commercial formulations containing MT.

O21- SIMULTANEOUS PASSIVE SAMPLING OF POLYCYCLIC AROMATIC HYDROCARBONS (PAHs) AND CURRENT-USE PESTICIDES AND THEIR SPATIAL AND TEMPORAL VARIATIONS IN THE ATMOSPHERE OF LUXEMBOURG

B. M.R. Appenzeller[1], O. Briand[2], M. Millet[3], L. Tuduri[4], C. Schummer[1,3*]

[1] CRP Santé, LNS, Laboratoire de Toxicologie, Université du Luxembourg, Campus Limpertsberg, 162A av. de la Faïencerie, 1511 Luxembourg (*claude.schummer@gmail.com).
[2] AFSSET, 253 avenue du Général Leclerc, 94701 Maisons-Alfort Cedex (France)
[3] LMSPC, Equipe de Physico-Chimie de l'Atmosphère, (UMR 7515 CNRS - Université de Strasbourg), 1 rue Blessig, 67084 Strasbourg Cedex (France).
[4] Institut des Sciences Moléculaires (UMR-5255 CNRS-Université Bordeaux 4), LPTC, Site Universitaire, 24019 Périgueux cedex (France)

Passive air sampling has been shown to be a very interesting alternative to high-volume sampling as it allows to overcome the disadvantages linked to this latter technique, like bulkiness or the need of electric power supply often absent in field situations. Though, to date, only limited data are available about passive air sampling of PAHs and current-use pesticides, actually among the most abundant organic pollutants in the atmosphere. To increase knowledge about passive air sampling of these compounds, XAD-2-resin based passive air samplers were deployed on five locations (two urban, one semi-urban, and two rural sites) in southern Luxembourg for one year, with durations of exposure varying from 30 to 81 days. Samplers were extracted using accelerated solvent extraction (ASE), and analyses were done using GC-MS/MS. The collected data were used to study the spatial and temporal variations of the atmospheric concentrations of the studied compounds.

15 PAHs with two to five aromatic rings were detected at concentrations ranging from 2,5 ng/sampler (pyrene) to 9727 ng/sampler (naphthalene), as well as 22 current-use pesticides with concentrations varying between 100 ng/sampler (Flusilazole) and 42100 ng/sampler (Dinocap). This shows that current-use pesticides were slightly higher concentrated than PAHs. Though, pesticides were only detected from March to October (according to the period of pesticide applications), while PAHs were detected quite regularly throughout the entire year of sampling. Concentrations of naphthalene were highest from October to December; which is in accordance with most studies having used high-volume sampling, while for other PAHs (e.g. acenaphthene, fluorene), highest concentrations were measured from April to June and, in parallel to naphthalene, from October to December. This indicates that some PAHs have a second important emission source causing large emissions of PAHs in springtime, and that does not produces particularly high amounts of naphthalene. Significant spatial variations of atmospheric PAHs were detected for acenaphthylene ($p = 0.049$), with highest concentrations on the urban sites and lowest concentrations on the rural sites. The opposite was observed for atmospheric pesticides, where most detections and highest concentrations were measured on the rural sites, except for Dinocap and Chlorothalonil of whom the highest concentrations were measured on an urban site.

This study shows that multiple classes of organic pollutants can be sampled simultaneously in the air using XAD-2-resin based passive samplers. Spatial and temporal variations were observed for both compound classes suggesting that the samplers can give quite accurate information about the pollution on urban and rural sites, though in further studies it should be tried to reduce the duration of the exposure of the samplers to improve precision in time of the measured concentrations.

O22- SOLID-CONTACT SULFIDE-SELECTIVE SENSOR FOR ITS FLOW INJECTION DETERMINATION IN ENVIRONMENTAL WATER

M. N Abbas, A. L. A. Radwan

National Research Centre, Tahrir st., Dokki, Cairo (Egypt)

A solid-contact sulfide-selective potentiometric sensor based on the ceric complex of N`-Acetyl-2-(benzo[d]thiazol-2-yl)-3-(3-chloro-5-methyl-4H-pyrazol-4-yl) acrylohydrazide covalently attached to polyacylamide as a charged ionophore. The ionophore dissolved in a plasticizer-free poly butylmethaacrylate–dodecylmethaacrylate copolymer (PBDA) was coated onto the top of a gold wire that was pre-coated with poly (3,4-ethylenedioxythiophene)-polystyrene sulfate PEDOT(PSS) as an ion-to-electron conducting polymer. The proposed sensor possessed a stable Nernstian slope of -29.7 mV/decade over a pH range of 6- 9.5 with a linear range of sulfide ion concentration of $2.0X10^{-7}$ – $1.0X10^{-2}$ mol L^{-1} and a detection limit of $2.0X10^{-8}$ mol L^{-1}. The fast dynamic response of the sensor has allowed its utilization as a detector for the FIA of sulfide ion in environmental water samples.

O23- DETERMINATION OF PESTICIDE RESIDUES IN WATER SAMPLES BY DISPERSIVE LIQUID–LIQUID MICROEXTRACTION WITH CHEMOMETRIC APPROACH COUPLED WITH GC-MS

A. Akdoğan, Ü. Divrikli, L. Elci

Chemistry Department, Science and Arts Faculty, Pamukkale University,
20017, Denizli (Turkey)

Pesticides used in agriculture to control pests, such as insects, weeds, and plant diseases, especially in grape-growing areas. The use of pesticides provides benefits for increasing agricultural production, but by bioaccumulation through the food they can eventually become a risk or threat to both animals and humans [1-3]. Migration of these pesticides from soil to water lead to accumulation in the water and may occur environmental contamination. The interest in the probable contamination of water resources has resulted in major focus on monitoring the residue of such compounds in water. The European Union (EU) allows a maximum concentration of 0.1 µg L^{-1} for each individual pesticide and 0.5 µg L^{-1} of the sum of pesticides in drinking water [4].

A simple procedure for the determination of organophosphorus pesticides (OPPs) and azole group fungicide in water samples using dispersive liquid-liquid microextraction (DLLME) was developed. The analysis was carried out by gas chromatography-mass spectrophotometer (GC-MS). DLLME method was optimized with experimental design. A Placket-Burman factorial design was used in order to define the considerable experimental variables (extraction solvent, extraction solvent volume, dispersive solvent, dispersive solvent volume, extraction time, sample volume and centrifuged speed) then optimized experimental conditions for DLLME extraction of analytes from water samples. The detection limits of these pesticides were between 48.8 and 68.7 ng L^{-1}. The relative standard deviation (RSD) at the 4.8 µgL^{-1} levels was in the range of 0.9-15.7 %. The proposed method was acceptable in the analysis of pesticides in natural water samples.

[1] J. Zeng, J. Chen, Z. Lin, W. Chen, X. Chen, X. Wang, Anal. Chim. Acta. 619, 59-66 (2008).

[2] R. M. González-Rodríguez, R. Rial-Otero, B. Cancho-Grande, J. Simal-Gándara, J. Chromatogr. A. 1196-1197, 100-109 (2008).

[3] J. Xiong, B. Hu, J. Chromatogr. A. 1193 7-18 (2008).

[4] Transposition of the 'Council Directive 98/83/EC of 3.Nov.1998 on quality of water intended for human consumption' into the national laws in the EU associated countries, Prague, 1999.

O24- DETERMINATION OF CHLOROPHENOLS IN WATER SAMPLES USING DISPERSIVE LIQUID–LIQUID MICROEXTRACTION COMBINED WITH GC-MS

A. Arslan Kartal, L. Elçi

Pamukkale University, Faculty of Science & Arts, Department of Chemistry,
Denizli (Turkey)

Chlorophenols (CPs) are significant contaminants that extensively exist in environmental samples as a result of their industrial applications. All chlorophenols are toxic and especially 2,4,6-trichlorophenol and pentachlorophenol are carcinogenic [1]. CPs are in the priority environment pollutants list of the EPA and EU [2-5]. European Union directives on drinking water at a maximum concentration of total phenols is 0.5 µg L^{-1} and limit for each phenol is 0.1 µg L^{-1} [6]. Therefore, developing reliable, sensitive and easily operating detection methods are of great interest for the determination of these compounds in environmental samples.

In this study, before GC-MS determination, preconcentrations of 2,4-dichlorophenol, 2,6-dichlorophenol, 2,4,6-trichlorophenol, 2,3,4,6-tetrachlorophenol and pentachlorophenol were performed with dispersive liquid-liquid microextraction (DLLME). Sample volume, pH, dispersive solvent type and volume, extraction solvent type and volume and extraction time which are variables of DLLME method were optimized with Plackett-Burman factorial experimental design. The recoveries of CPs varied from 69 % (2,4-DCP) to 101 % (PCP). The RSDs were less than 6.6 %. Calibration curves were obtained in the range of concentration between 10.0 and 800 µg L^{-1}.

[1] L.W. Chung, M.R. Lee, Talanta. 76 (2008) 154.

[2] EPA Method 604, Fed. Rep. 26 October, part VIII, 40 CFR Part 13b, Washington, DC, 1984, p. 58.

[3] Directive 80/77/CE 157-1990, Off. J. Eur. Commun., 30-8-1990, European Community, (1990), Brussels.

[4] J.W. Moore, S. Ramamoothy, Editors, (1984) Organic Chemical in Natural Waters: Applied Monitoring and Impact Assessment, Springer–Verlag, New York.

[5] Drinking Water Directive 80/778/EEC, Commission of the European Communities, (1980), Brussels.

[6] M.C. Quintana, L. Ramos, Trends in Anal.Chem. 27 (2008) 5.

O25- MULTIVARIATE CURVE RESOLUTION ALTERNATING LEAST SQUARES ASSISTED DETERMINATION OF FORMALDEHYDE IN INDUSTRIAL WASTE WATER BY SPECTROPHOTOMETRY

M. Khanmohammadi[1*], N. Dallali[2], F. Karami[2], A. Bagheri Garmarudi[1,3]

[1]Chemistry Department, Faculty of Science, IKIU, Qazvin (Iran)
[2]Chemistry Department, Faculty of Science, Zanjan University, Zanjan (Iran)
[3]Department of Chemistry & Polymer Laboratories, Engineering Research Institute, Tehran (Iran)
[*]mrkhanmohammadi@gmail.com

The high rate increment in production and consumption of formaldehyde has caused harmful problems for both human and environment. It has already been known as a very toxic, mutant and carcinogen causing chemical which affects human eyes, membranes, and respiration systems. Its irritant properties such as dermatitis, eye irritation, respiration, asthma and pulmonary edema have been reported previously. Formaldehyde has been classified as one of the major pollutants due to its toxicity. It tends to form nitric acid and peroxide acetyl nitrate through a photochemical reaction. It is also known as a pollutant which has the potential to react with hydrochloric acid to form bis(chloromethyl)ether, a well known carcinogen. There are several reports indicating the analytical methods for determination of formaldehyde. Gas chromatographies (GC), high performance liquid chromatography (HPLC), GC with electron-capture detector (ECD) or flame ionization detector (FID) are some of the confirmed methods. Combination of the HPLC and preconcentration by solid-phase extraction (SPE) with C18 cartridges has been also reported as a sensitive technique; Solid phase spectrophotometric method in association with flow injection analysis is also used for determination formaldehyde with direct spectrophotometric measurement in C18 material. Trace amounts of formaldehyde in textiles is determined by discoloring kinetic spectrophotometry; Food samples are also analyzed by flow injection spectrophotometry using phloroglucinol as chromogenic agent to determine formaldehyde. This study proposes a UV-Vis spectrophotometric based method for determination of formaldehyde. The method is based on reaction between the analyte and Fluoral p. Spectral changes during the time were mathematically analyzed using a chemometrics technique, called "multivariate curve resolution based on alternating least squares" (MCR-ALS). Data processing by this chemometrics technique, introduces the UV-Vis spectrophotometry as a reliable method for quantitative analysis of formaldehyde in real samples and environmental protection.

O26- NANO-LIQUID CHROMATOGRAPHY-NANOSPRAY-MASS SPECTROMETRY FOR THE DETECTION AND QUANTIFICATION OF TRACES OF ENDOCRINE DISRUPTORS IN BENTHIC INVERTEBRATES

R. Baudot[1], A. Bulete[1], C. Cren-Olive[1], J. Garric[2],
M. Gust[2], L. Wiest[1]

[1]USR 059 Service Central d'Analyse du CNRS, échangeur de Solaize, chemin du canal,
69360 Solaize (France)
[2]Cemagref UR Milieux Aquatiques, Ecologie et Pollutions Laboratoire d'écotoxicologie
3 bis quai chauveau -CP 220 69336 Lyon (France)

Due to industrialization and use of chemical products in everyday life, different kinds of drugs or pesticides are present in our environment, causing negative impacts and threats on humans. Consequences of these pollutions are gradually highlighted and one of the challenges of environmental science is to evaluate risks.

The objective of this study is to develop analytical tools for extraction and analysis of traces of endocrine disruptors in biotic environmental matrices like water's benthic invertebrates. These gastropods, weighing just a few milligrams, are used to evaluate ecosystems state.

With such a small sample size, extraction step and analysis are more difficult. So, advanced technologies are required to seek drugs traces in complex matrices like gastropods: nano-chromatography coupled with mass spectrometry (nano-LC-nano-ESI MS/MS) increases sensitivity, reduces the required initial sample amount and is a good tool to answer this ecotoxicological issue.

Experimentation

In this context, we developed a new methodology using nano-LC-nano-ESI MS/MS to quantify traces of two substances (a neuropharmaceutical, fluoxetine and an anticonvulsant, carbamazepine) in two gastropods (10 to 20mg): Potamopyrgus antipodarum and Valvata piscinalis prosobranch gastropods. An easy and quick extraction method was developed. The procedure involves an extraction of about 10 milligrams of matrix by 500µL of a mix of acetonitrile:water:hexane (50/20/30) and 100mg of buffer salt. Recoveries were 86% for carbamazepine and 87% for fluoxetine.

Nano-LC-nano-ESI MS/MS analysis was performed with a nano Ultimate3000 (Dionex®) coupled with a Qtrap3200 detector (AB Sciex®). MS/MS detection was performed in MRM mode using a NanoSpray ® II (AB Sciex®) in the positive mode.

Validation

The developed method presents a good robustness and obtained limits of detection and quantification are enough low to detect contaminants in the environment: for carbamazepine and fluoxetine, LOD was respectively of 4ng/g and 30ng/g with only 10 milligrams of matrix. The validation was carried out over three days: within-day precision, inter-day variation and recoveries were determined.

Conclusion and perspectives

In order to handle small volumes, to work with a limited matrix quantity and to keep analysis sensitivity, an analytical method was developed using nano-LC-nano-ESI MS/MS. After a short exposure (14 days) at different doping concentrations, we studied bioaccumulation of fluoxetine in the two gastropods. As this method was carried out on one gastropod, a metabonomics approach could be possible to characterize biological responses.

O27- SEMI-AUTOMATED LIQUID CHROMATOGRAPHY - MASS SPECTROMETRY (LC-MS/MS) METHOD FOR MICROCYSTINS IN LAKEWATERS

B. A. Dineen[1], M. G. Cahill, J. O'Hallorn[2], F. van Pelt[2] and K. J. James[1,2]

[1]PROTEOBIO (Mass Spectrometry Centre), Cork Institute of Technology, Bishopstown, Cork, Ireland
[2]Environmental Research Institute, University. College Cork, Lee Road, Cork (Ireland)

Cyanobacteria (blue-green algae) are a common component of many freshwater and marine ecosystems that occur in eutrophic lakes and drinking water treatment plants and have a potential to produce several different biotoxins. The most commonly occurring class of freshwater biotoxins are the microcystins (MCs), which are cyclic heptapeptides that display potent hepatotoxicity and tumour promotion and to-date over 90 analogues have been characterised.[1,2] An automated LC-MS/MS method has been developed and validated for the direct analysis of MCs in lakewaters without pre-concentration. Large volume (1.5 mL) injection and an on-line analyte trapping column were used to achieve a detection limit < 0.03 µg/L MC-LR, which permits this automated method to be applied to monitor for compliance within the World Health Organisation Guideline limit of 1.0 µg/L MC-LR in drinking water. Reversed-phase liquid chromatography (LC) using a methanol/water gradient was used for the MRM LC-MS/MS determination of six microcystins. Using a heated electrospray ionisation (HESI) in positive mode, four precursor-product ion combinations for each toxin were used for MRM experiments. The method validation included the limits of detection, limits of quantification, mean recoveries, accuracy and precision, specificity and evaluation of matrix effects. The following calibration and reproducibility data were obtained for MC-LR; using LC-MS/MS; 0.25-10 µg/L, r^2=0.9992 (n=5); % RSD ≤ 7.3 at 0.25 µg MC-LR/L, (n=5). Using this method, microcystin-LR and microcystin-WR were identified in a number of lake water samples from Iniscarra Lake, County Cork, Ireland. Analyte confirmation was carried out by carrying out a Quantitation-Enhanced-Data-Dependant MS/MS (QED-MS/MS) scan also known as a reverse energy ramp (RER) which provided rich product ion spectra of the sample analytes.

[1] T.TU, A., Handbook of Natural Toxins: Marine Toxins and Venoms. Vol. 3.
[2] Botana, L.M., Seafood and Freshwater Toxins, Pharmacology, Physiology and Detection , Second Edition 2008.

O28- FLOW-INJECTION SPECTROPHOTOMETRIC DETERMINATION OF NITRITE IN MEAT AND NITRATE IN WASTE WATER SAMPLES USING DIAZOTIZATION COUPLING REACTION

H. A. Kadir and N. A. Fakhre

Dept. of Chemistry, College of Education/ Scientific Depts., University of
Salahaddin, Kirkukn Street, 009647504661563, Erbil (Iraq)

Nitrite and nitrate ions have been considered as a suspected carcinogen (because nitrite can react with secondary or tertiary amines to form N-nitrosamines, which are potent carcinogens), an environmental pollutant and a precursor of acid rain. Their salts are used as preservatives in the food industry such as curing of meat because under certain conditions, nitrite plays an important role in retarding and inhibition the growth of many kinds of bacteria which they spoilage a meats. Nitrate is an important intermediate in the biogeochemical cycling of nitrogen in natural water. They are present in soils, waters, food, wastewaters, plants, airs (as nitrogen dioxide) 1 . Because of the relative stability of the nitrate ion, most nitrogenous materials in environmental media tend to be converted to nitrate. Therefore, all sources of nitrogen (including organic nitrogen, ammonia and fertilizers) should be considered as potential sources of nitrate. Because nitrate salts are very soluble, nitrate is highly mobile in soil and migrates readily to the water table when present in excess of the amount utilized by plants as an essential nutrient. It comprises liquid waste discharged by domestic residences, commercial properties, industry, and / or agricultural and can encompass a wide range of potential contaminants and concentrations. In the most common usage, it refers to the municipal wastewater that contains a broad spectrum of contaminants resulting from the mixing of wastewater from different sources.

The development and application of a simple and sensitive batch and flow -injection spectrophotometric method for nitrite and nitrate determinations had been described. In this study, the method was based on the diazo-coupling reaction between acidified NDMPDAH and resorcinol. Under alkaline conditions the azo dye was formed, which absorption reaches maximum at 472 nm. Nitrate was reduced to nitrite in amalgamated cadmium reductor column and analyzed as nitrite. The influences of some interference on the batch and flow-injection spectrophotometric determination of nitrite and nitrate had been described. To eliminate the effect of some cationic interferences such as (Cr3+, Cd2+, Co2+, Fe3+, Ni2+, Mn2+ and Cu2+) two methods have been used; the first was column of cationic exchanger (H+–form), while the second was using 5.0% of EDTA solution, the results showed that EDTA solution gave superior results in both methods. Nitrite content of different curing meat samples and nitrate content of wastewater samples in different locations in Erbil city have been successfully determined with the proposed batch and flow-injection analysis methods. The results in batch methods were compared to those obtained with standard NEDA method.

[1] G. Ishiguro, T. Kawabe, N. Nakano and K. Nagashima, Anal. Sci., (2006), 22, 789 – 91.

O29- UPLC-ESI-MS/MS METHOD FOR THE DETERMINATION OF FDA APPROVED ANTI-INFLUENZA PHARMACEUTICALS IN WATER ENVIRONMENT

G. C. Ghosh, H. Tanaka, N. Yamashita, N. Nakada, T. Azuma

Kyoto University, Research Centre for Environmental Quality Management,
1-2 Yumihama, Otsu-City, Shiga-Prefecture, 520-0811(Japan)

Recently, a novel influenza A (H1N1) virus has spread rapidly across the globe and a pandemic alert was announced by World Health Organization (WHO) on April 29, 2009. As of January 10, 2010, more than 208 countries have reported laboratory-confirmed cases of the novel influenza A (H1N1) infections, including at least 13,554 fatalities (WHO 2010) . Two groups of anti-influenza drug have become available for the treatment of influenza infections are the neuraminidase inhibitors (oseltamivir and zanamivir) and the M2 ion channel inhibitors (amantadine and rimantadine). Oseltamivir phosphate (OP) which is marketed as Tamiflu is recommended by WHO for both treatment and prophylaxis of influenza pandemic. OP is a pro-drug, extensively metabolized (approximately 80%) in the human liver to oseltamivir carboxylate (OC)-the active metabolite which is excreted unchanged. On the other hand zanamivir, amantadine and rimantadine are excreted unchanged. The expected widespread use of anti-influenza pharmaceuticals during a severe pandemic are of environmental concern due to their eco-toxicological risk to aquatic organisms, possible anti-flu resistance in environment and drinking water contamination.

Analytical methods for the quantification of anti-influenza pharmaceuticals in water environment are relatively scarce and detection methods only for OP and OC are available [1, 2, 3]. Here we report on the development of an analytical method (SPE followed by UPLC-ESI-MS/MS) for quantitative determination of all FDA approved anti-influenza pharmaceuticals (OP, zanamivir, amantadine, rimantadine and OC-the active metabolite of OP) in water environment.

[1] Fick, J., Lindberg, R. H., Tysklind, M., Haemig, P. D., Waldenström, J., Wallensten, A.,Olsen, B., PLoS ONE 2 (10) e986 (2007).
[2] Ghosh, G. C., Nakada, N., Yamashita, N., Tanaka, H., Environ. Health Perspect. 118(1), 103-107 (2010).
[3] Prasse, C., Schlüsener, M.P., Schulz, R., Ternes, T.A., Environmental science & technology, 44(5), 1728-35 (2010).

O30- NOVEL ZrO^{2+} ION-SELECTIVE ELECTRODE BASED ON A HEXA COSINE COMPOUND AS NEUTRAL CARRIER IN PVC MATRIX

M. Giahi[1*], M.R. Rahimibashar[2]

[1]Department of Chemistry, Faculty of Science, Lahijan Branch, Islamic Azad University,
P.O. Box: 1616, Lahijan (Iran)
[2]Department of Marine biology, Faculty of Science, Lahijan Branch, Islamic Azad University,
P.O. Box: 1616, Lahijan (Iran)
[*]giahi_m@yahoo.com

In this work, a novel ZrO^{2+} PVC-based membrane sensor based on 4,7,13,16,21,24-hexa oxa-1,10- diazabicyclo [8,8,8]- hexa cosane (HODBHC) as a new ionophore is presented. The sensor displays a linear dynamic range between 1.0×10^{-1} and 1.0×10^{-6} M, with a near Nernstian slope of 29.9 ± 0.4 mV per decade in an acidic solution (pH=1). The limit of detection is 8.0×10^{-7} M. The electrodes possess advantages of low resistance, very fast response time, relatively long lifetimes and, especially, good selectivities relative to a wide variety of other cations. It was used as indicator electrode in potentiometric determination of ZrO^{2+} ion by standard addition method at pH 1.0 in two samples.

References

[1] M.B. Gholivand, A. Babakhanian, M. Joshaghani. Analytica Chimica Acta **2007**,584, 302.
[2] Chen, L.; Zeng, X.; Ju, H.; He, X.; Zhang, Z., *Microchemical Journal* ***2000,*** *65, 129.*
[3] Buhlmann, P.; Pretsch, E.; Bakker, E., *Chem.Rev.* ***1998,*** *98, 1593.*

O31- MODIFIED DIFFUSIVE GRADIENT IN THIN FILMS TECHNIQUE IN DETERMINATION OF URANIUM IN SEDIMENTS

M. Gregusova[1,2,*] and B. Docekal[1]

[1]Institute of Analytical Chemistry ot the ASCR, v.v.i, Veveri 97, 602 00 Brno (Czech Republic)
[2]Department of Environmental Analytical Chemistry, Faculty of Chemistry,
Brno University of Technology, Purkynova 118, 612 00 Brno (Czech Republic)
[*]gregusova@iach.cz

The diffusive gradients in thin film technique (DGT) is a relatively new analytical technique capable of measuring in situ concentrations of trace metals in an aquatic environment [1]. It is largely used for measuring kinetically labile metal species in natural waters or trace metal fluxes in sediments and soils.

The DGT employs a hydrogel layer to control the diffusive transport of metals to a cation-exchange resin, usually Chelex 100, which is selective in free or weakly complexed metal ion species. This study deals with a new resin gel based on Spheron-Oxin® (5-sulphophenyl-azo-8-hydroxyquinoline) [2] ion exchanger for DGT technique. This new binding phase with a higher selectivity for trace metal species than Chelex 100 could potentially provide more information on metals speciation in aquatic systems.

The performance of this new binding phase was tested for the determination of Cd, Cu, Ni, Pb by ET AAS and U by ICP MS under laboratory conditions. Uranium, analogously to other heavy metals, forms various complexes in natural waters with a variety of ligands. Depending on pH of the solution, uranyl species in form of stable hydroxide and, especially carbonate complexes are present in aquatic systems. Different uranium species with different biological effects can be measured by selecting DGT binding phases. Comparison of DGT devices with embedded Chelex 100 and Spheron-Oxin® resin gels in carbonate solutions showed that different fractions of uranium can be measured.

The sedimentary column is one of the most important stocks of contaminants in the aquatic environment. DGT probes are used to obtain resolution data of metal mobilization in marine and river sediments. Modification of DGT sediment probe for measurement depth profiles of uranium isotope abundance by ICP MS in river sediments to spatial resolution of 1 mm.

[1] Davison, W., Zhang, H., Nature 367, 546-548 (1994).
[2] Slovák, Z., Bulletin n.p. Lachema Brno 30-34 (1979).

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O32- OPTIMIZATION OF DISPERSIVE LIQUID-LIQUID MICROEXTRACTION OF NICKEL(II) BY ATOMIC ABSORPTION SPECTROMETRY

A. Höl, L. Elçi

Pamukkale University, Faculty of Science and Arts, Department of Chemistry,
20017 Kinikli Denizli (Turkey)

Sample preparation has a direct impact on accuracy, precision and quantitation limits and is often the rate determining step of the analytical process, especially when trace determination has been the purpose. Conventional liquid-liquid extraction (LLE) is the most widely used sample pre-treatment technique in routine analyses for trace metal determination due to its simplicity and adaptability. However, some shortcomings like the use of large sample volumes and toxic organic solvents make LLE expensive, time-consuming, laborious and unfriendly for the environment. Recently, efforts have been focused on the miniaturizing of the LLE procedure by reducing the organic solvent, leading to the development of micro extraction methodologies [1]. Dispersive liquid-liquid microextraction (DLLME) is a miniaturized LLE that uses microliter volumes of extraction solvent. The advantages of DLLME method are simplicity of operation, rapidity,low cost, high-recovery high enrichment factor and environmental benignity, with wide application prospects in trace analysis [2].

In this study a DLLME method was investigated for the preconcentration of Ni^{2+} ions. 8-Hydroxy quinoline was used as a chelating agent prior to extraction. The effect of various experimental parameters on the extraction was investigated using Plackett-Burman design and full factorial design. Disperser and extracting solvents, dispersive solvent volume, extracting solvent volume, pH, extraction time were selected as design variables. Through factorial design the best efficiency of extraction acquired using methanol and chloroform as dispersive and extraction solvents respectively. Design optimization resulted in 1.0 mL of dispersive solvent, 300 mL of extraction solvent, sample size 7.5 mL. Flame atomic absorption spectrometry was used for quantitation of the analyte after preconcentration. The developed method was evaluated by analyzing certified reference material and applied successfully to the analysis of environmental water samples.

[1] A. N. Anthemidis, K.-I. G. Ioannou, On-line sequential injection dispersive liquid–liquid microextraction system for flame atomic absorption spectrometric determination of copper and lead in water samples, Talanta 79, 86–91, 2009.

[2] Zang Xiao-Huan, Wu Qiu-Hua, Zhang Mei-Yue, Xi Guo-Hong, Wang Zhi, Developments of dispersive liquid-liquid microextraction technique, Chıınese Journal of Analytıcal Chemistry, 37(2), 161-168, 2009.

O33- ASSESSMENT OF ANTIFOULING BIOCIDES CONTAMINATION IN DIFFERENT COASTAL AREAS OF ITALY

G. Ansanelli[1], S. Cannarsa[2], S. Chiavarini[3], C. Cremisini[3], G. Di Landa[1],
M. Fantini[3], P. Massanisso[3], M. Pezza[3], C. Ubaldi[3]

[1]UTTP-CHIA, ENEA, Portici Research Centre , Via Vecchio Macello, 80055 Portici (Italy)
[2]UTMAR-ECOL, ENEA, S. Teresa Marine Environment Centre, 19036 Pozzuolo di Lerici (Italy)
[3]UTPRA-GEOC, ENEA, Casaccia Research Centre, Via Anguillarese 301, 00123 Rome (Italy)

Due to the large use of biocides as active components in antifouling paints, their release from maritime traffic represents one of the main problems of direct, diffuse and continue contamination of the marine environment (1).

The presence of four common antifouling biocides (irgarol 1051, diuron , dichlofluanid and chlorothalonil) was investigated in different coastal areas of Italy. Even if Tributyltin (TBT)-based antifouling paints was recently banned (2), due to the significant toxic effects and bioaccumulation of this compound, the presence of TBT was also investigated to evaluate the residual level of this contaminant.

Several studies have demonstrated the presence of these biocides in marina, harbor and coastal waters of many European countries both in the Northern and Mediterranean areas. As far as we know, up to know only few survey of these compounds has been carried out in Italy, except for TBT.

In the two sampling campaigns organized in 2010, samples of seawater, sediment and mussels were collected in the Gulf of Napoli and Gulf of La Spezia.

The analytical method utilized for the determination of the biocides in seawater involves off-line solid phase extraction (SPE) or liquid/liquid extraction (LLE). The biocides extraction from sediments and mussel was carried out with solvent mixtures in concert with various extraction devices, such as Soxhlet, ultrasonic bath and pressured liquid extraction (PLE).

The data obtained were evaluated considering the local condition in terms of maritime traffic and activities. Moreover, the results were compared with previous monitoring campaign (3, 4) to evaluate the trend of the concentration of these biocides in water sediments and mussels in the studied areas.

[1] Mazziotti, I., Massanisso, P., Cremisini, C., Chiavarini, S., Fantini, M. and Morabito, R., Energia, Ambiente e Innovazione 5, 34-54, (2005).

[2] International Maritime Organization (IMO). International convention on the control of harmful anti-fouling systems on ships, (2007) Available from: http://www.imo.org/ includes/blastDataOnly.asp/data_id%3D20019/14.pdf

[3] Caricchia, A.M., Chiavarini, S., Cremisini, C., Fantini, M. and Morabito, R., Science of the Total Environment 121, 133-144, (1992).

[4] Di Landa, G., Ansanelli, G., Ciccoli, R. and Cremisini, C., Marine Pollution Bulletin 52, 1541-1546, (2006).

O34- AN ON-LINE ANALYTICAL EQUIPMENT TO DETECT H_2O_2 RESIDUES IN WARM-WATER DISTRIBUTION SYSTEMS DISINFECTED WITH H_2O_2 – Ag^+ AGAINST *LEGIONELLA*

L. Achene[1], V. Melini[1], M. Ottaviani[1], M. L. Ricci[2], E. Veschetti[1]

[1]Istituto Superiore di Sanità, Dep. of Environment and Primary Prevention,
Viale Regina Elena 299, 00161 Rome (Italy)
[2]Istituto Superiore di Sanità, Dep. of Infectious, Parasitic and Immune-Mediated Diseases,
Viale Regina Elena 299, 00161 Rome (Italy)

Bacteria with harmful action on human health can colonise warm-water distribution systems and cause serious diseases especially in otherwise healthy individuals. A wide range of disinfection methods, both systemic and localised, is usually used in hospital to control bacteria growth thus preventing fatal diseases. A relatively recent disinfection technique is hydrogen peroxide - silver treatment whose efficacy requires further experimental confirmations. The lack of the efficacy evaluation for this treatment is, in fact, mainly due to the absence of an efficient system for the periodic determination of disinfectant residues in water distribution systems. In a previous study we randomly measured hydrogen peroxide concentrations in hospital warm-water distribution systems and we observed considerable fluctuations during the time. Those were mainly due to the variability of the water flow during the day and to the interaction between disinfectant and materials in contact with water. So that experience showed it was necessary to monitor periodically, even during the night, the disinfectant concentration at any remote point of the warm-water distribution systems to develop an effective bacteria controlling strategy.

In order to tackle this problem, an automatic on-line apparatus that can monitor automatically and periodically the concentration of hydrogen peroxide, has been recently developed by our research team. Hot water aliquots are cooled down in Teflon pipes, degassed in a lab-made camera and pumped into a flow injection system where vanadate ion is added at acid pH. The product of the colorimetric reaction is then determined by a UV-VIS detector operating at 427 nm. The optimization of this innovative equipment required efforts in studying water and reagent flow ratio, pump tube section, reaction pH and complex absorption wavelength. This equipment has been installed in four Italian hospitals to monitor the residual concentration of a H_2O_2 - Ag^+ 10^3:1 commercial solution used to disinfect the warm water at the nominal concentration of 10 mg/L H_2O_2. The actual concentration of the disinfectant components was monitored every 90 min for at least 48 hours immediately after the addition point of the disinfectant and at the most remote sampling points. A significant variability of disinfectant residues was observed during the experimental time and the identified fluctuations matched the variability of microbiological results.

O35- DETERMINATION OF LIPOSOLUBLE NEUTRAL Cu(II) COMPLEXES IN NATURAL WATERS USING A PERMEATION LIQUID MEMBRANE PRECONCENTRATION PROBE

N. Parthasarathy, M. Pelletier and J. Buffle

Department of Inorganic and Analytical Chemistry, University of Geneva, Sciences II,
30 Quai E.-Ansermet, CH-1211 Geneva 4 (Switzerland)

Metal ions, such as Cu (II), Pb(II) and Cd(II), are present under a wide variety of chemical forms in natural water, e.g. free metal ions, hydrophilic charged complexes and neutral lipophilic complexes. Their bioavailability or toxicity to microorganisms depends on the specific form, particularly the free metal ions are the most toxic and labile metal complexes and neutrally charged lipophilic complexes are potentially toxic or bioavailable. The determination of these complexes is important in order to correctly interpret their environmental impact, but these species are present at trace levels, typically at subnanomolar level, and very few methods allow their determination under natural water conditions. Due to lack of sensitive methods, especially for lipophilic complexes detection, their contribution to biouptake is poorly understood. Hence, an analytical technique, based on permeation liquid membrane (or supported liquid membrane) (PLM or SLM) has been investigated for the determination of lipophilic metal complexes. Permeation liquid membrane technique is based on liquid-liquid extraction principles and their attractive features are that extraction, back extraction and preconcentration can be done in one step. Previous studies of Cu(II) speciation in natural waters showed that high preconcentration factors can be obtained using a hollow fibre PLM (HFPLM) and subnanomolar concentrations of free Cu(II) can be determined [1]. Whereas metal ion separation by PLM is mediated by metal carrier in the organic membrane phase, separation of neutral complexes may be achieved in the absence of carrier. To our knowledge, determination of lipophilic complexes in natural water using PLM preconcentration probe has not been reported. The aim of this study was to use hollow fibre permeation liquid membrane for such a determination. For this purpose the PLM parameters, such as the nature of solvent, diffusion coefficient in the membrane, partition coefficient between the solution and the membrane, and permeability coefficient were evaluated for optimization of the method. Copper–8-hydroxyquinolate, CuQ_2^0, was chosen as model lipophilic complex. It is used as a pesticide and may be present in natural waters. The effects of pH, on CuQ_2^0 transport were also studied. The results showed that the neutral species is transported efficiently across the membrane containing toluene/phenylhexane mixture. The application of PLM method was tested for trace level determination of lipophilic complexes by using hollow fibre permeation liquid membrane to preconcentrate the analyte. High preconcentration factor for CuQ_2^0 was achieved using the designed HFPLM device. Finally, the applicability of this method to CuQ_2^0 was tested in natural water by spiking it with 8-hydroxyquinoline (10 µmol L^{-1}). The results showed a quantitative recovery. The theoretically estimated LOD is few pmol L^{-1}[2].

[1] Parthasarathy, N., Pelletier, M. and Buffle, J., Chrom. A 1025, 33-40 (2004).
[2] Parthasarathy, N., Pelletier, M. and Buffle, J., J. Memb. Sci. 355(1-2), 78-84 (2010).

O36- PAHs IN ARCTIC SNOW

Z. A. Zhakovskaya, V. A. Nikiforov, V. N. Petrova

Department of Ecological and Chemical Research, St.-Petersburg Scientific Research Center for Ecological Safety, Russian Academy of Sciences,
Korpusnaya st. 18, 197110 St.-Petersburg (Russia)

The study was focused on surface snow, located in the area of Norwegian settlement Longyearbyen, where the samples were collected from the 7 characteristic stations in April 2009. The study included the analysis of accumulation and distribution of 16 priority polycyclic aromatic hydrocarbons (PAHs). The determination of quantitative relationships between individual PAH components allowed to obtain snow pollution PAH profiles and to determine the character of the dominating source of their input into the environment [1, 2]. The investigation of Arctic snow cover on Svalbard showed the comparatively high total PAH levels, which could be the local characteristic. The values of fluoranthene/fluoranthene+pyrene ratio (Fl/Fl + P) in the examined snow samples vary from 0.4 (6th station) to 0.9 (5th station). The snow cover in the region under study features relatively low concentrations of fluoranthene and pyrene; therefore, the ratio of these components is sensitive to even small input of organic matter burning products. The values of the anthracene/anthracene+phenanthrene (An/An+Phen) suggested a mixed type of pollution with a shift toward pirogenic origin. As a result the pirogenic prevailing PAH source was determined for the observed area. It should be also mentioned, that some potentially carcinogenic polychlorinated naphthalene was found on the 8th station. The fact is that these PAHs, which were already observed on Svalbard before, have very high toxicity but no international norms or permissible levels for their presence in the environment.

[1] Dahle S., Savinov V., Petrova V. et al. Polycyclic aromatic hydrocarbons (PAHs) in Norwegian and Russian Arctic marine sediments: concentrations, geographical distribution and sources. Norwegian Journal of Geology 86, 41-50 (2006).
[2] Halsall C. J., Barrie L. A., Fellin P. et al. Spatial and Temporal Variation of Polycyclic Aromatic Hydrocarbons in the Arctic Atmosphere. Environ. Sci. Technol. 31 (12), 3593-3599 (1997).

O37- DEGRADATION OF FLUOROQUINOLONE ANTIBIOTIC PEFLOXACIN BY UV PHOTOLYSIS, OZONATION AND THEIR COMBINATION

A. Dombi[1], K. Gajda-Schrantz[1], E. Illés[1], L. Nováková[2], M. Seifrtová[2], P. Solich[2]

[1]Department of Inorganic and Analytical Chemistry, University of Szeged, Research Group
for Environmental Chemistry, ReGECh, P.O. Box 440, H-6701 Szeged (Hungary)
[2]Department of Analytical Chemistry, Faculty of Pharmacy, Charles University, Heyrovského 1203,
500 05 Hradec Králové (Czech Republic)

Advanced oxidation processes (AOPs) such as ozonation or UV photolysis are promising tools for the removal of persistent pharmaceutical compounds from water. AOPs are able to generate hydroxyl radical which is one of the strongest known oxidant and it is able to oxidize and mineralize almost every organic molecule into a CO_2 and inorganic ions. It can be used in advanced treatment of secondary wastewater effluent as it has potential to disinfect primary wastewater effluents and can accomplish the water treatment process and avoid to release of pharmaceuticals into surface waters.

In this work the degradation of fluoroquinolone type antibiotic, pefloxacin was done using ozonation, UV photolysis at 254 nm and their combination, in order to compare the efficiency of these processes. The results showed that ozonation is the most efficient method for the degradation of pefloxacin, followed by ozonation/UV and UV photolysis. The degradation can not be explained with simple first order kinetics. The changes of the dissolved O_3 concentration during the degradation as well as the different kinetics of the formation and decomposition of the by-products make this process very complex.

In order to obtain information about the rate of mineralization of pefloxacin TOC measurements were performed. Although, the total degradation of pefloxacin was observed, total organic carbon analysis showed no mineralization indicating the transformation of pefloxacin into some stable organic byproducts. Although the total mineralization would be suitable for the water treatment process, the formation of hydrophilic biodegradable products with no toxicity could be also acceptable for the treatment process in wastewater treatment plants. For this reason, future work in the evaluation of the toxicity of the degradation products of pefloxacin will be done.

The formed degradation products were studied by UPLC-MS/MS with electrospray ionization in positive mode. The analysis of the degradation products in case of pefloxacin showed the formation of degradation products with molecular weights of 363, 319, 335, 349 and 301. Structures of byproducts were suggested on the basis of exact mass measurements and specific MS fragmentation.

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O38- OPTIMIZATION OF FENTON'S PROCESS FOR THE DECOLORIZATION OF AZO DYES

S. Ali[1], S. A. S. Chatha[1,2] , A. I. Hussain[2] and A. Shoukat[2*]

[1] Department of Chemistry & Biochemistry, University of Agriculture, Faisalabad-38040 (Pakistan)
[2] Department of Industrial Chemistry, Government Collage University, Faisalabad-38000 (Pakistan)
[*]aizachemist@yahoo.com

Colored azo dye effluents from different dying units, poses a threat to the aquatic environment due to their non bio degradable, toxic and carcinogenic nature. It is imperative to treat these effluents before discharging in to water bodies. In the present research, Fenton's process was employed to treat the industrial effluents and further different working parameters like pH, temperature and doses of H_2O_2 and Fe (II) were also optimized to achieve the better efficiency of process. Decolorization efficacy of process was evaluated by measuring the absorbance spectrophotometrically. It was observed that the degradation rate of azo dyes was strongly dependent on pH, temperature and doses of Fe (II) and H_2O_2. Furthermore, water quality parameter, COD was conducted through standard methods the extent of mineralization. These investigations can provide a fundamental knowledge for the treatment of wastewater containing red azo dye by Fenton oxidation process.

O39- THE EFFECT OF HAIR CHARACTERISTICS AND TREATMENTS ON MINERAL COMPOSITION OF SCALP HAIR

K. Chojnacka, I. Michalak, A. Zielińska

Institute of Inorganic Technology and Mineral Fertilizers, Wroclaw University of Technology,
Smoluchowskiego 25, 50-372 Wroclaw (Poland)

Hair mineral analysis (HMA) is used in biomonitoring of exposure from the environment, evaluation of systematic intoxication, determination of nutritional status of individuals and in diagnosis of various diseases [1], metabolic disorders [2] and also in the assessment of exposure at the workplace [3]. Recently, a particular attention has been paid to supplementation of minerals to treat mineral imbalance. In order to elaborate an efficient supplementation program, it is essential to determine the level of minerals in the body. Hair mineral analysis can be employed as a diagnostic tool [2].

In the present work, the effect of the type of hair (weak/strong, greasy/normal/dry, presence of dandruff) and cosmetic treatments (anti-dandruff shampoos, drying of hair) on hair mineral composition is discussed. The application of hair mineral analysis was exemplified by identification of exposure to elements from deodorants. Hair was sampled from 117 individuals, who were asked to fill a questionnaire. The elemental composition of hair was determined by ICP-OES (macroelements and major microelements) and ICP-MS (minor microelements, toxic elements and other trace elements). The results were elaborated statistically by *Statistica 8.0*. Statistical significance of differences was determined by U Mann-Whitney test ($p<0.05$, $p<0.1$). For elements, the content of which differed between the groups, the reference ranges were elaborated, as the values within 10th and 90th percentile. Healthy and strong hair which were not dried with dryer contained statistically significantly more K and La and less Co and Ca than destroyed, weak, dried hair and hair with dandruff. In hair with dandruff, statistically higher level of Hg was found. The results of hair mineral analysis showed that Zn and Se are deposited on hair follicle exogenously from medicated anti-dandruff shampoo from active ingredients. This technique was used to assess dermal exposure from deodorants. Individuals which use stift which contain the compound of Zr as antiperspirant, contain 3 and 5 times higher level of this elements than those which use deo-roll or spray, respectively.

[1] Saiki, M., Alves, E.R., Jaluul, O., Sumita, N.M. and Jacob Filho, W., J. Radioanal. Nucl. Chem. 276, 53–57 (2008).
[2] Hong, S.R., Lee, S.M., Lim, N.R., Chung, H.W. and Ahn, H.S., Nutr. Res. Prac. 3, 212-219 (2009).
[3] Pereira, R., Ribeiro, R. and Goncalves, F., Sci. Total Environ. 327, 81–92 (2004).

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O40- LARGE SCREENING OF EMERGING POLLUTANTS IN SURFACE AND DEEP WATERS BASED ON ANALYSES BY LC/MS-MS

R. Baudot, C. Cren-Olive, E. Vulliet, L. Wiest

Service Central d'Analyse du CNRS, USR59, Echangeur de Solaize,
Chemin du Canal, 69360 Solaize (France)

Industrialization and the use of an increasing number of chemicals and drugs in everyday life are responsible for the environmental release of various substances whose effects are only gradually being identified. The so called emerging pollutants are not necessarily new chemicals and some of them have often long been present in the environment, but their presence and significance are only now being elucidated.

As part of a national screening to evaluate the risk exposure of populations to certain classes of emerging substances, several families of pharmaceuticals and endocrine disruptors (including hormones and industrial compounds) were investigated in surface and deep waters intended to drinking.

Today, the technique of choice for analysis of these substances in environmental compartments is liquid chromatography coupled to tandem mass spectrometry (LC-MS/MS), which offers the selectivity and sensitivity required. In this context, multi-residue LC-MS/MS methodologies were developed and applied to the analysis of 71 surface and 70 ground-waters of the Rhône-Alpes region (France). Were also included influents and effluents of 8 drinking water treatment plants, in order to assess the potential for these compounds to resist to drinking water treatments.

The developed methods allowed the detection of the target compounds at the low ng/L levels. Results indicate that no water was free of pollutants, regardless of its origin (surface or ground-water) and the season of collect. The nature and levels of pollutants, however, vary depending on the origin of water and the season. Generally, the levels found were low, rarely exceeding 50 ng/L in the case of pharmaceuticals and industrial compounds and rarely superior to 3 ng/L in the case of hormones. With exceptionally low detection limits of the analytical methods, the results also reveal the presence of compounds in drinking waters, indicating that most of treatments failed in their elimination.

O41- ARTIFICIAL SWEETENERS AND FLUORESCENCE WHITENING AGENT IN SURFACE WATERS: DETERMINATION AND APPLICATION AS CHEMICAL TRACERS

J. Wu, Z. Yang, L. Zhang

Center for Advanced Water Technology, Public Utilities Board, 82, Toh Guan Road East,
WaterHub, #C4-03, Singapore 608576 (Singapore)

Artificial sweeteners are used as sugar substitutes in remarkable amounts in food, drinks, drugs as well as sanitary products [1]. Among them, acesulfame, cyclamate, saccharin, sucralose and aspartame are approved by the US Food and Drug Administration. After ingestion, these sweeteners can pass through the human metabolism largely unaffected, then reach the domestic wastewater, and even transport to surface waters because of their relatively high mobility [2]. Fluorescent whitening agents (FWAs) are extensively applied in household detergents and usually discharged though wastewater treatment facilities or directly into surface waters [3, 4]. Among FWAs, 4,4'-Bis(2-sulfostyryl)-biphenyl (DSBP) has been predominantly detected in surface waters [3].

In this work, an analytical method for the simultaneous determination of five artificial sweeteners (acesulfame, cyclamate, saccharin, sucralose and aspartame) in water is reported. After solid phase extraction with Waters HLB cartridge at pH 2, target analytes were analyzed by liquid chromatography-electrospray ionization tandem mass spectrometry (LC-MS-MS) in negative ionization mode. In the optimized conditions, recoveries higher than 70% were obtained for all of target compounds. And detection limits ranged from 10 to 30 ng/L when 100 mL of water sample was used. For the determination of DSBP, one of FWAs, PerkinElmer LS-55 fluorescence spectrometer was employed with 350nm as excitation wavelength and 442nm as emission wavelength. Good linearity of response ranging from 1 to 50µg/L with the coefficients of determination, r^2, 0.9998 was obtained. The possibility of employing artificial sweeteners and DSBP as chemical tracers in tropical urban marine system was examined. Surface water samples were collected from 17 locations of Marina Bay, rivers or canals connected, and drainages released to the canal around Marina Bay. Acesulfame, cyclamate, saccharin were consistently detected in surface waters with concentration of 12-98.8 ng/L, 5.5-315 ng/L, 51-587 ng/L, respectively. Sucralose was observed in 74% of the investigated water samples. And aspartame was only detected in 12% of surface waters. FWA expressed as DSBP was observed in all of studied waters with concentration of 0.75-12.48 ng/mL. The highest concentrations of target compounds were observed in drainages, followed by canal waters. The correlation analyses for fecal coliforms, *E.coli* with these chemical tracers were investigated. It was found the high correlation exists between saccharin and fecal coliforms or *E.coli* (Pearson correlation coefficient r, 0.68), FWA expressed as DSBP and fecal coliforms or *E.coli* (Pearson correlation coefficient r, 0.64), respectively, in surface waters, demonstrating that saccharin and FWA are highly related to the human-source contamination and suitable for chemical tracers.

[1] Buerge, I.J., Buser, H.-R., Kahle, M., Müller, M.D. and Poiger, T., Environ. Sci. Technol. 43, 4381-4385 (2009).
[2] Scheurer, M., Brauch, H.-J., Lange, F.T., Anal. Bioanal. Chem. 394, 1585-1594 (2009).
[3] Shu, W.-C., Ding, W.-H., J. Chromatogr. A. 1088, 218-223 (2005).
[4] Hayashi, Y., Managaki, S., Takada, H., Environ. Sci. Technol. 36, 3556-3563 (2002).

O42- OFF-FLAVOR ODOROUS COMPOUNDS IN WATER AND THEIR DETERMINATION

X. Qian, R. Hu, Z. Yang and L. Zhang

Centre for Advanced Water Technology, BUB, The Toh Tuck Complex, 80/82,
Toh Guan Road East, #C4-03, 608575 (Singapore)

Off-flavor problems are significant for water suppliers, first because tastes and odors are regulated by guidelines for potable water and, secondly, because consumers judge water by what they first perceive. Tastes and odors account for the largest single class of consumer complaints submitted to water utilities. Although the compounds responsible for taste and odor are normally not associated with adverse health effects, their presence can lead to the perception that the quality of the tap water is inferior. Among the eight odor groups described in the water flavor wheel, the earth-musty odors are specially troublesome because they are particularly unpleasant and often encountered in water (Suffet *et al*., 1996). These semi-volatile compounds have a muddy, musty odor described by the human nose when present at concentrations > 0.004–0.02 mg/L for geosmin and MIB (Mallevialle and Suffet, 1987; Krasner *et al*., 1983; Persson, 1983; Young *et al*., 1996), as well as 30 pg/L for haloanisoles in water (Malleret *et al*., 2001a,b). These olfactory detection limits are well below the conventional analytical methods.

In most cases, complaints concern about the chlorine and earthy/musty smelling compounds. However, better understanding the types of taste and odour and the chemical causes of the taste and odour problems would help in controlling the taste and odor problems. For determination of off flavor odours in water, two monitoring approaches can be applied: sensory human panel and advanced instrumentation. Sensory human panel will provide a broad screening tool for identifying the presence or absence of off flavors via threshold odour number. It also can provide qualitative information on the compounds likely to be responsible for the off flavors via flavor profile analysis. However, sensory human panel approaches are human nose dependant with inevitable human errors. The approach of advanced instrumentation involves chemical analysis of compounds that are commonly associated with the presence of off-flavors in water. Traditional analytical methods for monitoring these tastes and odors concentrations include closed-loop stripping, liquid–liquid extraction, steam distillation and purge and trap. Some of these methods have poor sensitivity, some of them are more complex for sample preparation or analysis. Most of the developments in the analysis of tastes and odor compounds focus on the extraction preconcentration technique, such as membrane based extraction (Zander *et al*., 1997), microliquid–liquid extraction (Bao *et al*, 1997) and stir bar sorptive extraction (Benanou *et al,* 2003). However, detection at picogram per liter level of the earthy-musty off-flavor compounds is still challenging, although numerous extraction techniques have been applied. In this paper, we would like to introduce a brief summary of the off-flavor compounds in water and their determination. We will also introduce types of analytical methods developed in our laboratory for determination of off-flavor compounds in water, inclusive of GC-MS, PTV-GC-MS, SPME-GC-MS, purge and tarp GC-MS, accelerated purge and tarp GC-MS, with their advantages and limitations being discussed. Many of the developed analytical methods have been successfully applied in our routine water quality monitoring for off-flavor control.

Bao M.L., Barbieri K., Burrinib D., Griffini O., and Pantania F., 1997, Determination of trace levels of taste and odor compounds in water by microextraction and gas chromatography-ion-trap detection-mass spectrometry, 31(7), 1719-1727

Benanou, D., Acobas F. and Roubin M.R.De., 2003, Stir Bar Sorptive Extraction: A New Way to Extract Off-Flavor Compounds in the Aquatic Environment, Agilent publication number 5988-8900EN

Krasner S. W., Huang C. J. and McGuire M. J., 1983, A standard method for quantification of earthy-musty odorants in water, sediments, and algal cultures, Water Sci. Technol. **15**(6/7), 127-138.

Malleret L ., Bruchet A., 2001, Application of large volume injection GC/MS to the picogram analysis of chlorinated and brominated anisoles in "earthy-musty" off-flavor water samples , Water Sci. Technol.Water Supply 1(4), 1-8.a

Malleret L ., Bruchet A., Hennion M.-C., 2001, Picogram Determination of "Earthy-Musty" Odorous Compounds in Water Using Modified Closed Loop Stripping Analysis and Large Volume Injection GC/MS, Anal. Chem. **73**, 1485-1490.^{b}

Persson P.-E. 1983, Off-flavours in aquatic ecosystems-an introduction, Water Sci. Technol. **15**(6/7), 1-11.

Suffet I .H., Corado A., Chou D., Butterworth S., MacGuire M.J., 1996, AWWA Taste and Odor Survey, J. Am. Water Works Assoc. **88**(4), 168-180.

Young W. F., Horth H., Crane R., Ogden T. and Arnott M.,1996, Taste and odour threshold concentrations of potential potable water contaminants. Water Res. **30**, 331-340.

Zander A.K and Pingert P., 1997, Membrane-based extraction for detection of tastes and odors in water, Water Research, 31(2), 301-309.

O43- COMBINED CHROMATOPROBE AND GC-MS ANALYSIS OF POLYBROMINATED DIPHENYL ETHERS IN INDOOR DUST IN THE PHILIPPINES

M. P. B. Espino

Institute of Chemistry, University of the Philippines, Diliman,
Quezon City 1101 (Philippines)

Polybrominated diphenyl ethers (PBDEs) are flame retardant chemicals added to plastic materials, electronic and electrical equipment, upholstery, and other modern materials. In time, PBDEs are released from these products and find their way into the different environmental compartments. Of late, trash burning and incineration of waste electronic and electrical equipment (e-wastes) have been implicated to contribute to environmental burdens [1,2]. In the Philippines, very little is known of the treatment and disposal of e-wastes. Broken or outmoded electronic and electrical equipment are commonly stored in homes and offices for extended periods of time. This study aimed to determine the levels of PBDEs in workplace environments in the country. An analytical method involving sonication-assisted hexane extraction and determination by combined chromatoprobe and gas chromatography-mass spectrometry (GC-MS) was developed for PBDEs in indoor dust. The extracts do not require cleanup before analysis by chromatoprobe injection-GC-ion trap MS. Recoveries of the PBDEs in indoor dust at 2500 and 4000 ng/g spike levels were from 59 to 134%. The PBDEs were identified by their mass spectra and retention times. The PBDE concentrations were determined using specific quantitation ions and calculated against standard calibration solutions. Good linearity of the chromatoprobe and GC-MS response was obtained in the concentration range of 4 to 283 ng/mL (R^2= 0.9938-0.9996). Based on S:N of 3:1, the detection limits were from 0.4 to 3 ng/mL. BDE-47, BDE-99, BDE-100, BDE-153, BDE-154 were detected in eight of the sixteen dust samples collected in indoor workplace environments at the University of the Philippines Diliman campus. The concentrations of these PBDE congeners are between 132 and 6900 ng/g and comparable to those determined in indoor dust in other countries [3,4]. The detection of these congeners was further confirmed by MS-MS analysis.

[1] Luo Q., Wong M., Cai Z. Talanta 72, 1644-1649 (2007).
[2] Deng W., Zheng J., Bi X., Fu J., Wong M. Environ. Int. 33, 1063-1069 (2007).
[3] Sjodin A., Papke O., McGahee E., Focant J., Jones R., Pless-Mulloli T., Toms L., Herrmann T., Muller J., Needham L., Patterson D. Chemosphere 73, S131-S136 (2008).
[4] Harrad S., Ibarra C., Diamond M., Melymuk L., Robson M., Douwes J., Roosens L., Dirtu A., Covaci A. Environ. Int. 34: 232-238 (2008).

O44- FIELD CALIBRATION OF PASSIVE BASED-XAD 2 AIR SAMPLERS FOR PCB ANALYSIS: INVESTIGATION IN GAS/PARTICLE DISTRIBUTION

F. Gueguen[1,2], M. Millet[1], P. Stille[2]

[1]Equipe de Physico-Chimie de l'Atmosphère, Laboratoire Matériaux, Surfaces et Procédés
pour la Catalyse, UMR 7515 CNRS, Université de Strasbourg,
1, rue Blessig, 67084 Strasbourg cedex (France)
[2] Laboratoire d'Hydrologie et de Géochimie de Strasbourg (LHyGeS),
UMR 7517 CNRS-Université de Strasbourg,
1, rue Blessig, 67084 Strasbourg cedex (France)

Atmospheric contamination of the air by Polychlorobiphenyls (PCBs) is commonly investigated by active sampling on glass fiber filters followed by Polyurethane foams (PUF plugs) or by passive sampling on PUF disks.

In the framework of a study on the potential influence of industrial activities in the Rhine river in the border of France and Germany, air samples were collected. Due to the important amount of sampling points needed for the characterisation of sources, passive sampling was chosen instead of active sampling more difficult to deploys in large areas. Passive samplers used were the same as those used for pesticides and consist of an mesh inox tube containing XAD-2 resin (XAD-2 PAS).

XAD-2 passive samplers were extracted by ASE, purified on a silica gel column, separated on two GC columns (one non polar and one semi-polar) and quantified by ECD. The first column was used for identification and the second for quantification.

In order to calibrate these samplers used for the first time for PCBs, different sampling campaigns were performed in winter 2009 (December) and spring 2010 in order to evaluate the sampling rate of these passive samplers. Experiments occurred in a garden, in an open space, by comparison of an active (Filter + XAD-2 resin) and passive (XAD-2) air sampler.

The sampling rate was studied in two contrasted seasons in order to evaluate the effect of temperature and gas/particle partitioning. Passive samplers were exposed for two weeks but traps of the active sampler were changed each 3 days in order to avoid volatilisation from filter. The total amount of air which go through the active sampler was measured by using a debimeter. For Two weeks periods the amount of air was measured of about 1 000 m^3.

First results indicate some variation in the sampling rate, especially when PCBs are present in particle phase in quantities. Thus, the season seems not to be the predominant factor.

The observation of the different PCB congener in XAD-2 PAS, resin and filter showed a different profile. Even if the particle phase is present at about 10% of total PCBs, the congeners distribution in PAS is different from the one from gas phase in active sampler. The sampling rate on the XAD-2 PAS is more correlated with the total concentration of PCBs (particle + gas) of the active sampler than with the only gas part of the active sampler.

Consequently, the nature of sample in passive air sample has to be better defined: either it is a mixture of gas and fine particle, or a loss of tri-PCB during the sampling session. These points needs to be considered and will be discussed in the presentation.

O45- MERCURY CONCENTRATION IN DIFFERENT ATMOSPHERIC PRECIPITATION SPECIES

A. Kowalski[1], I. Kurzyca[1], J. Siepak[1] and B. Walna[2]

[1]Department of Water and Soil Analysis, Adam Mickiewicz University, Drzymaly 24,
60-613 Poznan (Poland)
[2]Jeziory Ecological Station of Adam Mickiewicz University, 62-050 Mosina,
P.O. Box 40 (Poland)

Nowadays one of the major threats to the environment is mercury pollution, especially due to the high level of mercury emission and its dynamics caused by the unique physical, chemical, and bioaccumulative properties. Most of the anthropogenic mercury emission is released to the atmosphere. Therefore, the estimation of its concentration in wet deposition gives very important information about mercury immission. Moreover, the determination of mercury in different atmospheric precipitation species provides more specific data about mercury deposition not only with rain or snow but also with not commonly studied hoar frost and dew.

The research presents the results of observations of mercury deposition in different atmospheric species. The samples were collected in the years 2004 and 2008 – 2010, in western Poland, in the areas differing in human impact, i.e. a city agglomeration (above 500 thousand inhabitants) and in the Wielkopolski National Park (an element of the European Ecological Network Nature 2000). Different types of atmospheric precipitation species: rain, snow, hoar frost and dew were collected on a daily basis. The determination of mercury concentrations was performed by the cold vapour atomic fluorescence spectrometry (CV-AFS).

Over the study period, a significant differentiation of mercury concentrations was observed, with the values ranging from 1.3 – 148 $ng{\cdot}L^{-1}$ for rain and snow samples and from 1.4 – 210 $ng{\cdot}L^{-1}$ for hoar frost and fog in the city area, and, respectively, from 1.1 – 129 $ng{\cdot}L^{-1}$ and from 1.4 – 270 $ng{\cdot}L^{-1}$ in the area of the Park. The mercury concentration values did not usually exceed 50 $ng{\cdot}L^{-1}$. Incidental maximum concentration values were often accompanied by the increased content of other ions, which is confirmed by the major contamination of the samples. It was stated that the mercury content in the snow samples was often higher by approximately 10 $ng{\cdot}L^{-1}$ than in the rain samples (wet only), but lower by about 5-20 $ng{\cdot}L^{-1}$ than in the samples of bulk precipitation. Slightly higher mercury concentrations were observed in the hoar frost samples than in the dew samples. Moreover, the samples which occurred simultaneously in both locations (the same event) were analysed and local or cross-regional flow of pollutants was observed. The analysis of the correlation of mercury determination results with other ions indicated a positive correlation with sulphate ions ($r=0.78$). It was also found that over the study period the mercury concentration in precipitation changed depending on the season of the year, reaching the highest values in winter, which was caused by the heating period.

Some analytical problems of mercury determination in atmospheric precipitation samples have also been discussed.

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O46- SLURRY SAMPLING ICP-AES PROCEDURE FOR FAST AND ACCURATE DETERMINATION OF CRUSTAL AND TRACE ELEMENTS IN AIRBORNE PARTICULATE MATTER

A. Limbeck and A. Mukhtar

Institute of Chemical Technologies and Analytics, Vienna University of Technologies,
Getredemarkt 9/164, A-1060, Vienna (Austria)

Airborne particulate matter (APM) is introduced into the atmosphere through various natural as well as anthropogenic sources [1] and particles with diameter from nanometres to tens of micrometers can remain buoyant in the atmosphere for days, and can be transported over a long distance from the original source resulting in an enhanced level of ambient PM concentrations. Measurement of elemental composition of APM from various European cities have shown that crustal elements like Al, Ca, Mg, Fe and Si are major constituents of APM, and trace elements such as (Ba, Cu, Mn and Zn) are only minor contributors to PM10 masses [2]. The presence of these elements in APM with aerodynamic diameter less than 10µm (PM10) can pose serious risk to human health as these particles can easily enter into respiratory tract [3]. Therefore, routine monitoring of these elements in APM is highly needed for risk assessment, source identification and ambient level reduction.

For determining the elemental composition of atmospheric samples ICP-MS, ICP-AES and AAS in combination with digestion procedures or non-destructive techniques such as XRF, PIXE or INAA are preferably used [4]. However, all of these techniques suffer from distinct limitations like time demand, selectivity, sensitivity, problems in signal quantification, special laboratory arrangement and sample preparation through acid digestion. In this contribution a slurry procedure with ICP-AES detection is presented which combines the speed of solid sampling analysis with the accuracy of solution based measurement techniques. The procedure excludes troublesome sample preparation steps, reduces the risk of sample contamination and avoids possible analyte losses. In addition, the proposed slurry procedure is simple to implement, inexpensive and aqueous calibration can be used for signal quantification. The developed slurry ICP-OES procedure was applied to a set of PM10 samples collected from Getreidemarkt, Vienna in summer 2008. For quality assurance, collected filter samples were divided into two halves, one was analyzed using the slurry approach, the other filter half was digested using traditional microwave digestion procedure. ICP-AES analysis of the prepared slurries and sample digests revealed a good correlation, demonstrating the applicability of the presented approach.

[1] Nriagu J. O., Nature, 338, 47-49 (1989).
[2] Querola X., Alastueya A., Ruiza C.R., Artinanob B., Hanssonc H.C., Harrisond R.M., Buringhe E., Brinkf H.M., Lutzg M.,Bruckmannh P., Straehli P. and Schneider J., Atmos. Environ. 38, 6547-6555 (2004).
[3] Pope C. A., Burnett T. R., Thun M. J., MD; Eugenia E. C.; Daniel K.; Kazuhiko I.; George D. T.,JAMA, 287, 1132-1141 (2002).
[4] A. Najat, Saliba H., Kouyoumdjian M. and Roumie M., *Atmos Environ*, 41, 6497–6509 (2007).

O47- MONITORING THE FINGERPRINT OF SANTIAGO DE CHILE URBAN ATMOSPHERIC AEROSOL ON TRACE ELEMENTAL PROFILES OF SNOW PRECIPITATION IN THE ANDES

[1]F. Cereceda-Balic, [1]J. Christie, [1]X. Fadic, [1]J. L. Guevara, [1]A. L. Llanos, [2]C. Miro,
[3]M. R. Palomo, [3]E. Pinilla, [1] V. Vidal

[1]Environmental Chemical Laboratory, Environmental Technology Centre (CETAM), Technical University Federico Santa María, Av. España 1680, Casilla 110-V, Valparaíso (Chile)
[2]Department of Applied Physics, University of Extremadura, Av. de la Universidad sn, 10071-Cáceres (Spain)
[3]Department of Analytical Chemistry, Faculty of Science, University of Extremadura, Av. de Elvas sn, 06071- Badajoz (Spain)

Trace elemental profiles are key data sets for the assessment of potential aerosol toxicity and also for pollution sources identification and quantification [1]. Urban aerosol elemental profiles are usually evaluated on aerosol samples obtained at particular city locations or closely around, but these samples can be eventually affected by analytical noise due to rapid temporal changes of pollution sources, and also by the intrinsic heterogeneity of the urban areas. In contrast, remote sampling may provide a clearer information, aside of data about medium and long range transportation of atmospheric aerosol. In this work, we have evaluated snow precipitation at the Andes metropolitan region as an environmental indicator of Santiago de Chile atmospheric aerosol composition by measuring its trace elemental profiles by ICP-MS. Three winter sampling campaigns (2003, 2008 and 2009) were conducted for surface and deep snow at three sampling zones around El Colorado area, a Central Andes mountain chain sector near Santiago (36 km). Snow samples from Nevados de Chillán, an undisturbed sector of the mountain chain located about 500 km south from the metropolitan area, were sampled and assayed for comparison. Specific source markers were inspected for traffic (Pb, Cd, V, Cr, Mn, Fe, Cu, Zn, Ba, Sc, La, Mo and Sb), biomass burning (As and K), oil combustion (As, Pb, Ni, V, Cu, Zn, La, Sm, Mo and Sb), metallurgy (As, Pb, Cd, Ni, Ca, V, Cr, Mn, Fe, Cu, Zn and Mo), waste incineration (Zn, Cu, Pb and Sb) and mineral matter (Li, K, Ca, Mn, Fe, Rb, Sr, Cs, Ti and rare earth elements). Significantly lower snow concentrations of the anthropogenic marker elements were found at Nevados de Chillán comparing to El Colorado, thus reflecting the higher impact of human activities in the latter. Aerosol transport from Santiago is proposed as the main cause of snow elemental profile alteration respect to the background Nevados de Chillán area. Significant differences were found between the 2003, 2008 and 2009 source markers profiles at El Colorado sampling points, probably reflecting changes in the urban atmosphere of Santiago. The correlation with changes in metropolitan air quality data is discussed.

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[1] M. Viana, T.A.J. Kuhlbusch, X. Querol et al. Aerosol Science 39, 827–849 (2008).

O48- ELUDICATION OF ORGANIC VOLATILE COMPOUNDS IN ANTARCTIC AEROSOL PARTICLES

K. Hartonen[1], E.-M. Kyrö[2], J. Parshintsev[1], T. Petäjä[2], M.-L. Riekkola[1], J. Ruiz-Jimenez[1],
A. Virkkula[2] and M. Kulmala[2]

[1]Laboratory of Analytical Chemistry, Department of Chemistry, P.O. Box 55,
FI-00014, University of Helsinki (Finland)
[2]Division of Atmospheric Sciences, Department of Physical Sciences, P.O. Box 64,
FI-00014, University of Helsinki (Finland)

The number of organic compounds in aerosol particles may easily be several hundred, and the chemical composition depends on the emission source and on the particle size. Because the elucidation of the composition of the organic matter in atmospheric aerosol particles is demanding, only ~10 to 30% of the individual compounds in the particulate organic matter have been identified. Many studies have revealed that aerosol particles contain numerous organic chemical compounds belonging to different chemical groups, such as hydrocarbons, alcohols, aldehydes and carboxylic acids.

In this study comprehensive two dimensional gas chromatography – time-of-flight mass spectrometry (GCxGC-TOF-MS) was used for the identification and semiquantitation of organic volatile compounds in aerosol particles. Because compound volatility was required, some compounds were transformed via derivatization (silylation) into volatile ones. In the identification of the analytes the NIST database for TOF-MS was exploited.

GCxGC-TOF-MS was applied to the screening of organic volatile compounds in all sized Antarctic aerosol particles. Aerosol particles were collected during the Antarctic summer 2009-2010 for about two months at the Finnish Antarctic Research Station, Aboa (73°03′S, 13°25′W), located some 130 km away from the Antarctic coast. The total number of compounds identified in the Antarctic aerosol particles was as high as 1300. The distribution of these compounds into different chemical groups, such as hydrocarbons, halogenated compounds, organic compounds containing sulphur, organic compounds containing nitrogen, acids, alcohols, aldehydes and ketones, was clarified. The results were compared to those obtained for all sized biogenic aerosol particles collected in spring and autumn 2009 at the Station for Measuring Forest Ecosystem Atmosphere Relations (SMEAR II) in Hyytiälä (Finland).

O49- ACTIVE AND PASSIVE SAMPLING TECHNIQUES AND STRATEGIES FOR AIR MEASUREMENTS OF INORGANIC NITROGEN SPECIES TO MEET THE NEW DEMANDS IN TROPICAL AREAS

C. L. W. Arciniegas, V. P Campos, L. P. dos Santos, A. M. C. Silva,
S. T. Oliva, T. M. Tavares

Instituto de Química, Universidade Federal da Bahia, Campus Universitário de Ondina s/n,
40.170-290, Salvador, Bahia (Brazil)

Anthropogenic input of nitrogen into the atmosphere are generally in the form of NO, NO_2, N_2O, NH_3 and HNO_3, which react in the gaseous form and partially are transformed in fine atmospheric particles with diameter < 2.5 µm, affecting the natural cycle and causing damage to ecosystems – acid rain and soil acidity –, to human health and increase in climatic change. Traditionally the monitoring of these compounds in air have focused only on NO and NO_2 continuous monitoring, with high time resolution and involving costly equipment, operation and maintenance. More recently mathematical models and scenario building on regional, continental and global scales, studies of nitrogen cycle, balance of environmental gas fluxes as well as studies of environmental personal exposure are demanding other types of monitoring designs, where need for spatial resolution surpasses the one of temporal resolution: measurements in remote places, where no electric power nor trained human resources are available; validation of dispersion simulation by modeling; indoor measurements where people are acting and noise is restricted such as hospitals, schools and residences. This paper presents several active and passive sampling techniques developed or optimized with our group and applied to different Brazilian ecosystems and situations, from the Amazon forest to coastal marine areas.

Speciation sampling of volatile and semivolatile compounds containing the reactive species NO_3^- and NH_4^+ have been obtained by the combination of thermodiffusion prior to particle collection on a membrane using a noncommercial system with typical limits of determination (µg m^{-3}): HNO_3 0.03; NH_4NO_3 0.04; other nitrates 0.02; NH_4^+ 0.01. Continuous samples of HNO_3 in the gaseous phase for flux measurement from soil in forest and in different agriculture areas have been obtained with a semicontinuous wet diffusion battery operated system (29 W) specially constructed, with quantification limit of 0.20 µg m^{-3} for 1 hour sampling intervals . Air particles fractionated by 6 sizes ranges have been obtained with Berner cascade impactor, (LOQ for 27 m^3 samples is 1 ng m^{-3} for both NO_3^- and NH_4^+). NO_2 has been collected by locally constructed and validated passive samplers exposed for a minimum of 7 days, with limit of determination in µg m^{-3} of 0,21 for one week exposures and 0,06 for four weeks exposures, and maximum deviation of 7 % from average value of continuous monitor running in parallel when applied in the Amazon forest or a large petrochemical complex.

Campos, V.P., Cruz, L.P.S., Godoi, R.H.M., Godoi, A.F.L., Tavares, T.M., Microchemical Journal., 2010, doi: 10.1016/j.microc.2010.02.015

O50- DEVELOPMENT OF GAS CHROMATOGRAPHY-INDUCTIVELY COUPLED PLASMA ISOTOPE DILUTION MASS SPECTROMETRY FOR ACCURATE DETERMINATION OF KRYPTON AND XENON

H.T Zhang, G.Q Zhou, J.Yang, M. Li, L.X. Zhang

Northwest Institute of Nuclear Technology
P.O. Box 69-14, Xi'an,710024 (P.R.China)

It plays great roles for most efficient and high resolving capacity to analysis of element in environmental, industrial and biological samples with the combination of both gas chromatography (GC) and the high sensitivity capability of inductively coupled plasma mass spectrometry (ICP-MS)[1,2].In this paper, gas chromatography coupled with inductively coupled plasma mass spectrometry for analyzing krypton and xenon is described.

It is quite significantly important for interfacing of GC with ICP-MS that needs the requirement of the analytes remains in the gas phase during the transport from the GC column to the plasma. Therefore any condensation of the analytes should be avoided to assure not only no loss of analyte by also the peak sharpness necessary for high sensitivity and low detection limits. A home-made GC-ICP-MS interface was achieved by means of a relatively simple and rapid coupling procedure.

An Agilent 4890GC (Agilent Techonoloiges, Palo Alto,CA,USA) gas chromatography was utilized in this work. High purity Argon was used as carrier gas and the column flow was set at a constant value of 11 mL min^{-1}. A plot 5Å molecular sieve capillary column (30m, 0.53mm id, 0.5μm film thickness) was used for separation. Oven temperature was set as 100℃ An Element ICP-MS (Finnigan-MAT,German) with a home-made interface was employed. The conditions of ICP-MS were set as follows: plasma gas flow rate was 13.5 L min^{-1}, auxiliary gas flow rate was 1.05 L min^{-1}, forward power was 1300W and isotopes ^{84}Kr,^{86}Kr,^{129}Xe,^{131}Xe were monitored.

The limits of detection of GC-ICP-MS are 24pg and 301fg for krypton and xenon respectively. The accuracy of the system was confirmed by analysis of the certified gas samples by capillary gas chromatography coupled with ICP-MS. The technique of gas chromatography-inductively coupled plasma isotope dilution mass spectrometry for accurate determination of krypton and xenon coupling has expanded the applicability of each individual technique in the area of gas analysis. The coupling of GC to ICP-MS not only yields low detection limits but also represents an efficient way to perform isotopic analysis.

[1] Brice Bouyssiere,Joanna Szpunar,Ryszard Lobinski,Spectrochim. acta Part B, 2002,57:805-828.
[2] Jorgelina C.A. Wuilloud, Rodolfo G. Wuilloud, Anne P. Vonderheide, Joseph A. Caruso, Spectrochim. acta Part B, 2004,59:755-792.

O51- DETERMINATION OF EXPLOSIVES AND THEIR DEGRADATION PRODUCTS IN CONTAMINATED SOIL AREA

J. Bečanová, Z. Friedl, Z. Šimek and I. Ungrádová

Research Centre for Toxic Compound in the Environment, Faculty of Science,
Masaryk University, Kamenice126/3, 625 00 Brno (Czech Republic)

Energetic compounds like trinitrotoluene (TNT), RDX and HMX has been discharged into the environment by implication of military conflicts and activities [1, 2]. The result is significant contamination of soils and waters by residues of these compounds, their degradation products and by-products. TNTs, products of their degradation, aminonitrotoluenes and compounds formed during explosion have been found to be cytotoxic presumably due to induced oxidative stress and demonstrated mutagenic capability. Major factors affecting fate and transport of 2,4,6-TNT in the environment are biotic and abiotic transformations, adsorption and irreversible bonding into soil organic matter [3]. Therefore the knowledge of content of these compounds in environment connected to ecotoxicity of explosive, related compounds and their products of biodegradation is essential. Liquid chromatography (HPLC) with optic detection is recommended by EPA for the analysis of nitroaromatics due to its widespread availability. HPLC combined with mass spectrometers are less frequently available methods. Nevertheless, in order to identify and determine of concentration of explosive related compounds at relevant environmental level, the use of LC/MS/MS has to be applied. The specific goal of the present study was to optimise properties for simultaneous HPLC/UV/MS/MS determination of group of explosives and their degradation products in soil samples. Problems connected with extraction and isolation of compounds under investigation as the most important part of soil sample preparation is discussed. The possibility to use LS/MS/MS for analysis of new energetic compounds is assessed. The application of proposed methods for determination of low levels of nitroderivatives in soil samples collected in real contaminated area is presented.

[1] Pennington, J.C. and Brannon, J.M., Thermochimica Acta, 384(1-2), 163-172 (2002).
[2] Stuck, H., Chimera, 58(6), 409-413 (2004).
[3] Brannon, J.M. and T.E. Myers, Review of Fate and Transport Processes of Explosives. Army engineer waterways experiment station. Vicksburg MS. 32, (1997)

O52- ELUCIDATION OF THE MASS FRAGMENTATION PATHWAYS OF POTATO GLYCOALKALOIDS AND AGLYCONS USING ORBITRAP MASS SPECTROMETRY

M. G. Cahill, G. Caprioli, K. J. James and S. Vittori

PROTEOBIO (Mass Spectrometry Centre), Cork Institute of Technology, Bishopstown, Cork, Ireland
Environmental Research Institute, University College Cork, Lee Road, Cork (Ireland)
Dipartimento di Scienze Chimiche, Facoltà di Farmacia, Università di Camerino,
via S. Agostino 1, 62032 Camerino (Italy)

Potatoes (*Solanum tuberosum*) are considered as one of the most important crops for human consumption by providing energy, high-quality protein, fiber, vitamins, pigments, as well as other nutrients [1]. Glycoalkaloids protect the potato crop against adverse effects of hosts of predators including fungi, bacteria, viruses, and insects [2]. The two naturally occurring toxins, α-solanine and α-chaconine, comprise over 95% of the total glycoalkaloids in potatoes [3]. The mass fragmentation of potato glycoalkaloids, α-solanine and α-chaconine and the aglycons, demissidine and solasodine were studied using a hybrid linear ion trap (LIT) Orbitrap Fourier Transform (FT) mass spectrometer (MS). Using LIT MS, multi-stage collisional-induced dissociation (CID) experiments (MS^n) on the $[M+H]^+$ precursor ions were performed to aid the elucidation of the mass fragmentation pathways. In addition, higher energy collisional induced dissociation (HCD) mass spectra were generated for these toxins at an ultra high resolution setting (100,000 FWHM) in the Orbitrap. This hybrid MS instrumentation was exploited to produce MS^3 spectra by selecting MS^2 product ions, generated using LIT MS, and fragmentation using HCD. The accurate mass data in the MS^3 spectra aided the confirmation of proposed product ion formulae. The main pathways for the mass fragmentation of the six-ring aglycons were similar with cleavages at the B-rings and E-rings. The quality of the accurate mass determinations using the Orbitrap MS is demonstrated by the fact that all of the precursor and product ions in the range 300 – 900 *m/z* for α-solanine and α-chaconine were determined with error values less than 0.75 ppm. For demissidine and solasodine the error values were less than 0.57 ppm in the ranges 253 – 450 *m/z*. The toxic glycoalkaloids were separated on Luna PFP analytical column using a linear gradient mobile phase consisting of water and methanol respectively both containing 0.01% formic acid and were detected on the LTQ Orbitap MS using a resolution setting of 30,000 FWHM. α-Chaconine and α-solanine were detected in potato samples at concentrations of 117 and 47 mg/kg. As a result of high concentrations in potato samples, toxic glycoalkaloids can be detected in agricultural soil and leachates.

[1] Friedman M., J Chromatogr. A, 1054, 143–155 (2004).
[2] Friedman M., J Agric Food Chem. (21) 5751-5780 (2002).
[3] Machado R. M. D., Toledo M. C. F., Garcia L. C., Food Control, 18, 503-508 (2007).

O53- COMPARISON OF HYBRID LINEAR ION-TRAP ORBITRAP MASS SPECTROMETRY AND TRIPLE QUADRUPOLE MASS SPECTROMETRY FOR THE DETERMINATION OF POLYETHER PHYCOTOXINS CONTAMINANTS IN SHELLFISH

B. Carey[1], K. J. James[2], J. O'Halloran[3] and F. Van Pelt[4]

[1]PROTEOBIO Mass Spectrometry Centre, Cork Institute of Technology, Rossa Avenue,
Bishopstown, Cork (Ireland)
[2]PROTEOBIO Mass Spectrometry Centre, The Environmental Research Institute,
University College Cork, Cork (Ireland)
[3]Department of Zoology, Ecology and Plant Science, Distillery Fields, North Mall,
University College Cork (Ireland)
[4]Department of Pharmacology and Therapeutics, Clinical Investigations Building,
Cork University Hospital, Cork (Ireland)

Diarrhetic Shellfish Poisoning (DSP) is an international issue which can affect humans following consumption of contaminated filter feeding bivalves, such as mussels, clams, scallops and oysters. Bivalve molluscs feed on marine microalgae for essential nutrients. It is evident that due to the consumption of algae from the *Dinophysis* spp. or *Prorocentrum* spp., the shellfish become contaminated with toxins DSP toxins (1). The polyether toxins responsible include okadaic acid (OA) and dinophysistoxins (DTXs) (2). Okadaic acid and DTXs are polyether carboxylic acids containing seven rings. Dinophysistoxin-2 (DTX2) is an isomer of okadaic acid and they differ from each other in the methylation of their F and G ring systems. The analytical methods used for the analysis of okadaic acid and DTX2 to date, have failed to resolve okadaic acid and DTX2 by mass fragmentation. Previous methods have targeted the $[M+H]^+$ or the $[M-H]^-$ precursor ions which do not produce any distinguishing ions (3).

Two methods were developed using a hybrid LTQ Orbitrap MS and a triple quadrupole MS, TSQ Quantum Discovery Max (Thermo Scientific), both equipped with a heated electrospray ion (HESI) source for the analysis of okadaic acid, DTX2. The LTQ Orbitrap MS, method resolved okadaic acid and DTX2 both by chromatography and by mass fragmentation of their $[M+Na]^+$ adduct ions. This full scan MS method is a non-target analysis and therefore offers higher analyte screening capabilities than other methods. Analyte selectivity was improved by utilizing a very narrow mass tolerance window (±2 ppm) for the precursor ions, at a 30,000 (FWHM) resolution setting. High mass accuracy data were obtained for all characteristic product ions using higher energy collisionally induced dissociation (HCD), with accurate mass errors values < 2 ppm for all major ions. Further confirmation was obtained using collision induced dissociation (CID) spectra. For the first time, okadaic acid and DTX2 were distinguished by selecting characteristic SRM transitions. This allowed the development of an isocratic reverse phase LC method in which okadaic acid and DTX2 co-eluted and this proved to be an excellent method for rapid sample analysis. Both methods were shown to have high sensitivity and good linearity over a wide concentration range (0.02-1.7 µg/ml). Excellent reproducibility, specificity and recovery data were also obtained and these methods were applied to the analysis of these DSP toxins in mussels (*Mytilus edulis*) and marine phytoplankton.

[1] Lee JS, Yanagi T, Fraga S, Dahl E, Hovgaard P and Yasumoto T. J Appl Phycol 1, 147-152 (1989)
[2] Murata M, Shimatani M, Sugitani H, Oshima Y and Yasumoto T, Bull Jpn Soc Sci Fish 48, 549-552 (1982)
[3] Fernandez Puente P, Fidalgo Saez MJ, Hamilton B, Lehane M, Ramstad H, Furey A and James KJ, J Chromatogr A 1056, 77-82 (2004)

O54- DETERMINATION OF THE LEVELS OF POLYCYCLIC AROMATIC HYDROCARBONS (PAHs) IN TOASTED BREAD BAKED FROM BARLEY, BRAN, CORN, RICE, SOYA AND FLACKS MIXED WITH SUN FLOWER SEEDS FLOURS USING GAS CHROMATOGRAPHY MASS SPECTROMETRY

M. I. H. Helaleh, A. Al-Rashdan, A. Nisar, A. Ibtisam, Z. Al-Ballam

Kuwait Institute for Scientific Research (KISR), Central Analytical Chromatography (CAL),
Chromatographic Section, 13109 Safat, P.O. Box 24885 (Kuwait)

Concentrations of 16 polycyclic aromatic hydrocarbons (PAHs) in 6 bread samples and 6 flours of the same ingredient used to bake bread have been tested in this study. The following categories for this study are (1) bread baked from different ingredients, such as corn, rice, barley, bran, soya and flacks flour mixed with sun flower seeds, and (2) non baked flours of the different ingredient used for baking the bread. Analysis was performed by GC-MS after soxhlet extraction of the sample and clean up of the extract. Benzo[a] pyrene B[a]P was detected in 9 out of 12 samples of bread flours. The rest of 3 samples were not detected. The levels of B[a]P were found to be varied from 4.69-24.04 µg/kg and from 4.34-19.05 µg/kg for breads and flours, respectively. The levels of total 16 PAH including higher and lower PAHs were found to be higher in pure flours of various ingredients as compared to the mixed flours. The followings are the concentration of the mixed flours: 256.39 µg/kg, 167.92 µg/kg, 173.59 µg/kg, 145.45 µg/kg, 138.69 µg/kg and 261.77 µg/kg for barley, bran, rice, corn, flacks flour mixed with sun flower seeds and soya, respectively. Six commercial toasted bread samples were collected and analyzed by the proposed method and the levels are ranged as follow: 108.21 µg/kg, 25.99 µg/kg, 1814.75 µg/kg, 10.58 µg/kg, 11.56 µg/kg and 31.83 µg/kg for barley, bran, rice, corn, flacks flour mixed with sun flower seeds and soya, respectively.

O55- PROXIMATE ANALYSIS, MINERAL COMPOSITION AND ANTIOXIDANT POTENTIAL OF SOME LOCALLY GROWN VARIETIES OF TOMATO (*LYCOPERSION ESCULANTUM*)

S. A. S. Chatha, A. I. Hussain*, and Z. Nawaz

Department of Chemistry, GC University, Faisalabad (Pakistan)
*ai.hussain@yahoo.com

The aim of the present study was investigated for proximate composition, minerals profiles and antioxidant potential. Tomato fruits were found to be a poor source of protein and fiber. ICP-OES analysis revealed that the contents of Na, K, Ca, Mg, Fe, Cu, Mn and Zn were found to be 17.0 to 20.0, 200.0 to 275.5, 6.4 to 11.3, 7.0 to 8.7, 0.20 to 0.33, 0.03 to 0.05, 0.02 to 0.04 and 0.05 to 0.07 mg/100g, respectively. Yield of extracts of different tomatoes varieties were found to be 3.8 to 5.0 g/100g. Methanol extracts of tomatoes exhibited a good antioxidant activity as determined in terms of measurement of total phenolic contents, percent inhibition of peroxidation, reducing power, and bleaching *β*-carotene. The results of the present analytical study revealed these 4 tomatoes varieties to be a potential source of antioxidants and minerals all of which are linked with positive health benefits.

O56- ECOTOXICITY OF KETOPROFEN DEGRADATION PRODUCTS

A. Dombi, K. Gajda-Schrantz, E. Illés, E. Szabó

Research Group of Environmental Chemistry at the Department of Inorganic and Analytical Chemistry,
University of Szeged, Dóm tér 7, Szeged, H-6720 (Hungary)

Due to the large-scale use, excretion and the high persistence of some pharmaceuticals, they can be found in surface and ground waters in the original form and/or in the form of metabolites. In long-term exposure these organic pollutants can have carcinogenic, mutagenic or toxic effects and in case of their co-occurrence synergic effects can arise [1]. Their degradation products may have similar risks or in some cases can be even more toxic than the parent molecule. In numerous European countries the chemical parameters of the treated sewage-water have to be supplemented with the toxicity tests. The goal of the toxicity tests is to establish the influence of the drain water to the recipient ecosystems [2].

An efficient method for the degradation of the persistent trace pollutants are the Advanced Oxidation Processes (AOPs), based on the generation of ·OH radicals. In this work ozonation and the O_3/UV (254 nm) combined method was used for the degradation of one NSAID, ketoprofen. The degradation process was followed by HPLC, and the by-products were identified using HPLC-MS. The toxicity tests of the target compound and the formed degradation products were done on *Selenastrum capricornutum* microalgae culture (ALGATOXKIT F^{TM}) and *Daphnia magna* zooplankton (DAPHTOXKIT F^{TM}).

The ketoprofen solutions at the initial concentration of 1×10^{-4} molL^{-1} were ozonized or treated by O_3/UV combined method during one hour. During ozonization one of the major by-products, the 3-(1-hydroperoxyethyl)benzophenone decomposed completely, while the other three were still present in traces after the treatment. Although all major by-products decomposed using O_3/UV combined method in 60 minutes, the complete mineralisation was not achieved. Small molecular weight acids (e.g. propionic, malic and succinic acid) were still present in the solution.

Based on the toxicity results the ketoprofen itself can cause high inhibition in the algal growth. With the degradation of the target molecule the toxicity is reduced, but can still be measured due to the degradation products. In larger dilution the ozonization could completely reduce the inhibition. The combined method was more efficient. Although the growth inhibition can still be measured, it is significantly lower than using ozonization. Similar observations were made with *Daphnia magna* zooplankton test. Ketoprofen, except in high dilution, caused 100% mobility inhibition. After the treatment with the two methods the inhibition decreased. The O_3/UV degradation was more efficient. Depending on the dilution some of the samples did not show any inhibition.

[1] Daughton, C. G., Emerging Polutants Workshop, Chicago, USA (2003)
[2] Kováts, N., Szalay, T., Kárpáti, Á., MaSzeSz Hírcsatorna July-August, 9-13 (2005)

O57- INTRINSIC PRODUCTION OF HYDROGEN PEROXIDE BY 172 nm PHOTOLYSIS OF WATER AND DURING THE PHOTOMINERALIZATION OF IBU- OR KETOPROFEN BY 172 nm AND/OR BY 185/254 nm LIGHT

A. Dombi[1], K. Gajda-Schrantz[2], T. Oppenländer[3] and E. Szakács[2]

[1] Institute of Material Sciences and Engineering, University of Szeged, Dóm tér 7,
6720 Szeged (Hungary)
[2]Department of Inorganic and Analytical Chemistry, University of Szeged, Dóm tér 7,
6720 Szeged (Hungary)
[3] Faculty of Mechanical and Process Engineering, Hochschule Furtwangen University,
Jacob-Kienzle-Str. 17, 78054 Villingen-Schwenningen (Germany)

Many publications can be found about the importance of the clean water for the life on Earth. However, the presence of emerging pollutants such as pharmaceuticals in surface waters can not be denied. Although their concentration range is very low (μg L^{-1} - pg L^{-1} [1]), they can still have negative effect on the aquatic life, since their input is permanent and some of them can be accumulated. Advanced Oxidation Processes (AOPs) might be effective and economic methods to oxidize and mineralize the organic substrates by generating short-lived, non selective and highly reactive radicals (mainly •OH). Hydroxyl radicals can be generated for example through vacuum-ultraviolet (VUV) irradiation of aqueous solutions or hydrogen peroxide [2, 3].

During bilateral researches of the Furtwangen University and the University of Szeged the efficient photomineralization of two non-steroidal anti-inflammatory drugs (NSAIDs: ibu- and ketoprofen) was achieved by the combination of VUV and UV induced Advanced Oxidation Processes. The experiments were performed using a xenon excimer flow-through photoreactor (Xe_2* excilamp: 160 nm < λ < 200 nm, λ_{max}= 172 nm) with an integrated ceramic gassing unit and/or by using a conventional low pressure mercury lamp (LP lamp: 185/254 nm).

During the 172 and/or 185/254 nm irradiation of the 10^{-4} mol L^{-1} aqueous solutions of the selected pharmaceuticals the intrinsic formation of hydrogen peroxide by the photolysis water (with 172 nm VUV light) contributed to the degradation of the pharmaceuticals. For this reason the formation of H_2O_2 in the presence and in the absence of ibuprofen and ketoprofen was investigated and rationalized. The generated H_2O_2 absorbed also the photons emitted by the Xe_2* excilamp or by the low pressure mercury lamp, resulting in hydroxyl radicals. The latter species contributed to the degradation of the dissolved pharmaceuticals and of their byproducts. The combined VUV/UV AOP using a modern Xe_2* excilamp and a conventional low-pressure mercury lamp led to efficient TOC diminution of aqueous solutions of ibuprofen and ketoprofen. This procedure can be an efficient process for decomposing organic matter and/or microorganisms in water.

[1] K. Kümmerer, "Pharmaceuticals in the environment: sources, fate, effects, and risks", Springer Verlag, Berlin Heidelberg (2004).
[2] O. Legrini, E. Oliveros and A.M. Braun, Chem. Rev., 93, 671-698 (1993).
[3] T. Oppenländer, “Photochemical purification of water and air”, Wiley-VCH, Weinheim (2003).

O58- OPTIMIZATION OF A SIZE-EXCLUSION METHOD FOR THE CHARACTERIZATION OF NATURAL ORGANIC MATTER USING EXPERIMENTAL DESIGN TOOLS

A. C. Duarte and R. Duarte

CESAM & Department of Chemistry, University of Aveiro, Campus Universitário de Santiago,
3810-193 Aveiro (Portugal)

Size-exclusion chromatography (SEC) represents a state-of-the-art technique to investigate the molecular weight distribution of natural organic matter (NOM) from different environments (water, soils, sediments, and air). Despite the widespread application of this technique for the analysis of NOM, the design of a suitable SEC procedure is still an enormous analytical challenge with no general consensus. The optimization of a SEC separation is frequently performed on the basis of the conventional one-factor-at-a-time method, which typically requires a relatively large number of experiments, being therefore time consuming. Statistical experimental designs, on the other hand, are more efficient and have been used for decades in diverse optimization strategies of chromatographic systems. In this work, the chromatographic conditions, selected to be suitable for the size-exclusion separation of NOM from atmospheric and aquatic environments, were optimized through two-level full factorial and central composite designs. The optimality criterion applied in this study was a chromatographic response function (CRF) developed in a previous work [1]. The experiments for the optimization were firstly conducted with a mixture of six organic compounds, which were selected on the basis of their chemical groups (monocarboxylic acids, carbonyls, amines, phenols and aromatics) that are recognized to be relevant to NOM from atmospheric and aquatic environments [2-4]. The optimum analytical conditions predicted by this strategy were then applied to a group of selected samples: water-soluble organic matter (WSOM) isolated from rural-coastal fine atmospheric aerosols collected during the Winter and Spring/Summer seasons of 2003 [4,5], and Pony Lake Fulvic Acid reference material obtained from the International Humic Substances Society (IHSS). The results are discussed in terms of chromatographic separation pattern and apparent molecular size range.

[1] Duarte, R.M.B.O. and Duarte, A.C., A new chromatographic response function for use in size-exclusion chromatography optimization strategies: application to complex organic mixtures, J. Chromat. A, *under review* (2010).
[2] Saxena, P. and Hildemann, L.M., J. Atmos. Chem. 24, 57-109 (1996).
[3] Kaiser, E., Simpson, A.J., Dria, K.J., Sulzberger, B. and Hatcher, P.G., Environ. Sci. Technol. 37, 2929-2935 (2003).
[4] Duarte, R.M.B.O., Silva, A.M.S. and Duarte, A.C., Environ. Sci. Technol. 42, 82248230 (2008).
[5] Duarte, R.M.B.O., Santos, E.B.H., Pio, C.A. and Duarte, A.C., Atmos. Environ. 41, 8100-8113 (2007).

O59- ELEMENTAL MIGRATION THROUGH NANO-AND SUBNANO-SCALE PORES IN GEOLOGICAL ENVIRONMENT

K. Sato[1], K. Fujimoto[1], M. Nakata[2], and N. Shikazono[3]

[1] Department of Environmental Sciences, Tokyo Gakugei University, Koganei,
Tokyo 184-8501 (Japan)
[2] Department of Astronomy and Earth Sciences, Tokyo Gakugei University, Koganei,
Tokyo 184-8501 (Japan)
[3] Department of Applied Chemistry, Keio University, Hiyoshi, Yokohama 223-8522 (Japan)

In geological environment, open pores offer the evolutionary pathway of elemental migration together with underground fluid. A series of long-term physicochemical reactions take place between pore wall and flowing fluid, influencing the precipitation, transformation, and dissolution of rock-forming minerals. It is thus of great significance to investigate open pores in natural rocks and rock-forming minerals to gain an insight into elemental migration in geological environment. Mercury porosimetry has been extensively employed for obtaining the information of pore sizes. This technique is however unsuitable for pores with a radius smaller than a few tens of nanometer, because quite large molecules of mercury have to be penetrated into the pores. Even recent technique of computed tomography using synchrotron x-rays is unable to differentiate the pores smaller than the order of micro-meter size. In the present study, we employed the positron (e+), antiparticle of electron (e-), to investigate open pores in natural rocks and rock-forming minerals [1-2]. Positronium (Ps) formation occurs with ortho-positronium (o-Ps) intensities ranging from a few % to 20 %, indicating a variety of nanopores. Size distributions of nanopores are evaluated from o-Ps lifetimes. The results will be discussed with respect to elemental migration in geological environment.

[1] K. Sato et al., Phys. Rev. Lett. 92, 127403 (2004).
[2] K. Sato et al., Phys. Rev. Lett. 96, 228302 (2006).

POSTERS

P1- APPLICATION OF A DNA-IL-CPE MODIFIED ELECTRODE AS AN ELECTROCHEMICAL BIOSENSOR FOR DETERMINATION OF TRACE AMOUNTS OF AFLATOXIN B1

M. H. Banitaba[1], A. Mehdinia[2], S. Seyedhosseinidavarani *[1]

[1] Department of Chemistry, Faculty of Sciences, Shahid Beheshti Universit G. C., Tehran (Iran)
[2] Department of Marine living science, Iranian National Center for Oceanography (INCO), Tehran (Iran)
*ss-hosseiny@cc.sbu.ac.ir

Aflatoxins are considered as natural contaminants of a variety of agricultural products [1]. It shows carcinogenic, mutagenic, hepatotoxic, and immunosuppressive effects on animals and humans [2].

It was shown before that Aflatoxin B1 bind to the DNA via N7 position of guanine [3]. This interaction can affect the oxidation process of guanine, which is shown in fig. 1. In this work we use a DNA-ionic liquid modified electrode for quantitative analysis of Aflatoxin B1 on the basis of variation in electrochemical oxidation of guanine in presence of Aflatoxin B1 using differential pulse voltammetry. For this purpose, a carbon paste electrode (CPE) was modified firstly with N-butyl pyridinium hexaflurophosphate ionic liquid (IL) as a binder. The replacement of non-conductive mineral oil, which weakens the electrochemical response of electrode, with this immiscible ionic liquid can improve the conductivity of electrode and sensitivity of determination. When IL-CPE was modified using ds-DNA via adsorption (DNA-IL-CPE), it shows an oxidation peak in about 0.93V which was due to the oxidation peak of guanine residue. Results show that peak current of the guanine oxidation decreases in presence of Aflatoxin B1 and these changes in various concentrations of Aflatoxin B1 can be used for quantitative determination of trace amounts of Aflatoxin B1and for determination of binding constant K_b between DNA and Aflatoxin B1. A linear dynamic range from 8.00×10^{-8} to 5.91×10^{-7}M and limit of detection of 2.00×10^{-8}M were resulted in DPV measurements. Also, the binding constant of DNA-Aflatoxin B1 was found to be 3.5×10^{6} M^{-1}.

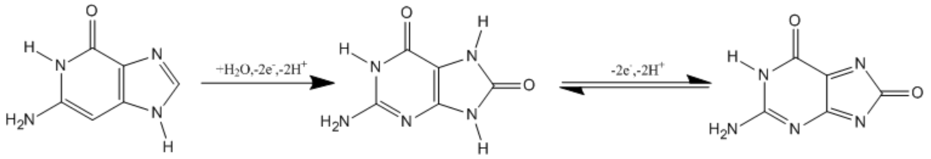

Fig. 1 electrochemical oxidation of guanine

References

[1] A. E. Khoury, T. Rizk, R. Lteif, H. Azouri, M. Delia, A. Lebrihi, Food and Chemical Toxicology 46 (2008) 2244–2250.

[2] V. Fernandez-Ibanez, A. Soldado, A. Martinez-Fernandez, B. de la Roza-Delgado, Food Chemistry 113 (2009) 629–634.

[3] Gunnar Boysen, Brian F. Pachkowski, Jun Nakamura, James A. Swenberg, Mutation Research 678 (2009) 76–94.

P2- MONITORING OF HYDROPHOBIC ORGANIC POLLUTANTS IN URBAN RUNOFF AND SEDIMENTS WITH PASSIVE AND ACTIVE SAMPLING

O. Bausheva and A. L. Rantalainen

Department of Environmental Sciences, University of Helsinki, Niemenkatu 73,
15140, Lahti (Finland)

Urban runoff is known to be contaminated with a range of hydrophobic organic compounds (HOCs) and often creates pollution load for surrounding ecosystems. Polyaromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs) are among the most widespread and toxic compounds. The city of Lahti has approximately 100 000 inhabitants and is a growing Finnish urban area. It abuts on Lake Vesijärvi, which is an important provider of recreational and fishing activities in the region. Most of urban runoff in Lahti discharged directly to Lake Vesijärvi. However, there is insufficient knowledge about the amount and fate of HOCs in stormwater. In previous studies PAH and PCB compounds were found in Lake Vesijärvi sediments and their concentrations tended to decrease with the distance from urban shore and stormwater outlets which could be possibly caused by the impact of urban surface runoff.

Present study aims to evaluate concentrations of HOCs in water and sediments from stormwater traps and possibly link them with contamination of the Lake Vesijärvi sediments. Semipermeable membrane devices (SPMD) were employed to monitor concentrations of pollutants in the liquid phase of urban runoff at three locations. Water samples were taken from the traps three times a week and transferred to the metal container. Control sample (tap water) has been also taken and treated similarly to others. Two SPMD samplers (each 15 cm long) were placed in each container. Water was continuously circulated by aquarium pump and replaced every second day with the new sample. Grab sediment samples were taken from stormwater traps at 15 locations. Areas with various degrees of urbanization (urban, mid-urban and suburban) were studied. Samples were analyzed for 16 PAHs (EPA) and 28 PCBs using isotope dilution technique and gas chromatography-mass spectrometry (GC-MS) method.

P3- STUDY ON HEAVY METAL RESISTANT BACTERIA IN OUED EL- HARRACH

Y. Benmalek

Laboratoire de Microbiologie, Département de BCM, Faculté des sciences biologiques,
Université des Sciences et de Technologie Houari Boumediene, Bab - Ezzouar,
Alger (Algérie)

Removal of heavy metals from wastewater needs advance chemical technology and is more expensively too. The cheaper alternative for this is the bioremediation using heavy metal resistant micro-organisms. In this study 20 heavy metal resistant bacteria were isolated from wastewater in El-HARRACH, Algiers/Algeria. These include lead-resistant bacteria, cadmium-resistant bacteria, chromium-resistant bacteria and zinc-resistant bacteria. Biochemical characterization showed that 18 metallo-resistant bacteria were Gram (-). Two metallo-bacteria were Gram (+) and spore-formed. All the isolates showed high resistance to heavy metals with Minimum Inhibitor Concentration (MIC) for heavy metals ranging from 200 – 1400µg/ml and they showed multiple co- resistance to other heavy ions. The 20 metallo- resistance bacteria were multi- antibiotic resistant.

P4- TRACE ANALYSIS OF 29 ENDOCRINE DISRUPTOR COMPOUNDS IN ENVIRONMENTAL SAMPLES BY LIQUID CHROMATOGRAPHY TANDEM MASS SPECTROMETRY

R. Baudot, J. Camilleri, C. Cren-Olive, E. Vulliet, L. Wiest

Service Central d'Analyse du CNRS, USR 59, Echangeur de Solaize, 69360 Solaize (France)

Many man-made or natural compounds are known or supposed to interfere with the endocrine, causing behaviour disorders [1], decreased fertility [2] and birth malformations [3]. Most of those compounds are listed as emerging contaminants by the European Union [4], [5] and need development of specific and highly sensitive methods to enable their monitoring in the environment. Endocrine disruptor compounds (EDCs) display a wide range of structural diversity and chemical properties and they occur in the aquatic environment at trace levels in complex matrices. Almost all available analytical methods only target one or two families of EDCs, such as steroids, pesticides or alkylphénols [6], [7]. In consequence, the development of a multi-residue methodology to surface water and river sediment analysis is necessary, in order to monitor as many EDCs as possible. Moreover, such a method should involve limited sample preparation steps with sufficiently selectivity and sensitivity.

In this context, the objective of this study was to quantify traces of 29 selected EDCs from various families in a single analysis using on line SPE coupled to liquid chromatography tandem mass spectrometry (LC/MS-MS) for surface water and pressurized liquid extraction (PLE) LC/MS-MS for river sediments. Molecules of interest have been chosen using lists of priority pollutants [4], [5] and compounds known or supposed to be EDCs : 6 hormones (estrone, 17β-estradiol, megestrol acetate, progesterone, testosterone and tamoxifen), 16 pesticides (2,4-dichlorophenoxyacetique acid, acetochlor, alachlor, atrazine, carbendazime, diuron, iprodion, linuron, prochloraz, thiram and ziram), 1 UV-filter (4-methylbenzyliden camphor), alkylphenols (tert-butylphenol, n-octylphenol, tert-octylphenol, n-nonylphenol and 4-para-nonylphenol), 3 phenolic compounds (2,4-dichlorophenol, bisphenol A and resorcine) and 3 pharmaceuticals used as pollution indicators (3,4-dichloroaniline, carbamazepine and diclofenac). The excellent selectivity and sensitivity allowed us satisfactory quantification and confirmation at the lower ng/L and ng/g range.

[1]. Madsen, S.S., Skovbølling, Christian Nielsen S. and Korsgaard, B., Aquatic Toxicol, 68, 109- (2004)
[2]. Giwercman, A., Rylander, L., and Lindberg Giwercman, Y., Reprod Biomed Online, 15, 633- (2007)
[3]. Schreinemachers, D.M., Environmental health perspectives A, 111, 1259 (2003)
[4]. Communication de la commission au conseil et au parlement européen sur la mise en œuvre de la stratégie communautaire concernant les perturbateurs endocriniens COM (2001) 262 final
[5]. European commission DG ENV, Towards the establishment of a priority list of substances for further evaluation of their role in endocrine disruption, bkh-annex 15
[6]. Baugros, J.B., Giroud, B., Dessalces, G., Grenier-Loustalot, M.F. and Cren-Olivé, C., Analytica Chimica Acta, 607, 191-203 (2008)
[7]. Barrek, S., Cren-Olivé, C., Wiest, L., Baudot, R., Arnaudguilhem, C. and Grenier-Loustalot, M.F., Talanta, 79, 712- (2009)

P5- TRACE METAL SPECIATION IN BLACK SEA WATERS EVALUATED BY CHITOSAN MEMBRANES AND DGT

G. Dakova[1], V. A. Dakov[2], I. B. Karadjova[1] and M. G. Karadjov[3]

[1]Department of Analytical Chemistry, Faculty of Chemistry, University of Sofia "St. Kl. Ohridsky",
J. Bourchier 1, 1164 Sofia (Bulgaria)
[2]Central University Laboratory, University of Forestry, Kl. Ohridsky 10, 1756 Sofia (Bulgaria)
[3] Geological Institute, Bulgarian Academy of Science, Acad. G. Bonchev St.,
Bl. 24, 1113 Sofia (Bulgaria)

The trace metals speciation and determination in aquatic environments is important task in the field of analytical chemistry, toxicology and environmental chemistry. Modern analytical methods could be applied for direct determination however this usually requires sample transport to the laboratory and eventual contamination or losses of trace elements and matrix interferences (sea water) during the analysis. Solid phase extraction procedures could be performed immediately after sampling thus avoiding any transformations, losses and contamination of trace elements and combining advantages of high preconcentration factors and interference free instrumental determination. Instead of column filled with particles, membranes have become increasingly attractive for efficient separation and preconcentration of metal ions due to their promosing properties such as easy and low energy of operation and high selectivity, and the resulting low cost of operation.

In the present investigation macroporous chitosan membranes (non-crosslined and crosslinked with glutaraldehyde or epichlorohydrin) are applied prior to ETAAS measurement of total dissolved metal content in sea water samples. Batch adsorption experiments were carried out as a function of pH, sorption and desorption time, sample and eluent volumes. The chitosan membranes permitted quantitative sorption (recoveries higher than 95 %) of Cd (II), Cu(II), Ni(II) and Pb(II) in the pH range 7-9. Several eluents (HCl, HNO_3, H_2SO_4) with different acidity were tested and it was found that 2 mol L^{-1} HNO_3 ensured quantitative elution for all studied elements. The influence of EDTA, citric and tartaric acids on the extraction efficiency were investigated. The most important interference except high salinity (sea water) is expected to come from competitive complex formation with humic substances (DOM) in the sample. Therefore model experiments were performed with humics (SRHF), in the sample solution and quantitative recoveries for elements like Cu, Ni and Pb obtained undoubtedly confirmed the applicability of the membranes for reliable and accurate direct determination of total dissolved concentrations of trace elements even in the water samples with high DOM content. Open pore diffusive gradients in thin films (DGT) were used for the estimation of kinetically labile inorganic and organic species of Cd, Cu, Ni and Pb in Black sea waters. Results obtained showed strong complexation for Cu and Pb with sea water dissolved organic matter, the ratio $[Cu]_{DGT}/[Cu]_{tot}$ and $[Pb]_{DGT}/[Pb]_{tot}$ was found in the range 0.20–0.38 and 0.21–0.36 respectively. The same ratios for Cd and Ni varied from 0.62 to 0.81 and from 0.68 to 0.72 respectively which means much higher degree of free, labile species of these metals in sea water.

P6- OPTIMIZATION AND DETERMINATION OF CADMIUM IN DIFFERENT ENVIRONMENTAL WATER SAMPLES WITH DISPERSIVE LIQUID–LIQUID MICROEXTRACTION PRECONCENTRATION COMBINED WITH INDUCTIVELY COUPLED PLASMA OPTICAL EMISSION SPECTROMETRY

F. Aflaki[1], G. Daneshvar[2*] M. Salahinejad[1*]

[1]Environmental Laboratory, Nuclear Science Research School,
Nuclear Science & Technology Research Institute, Atomic Energy Organization of Iran (AEOI),
North Karegar st, P. O. Box 11365-3486, Tehran (Iran)
[2]Exploration and Extraction Group, Nuclear Fuel Cycle Research School, Nuclear Science and
Technology Research Institute, Atomic Energy Organization of Iran (AEOI), P. O. Box 11365-3486,
Tehran (Iran)
*msalahinejad@aeoi.org; gdaneshvar@aeoi.org

Dispersive liquid–liquid microextraction (DLLME) followed by inductively coupled plasma-optical emission spectrometry (ICP-OES) has been investigated for determination of Cd (II) ions in water samples. Ammonium pyrrolidine dithiocarbamate (APDC) was used as chelating agent.

Several factors influencing the microextraction efficiency of Cd(II) ions such as extracting and dispersive solvent type and their volumes, pH, sample volume and salting effect were optimized. The optimization was performed both via one variable at a time and central composite design methods and the optimum conditions were selected. Both optimization methods showed nearly the same results: sample size 5 mL; dispersive solvent ethanol; dispersive solvent volume 2 mL; extracting solvent chloroform; extracting solvent volume 200 µL; pH and salt amount do not affect significantly the microextraction efficiency.

The limits of detection and quantification (LOD and LOQ) were 0.8 and 2.5 ng L^{-1} for Cd(II) ions respectively. The relative standard deviation (RSDs) for five replicate measurements of 0.50 mg L^{-1} of cadmium was 4.4 %. Tap, river, farm and dam water samples at spiking level of 0.50 µg mL^{-1} were analyzed for Cd(II) ion.

[1] Yamini, Y , Hejazi, L , Mohammadi, D E., MicrochimicaActa, 142,21-25 (2003)
[2] Rezaee, M , Assadi, Y , Hosseini, M M., J of Chromatography A, 1116, 1-9 (2006)
[3] Berijani, S , Assadi, Y , Anbia, M , Milani Hosseini, M R , Aghaee, E., *J of* Chromatography A, 1123,1-9 (2006).

P7- SCREENING AND RESOLUTION OF CARBAMIC AND ORGANOPOSPHATE PESTICIDES MIXTURE IN EXTRA VIRGIN OLIVE OIL WITH A BI-ENZYMATIC AMPEROMETRIC SENSOR

[1]D. Albanese, [1*] M. Di Matteo and [2]R. Pilloton

[1]Dipartimento di Ingegneria Chimica e Alimentare, Università di Salerno,
Via Ponte Don Melillo, 84084, Fisciano (Salerno) (Italia)
[2]ENEA, C.R. Casaccia, Via Anguillarese 301, I-00123, Roma (Italia)
[*]mdimatteo@unisa.it

A screen printed acetylcholinesterase-choline oxidase amperometric bi-enzymatic biosensor in a flow injection configuration has been assembled in order to quantitatively detect carbamic and organoposphourus pesticides mixture in extra virgin olive oil samples. The recognition of the two different pesticide classes by this biosensor has been carried out by exploiting the well known different inhibition mechanism of carbamic (reversible inhibition) and organoposphourus (irreversible inhibition) compounds versus acetyl cholinesteras activity. In order to eliminate extraction clean-up steps for pesticides detection in extra virgin olive oil, inhibition calibration curves and analyses of spiked real samples were performed using hexan as the carrier in the flow injection apparatus. The results of the calibration curves showed a different inhibition power versus acetyl cholinesterase in function of the specific compound and found that a probable interaction exists between two or more compounds that affected the toxic power of the single pesticide. The limit of detection (5µg kg^{-1}) obtained for the tested organoposphourus (Paraoxon; Fenitrothion), and carbamic (Methomyl; Carbaryl) pesticides was lower than residues established by European legislation, thus suggesting that the bi-enzymatic biosensor, extensively described in literature, can be a useful and economically convenient for quantitative screening methods in food security monitoring.

P8- THE USE OF AQUATIC MOSSES FOR MONITORING OF METAL POLLUTION IN MORAVA RIVER

P. Diviš and J. Machát

Brno University of Technology, Faculty of chemistry, Purkyňova 118, Brno 612 00
Masaryk University Brno, Kamenice 126, Brno 625 00 (Czech Republic)

Quantitative determination of metals in several compartments of aquatic ecosystems constitutes an important task for the identification of pollution sources, evaluation of contamination or decontamination trends and duality control. However, analytical results from river water sampling can give us information only on momentary state and represent partial approach for ecosystem assessment. In addition to that, collected water samples do not provide accurate information about the bioavailable fraction of metals. Living organisms are successfully used to gain time-integrated information about the biological impact of metal pollution. In the literature, different species of mollusks and bryophytes are described as biological indicators of metal pollution in aquatic environment. In this work *Fontinalis antipyretica* moss species were used for monitoring of metal pollution in down part of Morava River (Czech Republic, South Moravia). The sampling points were located at Spytihněv, Bělov and Uherské Hradiště. Approximately 20 grams of aquatic moss in the form of moss bags were deployed for 28 days in the river water. For analysis of accumulated metals, microwave assisted decomposition by nitric acid and hydrogen peroxide was performed and after flame atomic absorption spectrometry was used.

P9- DETERMINATION of CHROMIUM (VI) in ENVIROMENTAL SAMPLES by ELECTROTHERMAL ATOMIC ABSORPTION SPECTROMETRY AFTER LEACHING WITH SODIUM CARBONATE

Ü. Divrikli[1], A. Akdoğan[1], A. Hol[1], M. Soylak[2], L. Elçi[1]

[1]Chemistry Department, Science and Arts Faculty, Pamukkale University, 20017, Denizli (Turkey)
[2]Chemistry Department, Science and Arts Faculty, Erciyes University, 38039, Kayseri (Turkey)

Environmental pollution caused by toxic heavy metals is one of the most pressing problems in the world. Among toxic heavy metals, speciation of chromium as Cr(III) and Cr(VI) species is a problem of great scientific and practical importance, because their toxicity to aquatic important and terrestrial organisms, including humans, depends upon the oxidation state [1-3]. Although trivalent chromium (Cr(III)) is required in trace amounts for sugar and lipid metabolism in humans and its deficiency may cause a disease called chromium deficiency, hexavalent chromium (Cr(VI)) is extremely toxic and carcinogenic owing to its ability to oxidize other species. Chromium speciation analysis in solid samples, a number of methods using an alkaline Na_2CO_3 solution for leaching Cr(VI) were described [4]. The leaching with Na_2CO_3 solution for Cr(VI) speciation is based on transformation of insoluble Cr(VI) compounds into soluble form in an alkaline media forming Na_2CrO_4 while Cr(III) species form insoluble hydroxides or carbonates [5].

In the present study, speciation of chromium in some plant leaves, soil and sediment samples was carried out by selective leaching of Cr(VI) using a sodium carbonate leaching procedure. Total chromium from the samples was extracted using aqua regia and oxidative acid digestion, respectively. The concentrations of chromium species in the extracts were determined using by graphite furnace atomic absorption spectrometry (GFAAS). A limit of detection (LOD) for determination of Cr(VI) in 0.1 mol L^{-1} Na_2CO_3 solution by GFAAS was found to be 0.93 $\mu g\ L^{-1}$. The procedure was applied to environmental samples. The relative standard deviation, R.S.D. as precision for 10 replicate measurements of 20 $\mu g\ L^{-1}$ Cr in processed soil sample was 4.2%.

[1] Environmental Quality Standards for Water Pollution, Ministry of the Environment, Japan, http://www.env.go.jp/en/water/wq/wp.html.
[2] J.O. Nriagu, E. Nieboer (Eds.), Chromium in the Natural and Human Environments, vol. 20, Wiley, New York, 1988.
[3] J. Kota´s, Z. Stasicka, Environ. Pollut. 107 (2000) 263–283.
[4] M.J. Marques, A. Salvador, A.E. Morales-Rubio, M. De la Guardia, Fresenius J. Anal. Chem. 362 (1998) 239–248.
[5] G. Svehla, Vogel's Qualitative Inorganic Analysis, seventh ed., Longman Publishers, Singapore, 1996.

P10- ENVIRONMENTAL FATE OF TRAFFIC RELEASED RARE EARTH ELEMENTS

R. Djingova and V. Lyubomirova

Faculty of Chemsitry, University of Sofia, J. Bouchier str. 1, 1164 Sofia (Bulgaria)

A sequential extraction procedure (three-step), proposed by the Standards, Measurements and Testing Programme (formerly BCR) of the European Union, was applied to spiked soil and street dust samples for the determination of REEs. This procedure provides the determination of extractable metals such as acid-soluble, reducible, oxidisable and residual. Analyses were carried out using inductively coupled plasma-mass spectrometry (ICP-MS). The total REEs concentration in the street dust samples determined after aqua regia digestion was in very good agreement with the previously reported values. Higher percent of leached metals in the street dust samples compared to the soil samples show that PGEs are oxidized more efficiently under natural conditions. Additionally metals bound to humic acids were investigated using size-exclusion separation of soil humic acids and fractionation of rare earth elements in high- and low molecular humic acid fractions.

P11- ANALYSIS OF METABOLITES IN URINE AS BIOCHEMICAL INDICATORS OF HUMAN EXPOSURE TO ATRAZINE

V. Drevenkar[1], G. Mendaš[1], and M. Vuletić[2]

[1]Institute for Medical Research and Occupational Health, Ksaverska c. 2,
HR-10000 Zagreb (Croatia)
[2]PLIVA-Research & Development Ltd., Prilaz Baruna Filipovića 25, HR-10000 Zagreb (Croatia)

Human exposure to atrazine and other triazine herbicides results in urinary excretion of traces of parent compounds and of their metabolites formed by dealkylation or conjugation with mercapturic acid. The aim of this study was to develop and validate a method for simultaneous extraction of atrazine and its more polar metabolites from human urine and to test its applicability in monitoring of occupational exposure. Atrazine, three dealkylated atrazine metabolites, and atrazine mercapturate were extracted from acidified urine samples (pH 2) with ethyl acetate and the extracts were analysed using high performance liquid chromatography - tandem mass spectrometry (Q-TRAP LC-MS/MS system). At mass concentrations of 50 ng ml^{-1} to 200 ng ml^{-1} extraction recoveries of atrazine, monodealkylated atrazine metabolites, and atrazine mercapturate ranged from 53% to 73% (RSD 4 % to 9%). The detection limits based on treatment of 2 ml urine samples were 0.2 ng ml^{-1} for atrazine and atrazine mercapturate, 4 ng ml^{-1} for deethylatrazine, 10 ng ml^{-1} for deisopropylatrazine, and 100 ng ml^{-1} for didealkylated atrazine. Detection sensitivity of mono- and didealkylated atrazine metabolites was influenced by interferences generated by sample matrix. The method was applied for analysis of atrazine metabolites in spot urine samples collected from agricultural workers at the beginning and at the end of a working day and 12 hours after the end of work. Atrazine and its dealkylated metabolites were not detected in any of 27 analysed urine samples but traces of atrazine mercapturate were measured in all urine samples collected at the end of the work and 12 hours after termination of exposure. The mass concentrations of atrazine mercapturate in positive urine samples ranged from 0.2 ng ml^{-1} to 7.9 ng ml^{-1}. The results confirmed atrazine mercapturate as a sensitive and useful biochemical indicator of human exposure to atrazine.

P12- PERSISTENT ORGANOCHLORINE PESTICIDES, POLYCHLORINATED BIPHENYLS, POLYBROMINATED DIPHENYL ETHERS IN FISH FROM BIZERTE LAGOON, TUNISIA

M. R. Driss, W. Ben Ameur

Department of Chemistry, Laboratory of Analytical Chemistry and Environment,
05 UR/12-03 Faculty of Sciences Bizerte, 7021 Zarzouna (Tunisia)

Organohalogenated pollutants (OHPs), such as polychlorinated biphenyls (PCBs), polybrominated diphenyl ethers (PBDEs) and organochlorine pesticides (OCPs), are lipophilic substances that are a great cause of concern because of their persistent and bioaccumulative nature. They are also known to cause adverse health effects in humans and wildlife [1].

Contamination profiles of organochlorine pesticides (OCPs) polychlorinated biphenyls (PCBs) and polybrominated diphenyl ethers **(**PBDEs) were determined in muscle of three fish species from Bizerte Lagoon: Mullet (*Mugil cephalus*), bar (*Dicentrarchus labrax)* and sole (*Solea solea*). A total of 36 fish samples were collected.

PCBs, IUPAC nos. 105,118,138, 149 and 180 were detected in all the analyzed samples. PCB 138 and 180 were the prominent congeners. Among target OCPs , only p,p'-DDE , o,p'-DDD, p,p'-DDD, p,p'-DDT and cischlordane were detected in all the samples. The most detectable PBDEs congener was BDE-47. Concentrations of PCBs were predominant followed by OCPs and PBDEs.

Concentrations of total OCPs ranged from 53.71 to 738.01 ng/g, 94.03 to 1202.75 ng/g and 103.51 to 675.90 ng/g on lipid weight basis, respectively in samples of mullet, bar and sole . Concentrations of total PCBs ranged from 97.30 to 1251.74 ng/g, 259.76 to 3488.24 ng/g and 149.48 to 1109, 33 ng/g on lipid weight basis, respectively in samples of mullet, bar and sole. Among the compounds of DDT, p,p'-DDE was the most dominant molecule accounting for 28.97%, 34,18% and 34, 65 of the total OCPs respectively in the samples of mullet, bar and sole.

The comparison of our finding to those reported in some other studies shows that levels of pollutants in fish samples from the Bizerte Lagoon were lower or similar to levels measured in other fish species.

[1] Jones K.C. and P. de Voogt, Environ. Pollut. 100, 209–221 (1999).

P13- BTEX DETERMINATION IN UNDERGROUND WATER AT GAS STATIONS USING HS-SPME/GC – MS/MS IN CAMPO GRANDE, MS BRAZIL

N. Ré-Poppi, S. S. Gebara

Department of Chemistry of the Federal University of Mato Grosso do Sul. Av. Senador Felinto Müller, 1555 – Cidade Universitária, 79080-190, Campo Grande – MS (Brazil)

The contamination of underground water by leak in tanks at gas stations is a constant concern in Brazil. The storage tanks built in the 70s which have an average usefulness of 25 years are already compromised [1]. The monoaromatic hydrocarbons: benzene, toluene, ethylbenzene and xylenes (BTEX) are some of the relevant compounds in the evaluation of water and soil contamination. BTEX are extremely toxic to humans, presenting chronic toxicity even in small concentrations, which may cause lesions to the central nervous system (CNS) [2]. The Environmental Protection Agency (EPA/USA) determined as a maximum concentration level for drinking water 5 $\mu g\ L^{-1}$ of benzene, 1000 $\mu g\ L^{-1}$ of toluene, 700 $\mu g\ L^{-1}$ of ethylbenzene and 10000 $\mu g\ L^{-1}$ of xylenes [3]. In order to determine these compounds in underground water a methodology was developed using microextraction in solid phase through headspace (HS-SPME) analyzed in a gas chromatograph (GC 3900) coupled to the ion-trap (GC-EM/EM) Saturn 2100T/MS/MS (Varian) mass spectrometry, with 1177 injector.
The equipment used was a ValcoBond low bleeding capillary column with VB-5 stationary phase, 5% phenyl and 95% methypolysiloxane, 30m x 0.25 mm x 0.55 µm. The parameters set for the extraction with the DVB/CAR/PDMS 30/50µm fiber were: desorption time and temperature of 0.15 min and 260ºC, extraction time and temperature of 5 min and 25ºC. The addition of salt to the mean and pH variation did not change the results. Considering the BTEX maximum limits allowed by legislation, good linearity was observed in the 0.5-64 $\mu g\ L^{-1}$ range for each analyte (r: 0.991-0.997) and the first point of the curve was the limit of the quantification adopted. The precision and the accuracy of the method were evaluated through recovery experiments which presented values between 85.4 and 112.7% with variation coefficient between 4.3 and 18.6%. The developed method was applied in underground water samples near petrol stations in Campo Grande, MS. Among the analyzed samples, 33% presented higher concentrations them 1.48 $\mu g\ L^{-1}$ from the analyzed substances. No compound was detected in only 16% from the collected material. High amounts of benzene (above the maximum allowed) were found in 50% of the water samples. Preliminary data show low contaminant level in underground water and consequent risk to human health considering the fact that in Campo Grande there are 82 active underground water capture wells, which assist about 40% of the town population [1].

[1] Ezequiel, G.C.P.F., Oliveira, P.T.S., Ayres, F.M., Martins, I.P., Machado, N.M. Geoprocessing (GIS) as a tool in the environmental licensing of gas stations, Society & Nature, Uberlândia, 20, 87 – 99 (2008).
[2] CETESB, Companhia de Tecnologia de Saneamento Ambiental, (Company of Environmental Sanitation Technology). http://www.cetesb.sp.gov.br
[3] USEPA, List of Contaminants & Their Contaminant Level (MCL_s) in drinking water (2004) http://www.epa.gov/safewater/mel.html#organic

P14- A STUDY ON THE PARTITION COEFFICIENTS OF METALS IN TROPICAL SURFACE WATER

E. M. Deduch, S. R. G. Barreto and W. J. Barreto

Department of Chemistry, Universidade Estadual de Londrina, Campus Universitário,
86051-980, Londrina, Paraná (Brazil)

In aquatic environments metals are transported in the dissolved form or bound to suspended particulate matter (SPM), iron oxyhydroxides and organic matter (OM). The distribution coefficient (Kd) is the ratio of the particulate (m/m) to dissolved (m/v) metal concentrations and provides a measure of changes in the affinity of trace metals in the particulate phase. The objective of this study was to determine the availability of metals in a tropical aquatic environment through the calculation of the Kd values, and compare them with the Kd values of non-tropical environments. The quantification of dissolved metals and those bound to the SPM was carried out for water samples collected from 19 points in the Capivara lake. The determination of dissolved metals was performed on water samples which had been filtered, acidified and pre-concentrated from 1.5 L to 50 mL at 60 °C. For the quantification of metals in the SPM, before and after filtration the membranes were dried at 60 °C for 30 min and weighed. The mass of the SPM was obtained by mass difference. The digestion of the membranes was performed with 30 mL of *aqua regia* at 150 °C. The metals were determined by ICP-AES. Correlations (r^2) were determined and hierarchical cluster analysis (HCA) was carried out using the Tanagra software. The mean log Kd values for Cr, Cu, Ni and Zn in the reservoir water samples were 36.8, 24.7, 21.7 and 14.5% higher than the average reported by the EPA and for Cd and Pb were 19.1 and 1.96% lower [1]. The sequence of log Kd values for metals in the reservoir was: Cr (6.98 ± 0.41)> Mn (6.37 ± 0.49)> Fe (6.20 ± 0.36)> Cu (5.86 ± 0.41)> Zn (5.84 ± 0.42)> Ni (5.60 ± 0.66)> Pb (5.49 ± 0.42)> Ca (3.83 ± 0.32)> Mg (3.81 ± 0.27)> Cd (3.80 ± 0.78). The highest concentration of Fe and Mn in the SPM was attributed to the characteristics of the soil. The solubility of transition metals in natural waters can be explained by the tendency to form soluble complexes with OM in suspension. The AHA showed that Cr is associated with Fe and Cu, forming an isolated "cluster", confirmed by high coefficients (r^2) for the correlations between Cr and Fe (0.934) and Cr and Cu (0.844) at the 19 sites. Cadmium was the only metal that formed a cluster with the OM, which explains its greater solubility in relation to the other metals investigated and suggests its complexation with the OM. Metals with the weakest correlated with OM were those with the highest logKd; Cr (0.055), Mn (0.015) Fe (0.013) and Cu (0.060), indicating no complexation with the OM. The strong correlation between Cr and Fe and between Cr and Cu indicated that Cu and Cr must be quantitatively related to the Fe oxyhydroxides in the SPM. The metal with the weakest correlation with Fe was Cd (0.015) confirming the low affinity with OM. There was a high inverse correlation between SPM and logKd for Cr , Ca , Zn , Mg , Cu , Fe and to a lesser extent for Pb, Ni and Cd. The logKd values of tropical aquatic environments are different from the average found in the northern hemisphere (EPA), probably due to soil type and the amount of OM.

[1] Allison, J. D., T. L. Allison, U.S. Environmental Protection Agency, Athens, GA. Publication No. EPA/600/R-05/074 (2005).

P15- HAZARDOUS DYE REMOVAL BY POLYMERIC HYDROGEL

M.G. Gigimol[1] , K. R. Dhanya [2], M. Beena [3]

[1]Alphonsa College, Pala, Kottayam, Kerala (India), e-mail: mggigi2009@gmail.com
[2]Research Scholar, St.Thomas College, Pala, Kerala (India), email: k_r_dhanya@yahoo.co.in
[3] School of Chemical Sciences, M.G University, Kerala (India), e mail: beenamj@yahoo.com

When chemicals that are harmful to living things get in to water normally pollution happens. Water pollution affects physical, chemical and biological characteristics of aquatic ecosystem. Hazardous dyes when spread in to water, it can affect the whole aquatic ecosystem. Many textile industries use dyes in order to colour their products.

Brilliant Blue G (BBG) is a hazardous dye; known as acid blue 90 is toxic to mankind. Its ingestion can cause eye, skin and respiratory tract irritation. For the removal of BBG from water, suitable methods are developed. Adsorption is one of the best methods. For this NNMBA-crosslinked polyvinyl pyrrolidone is an efficient adsorbent. Solution polymerization is the suitable method for the preparation. Binding of BBG by NNMBA-crosslinked polyvinyl pyrrolidone was followed. From the binding studies, the effect of concentration, polymer added, pH, temperature and order of the reaction can be calculated. Adsorption of BBG has been correlated with second order kinetic equation. Synthesis of polymer, characterization, dye binding and various conditions are detailed in this paper.

P16- PROSPECTIVE OF EFFECTIVE SEPARATION OF FISSION PALLADIUM USING BIOMASS SORBENT

K. Hirota and D. Parajuli

Environmental and Industrial Materials Research Division, Japan Atomic Energy Agency,
1233-Watanuki, Takasaki, 370-1292 (Japan)

The radioactive waste, commonly known as high level radioactive waste (HLW), generated during the nuclear fuel procession contains substantial amount of platinoids like Palladium, Rhodium, and Ruthenium. Interestingly, the half lives of their isotopes are relatively very short and the radioactivity of some long half life isotopes is weak enough for various applications [1, 2]. However, the co-existence of highly radioactive isotopes of other elements is the big obstacle for their selective separation. The concentration Palladium in this complex mixture is about 2000 ppm. More importantly 83 % of Palladium is in stable form and the remaining 17 % radioactive isotopes 107Pd possesses poor intrinsic radioactivity. In order to recover this valuable resource, Cedar wood powder (CWP) was modified to thiamide type adsorbent and was studied for the separation of Pd(ll) from nitric acid medium.

The adsorbent was prepared by heating a 1:2 mixture of CWP and thiourea using a microwave. The product obtained after washing with water is named as CWP-TV. Because the high level waste is contained basically in nitric acid, the adsorption test was performed in nitric acid and found that Pd(ll) is adsorption is preferred from 3 M or higher concentration nitric acid solution. The Pd(ll) only selectivity was revealed by taking simulated HL W solution containing 15 different metals in same molar ratio as in the real fission waste. The feasibility of recovering Pd(ll) using CWP-TV from highly radioactive HL W solution was tested by irradiating the mixture of adsorbent and simulated HL W solution by gamma rays for 50 h with total dose of 500 kGy. The results show that, unlike on commercial synthetic extractants, there is no direct effect of radiation on the Pd(ll) binding ability of the sorbent. In addition, CWP-TV possesses an impressive loading capacity of as high as 1.0 mol/kg Pd(ll) in normal as well as in radioactive environment.

[1] Inoue, T., Sakata, M., Miyashiro, H., Matsumura, T., Sasahara, A., and Yoshiki, N., Nucl Technol. 93,206-220 (1991).
[2] Kolarik, Z., Renard, E.V., Platinum Metals Rev. 49, 79-90 (2003).

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P17- SIMULTANEOUS DETERMINATION OF METALS BY ICP-MS IN ENVIRONMENTAL WATERS USING SPE PRECONCENTRATION ON DIFFERENT SORBENTS

Z. Holubova, M. Moos, L. Sommer

Brno University of Technology, Chemistry and Technology of Environmental Protection,
Purkyňova 118, 612 00 Brno (Czech Republic)

A study has been conducted for the determination of eight elements (Be, V, Co, Ni, Y, Cd, Pb and Th) by inductively coupled plasma mass spectromentry (ICP-MS) in natural waters and waters after mining and processing of uranium. An ICP-MS spectrometer Agilent 7500ce, with a plasma generator of 27.12 MHz, power output 1500 W and concentric nebulizer MicroMist™ with a cooled Scott chamber was used. The matrix effects were eliminated by using a solution of internal standards ^{6}Li for ^{9}Be, ^{45}Sc (^{51}V), ^{72}Ge (^{59}Co, ^{60}Ni, ^{89}Y), ^{103}Rh (^{111}Cd), ^{209}Bi (^{206}Pb, ^{207}Pb, ^{208}Pb, ^{232}Th).

Monitored interfering elements were K^{+}, Na^{+}, NH_4^{+}, Fe^{2+}, Ca^{2+}, Mg^{2+}, Al^{3+}, NO_3^{-}, NO_2^{-}, SO_4^{2-}, Cl^{-}, HCO_3^{-}. The non-polar sorbents based on Silica (C18, C8 and Phenyl) were conditioned with the Benzyldimethyltetradecylammonium chloride (Zephyramine) or 1-etoxycarbonyl-pentadecyltrimethylammonium bromide (Septonex®).

The sorption process for the preconcentration of target elements was realized in the presence of 4-(2-pyridylazo) resorcinol, Ammonium pyrrolidinedithiocarbamate, 8-Hydroxyquinoline-5-sulphonic acid and Alizarine S at pH 5-9. The elution mixture was acetone and ethanol (1:1) in presence of 1 mol·l^{-1} HCl. The excess of acid and organic solvents were evaporated in Teflon® dish prior to the determination by ICP-MS.

P18- HEAVY METALS IN FLOODPLAINS SEDIMENTS THE ROLE OF SAMPLING AND EXTRACTION PROCEDURES

G. Głosińska[1], A. Ibragimow[1], M. Siepak[2] and B. Walna[3]

[1]Collegium Polonicum Słubice, Adam Mickiewicz University, Kościuszki 1,
69–100 Słubice (Poland)
[2]Institute of Geology, Department of Hydrogeology and Water Protection, Adam Mickiewicz University, Maków Polnych 16, 61–606 POZNAŃ (Poland)
[3]Jeziory Ecological Station of Adam Mickiewicz University, P.O. Box 40, 62–050 Mosina (Poland)

The paper presents the results of determination of heavy metals (Cd, Cr, Cu, Fe, Mn, Ni, Pb, Zn) in fluvial sediment samples collected from the surface and subsurface layer on the flood plains of the Odra River (western Poland). The forms of metals were obtained by single extraction procedures: 0.05 EDTA and 0.005 DTPA with different ratios of sediment samples to solution. The concentrations of metals were determined using the technique of atomic absorption spectrometry with flame atomisation (F-AAS). The concentration of heavy metals in sediment samples varied in the investigated samples and depended on the distance from the Odra River, depth and the extractant used. 0.005M DTPA with the ratio of sediment samples to solution 1:2 dissolved about ($mg \cdot kg^{-1}$): 0.20 – 79.3 of Cu, 2.25 – 86.1 of Mn, 11.21 – 554 of Fe, 0.12 – 9.64 of Ni, <0.01 – 5.28 of Cd, 0.174 –13.8 of Pb, 0.29 – 201 of Zn,<0.02 – 0.65 of Cr. 0.005M DTPA with the ratio of sediment samples to solution 1:10 dissolved about ($mg \cdot kg^{-1}$): 32.98 – 114 of Cu, 23.8 – 190 of Mn, 95.2 – 2520 of Fe, <0.03 – 23.7 of Ni, 0.01 – 8.31 of Cd, 0.03 – 70.3 of Pb, 19.58 – 597 of Zn, <0.02 – 1.24 of Cr. 0.05M EDTA with the ratio of sediment samples to solution 1:10 dissolved about ($mg\ kg^{-1}$): 0.26 – 148 of Cu, 15.8 – 1008 of Mn, 28.1 – 2777 of Fe, 0.45 – 16.7 of Ni, <0.01 – 5.84 of Cd, 1.95 – 157 of Pb, 1.33 – 460 of Zn. The research demonstrated that the sampling depth and extraction procedure play a significant role in the determination of heavy metal concentration in sediment samples. In addition, using the same extractant with different ratios of sediment samples to solution can also give different results.

P19- SPECTROFLUORIMETRIC DETERMINATION OF ANIONIC SURFACTANTS USING RHODAMINE 6G

M. Idouhar, A. Tazerouti

Laboratoire de Chimie Organique Appliquée, Faculté de Chimie, Université des Sciences et de la Technologie Houari Boumediene, BP 32 El-Alia Bab-Ezzouar, 16111 Algiers (Algeria)

Determination of traces of organic pollutants takes great importance in environment. Anionic surfactants are often be present in sea waters and their determination become necessary. Development of the spectrofluorimetry method witch is based on the extraction of anionic surfactants with a fluorescent organic dye as ion pairs [1]. Fluorescent molecules have possibility in having absorption and emission at different wavelength.

The main advantages of this method are the elimination of the absorption of all other molecules which may be present in the samples except that of the fluorescent agent in the same field of absorption, and the detection of week emission leading to the determination of low fluorescence intensity of every sample [1]. Rhodamine group are used in the extraction of different metals and compounds [2, 3]. In this way, the method of determination of low anionic surfactant concentrations is setup and optimised.

In the Rhodamine 6G- Benzene system, the ion pair Rhodamine 6G- Sodium Dodecylsulfate produces maximum emission at wavelength 559 nm. The calibration curve obtained by the recommended procedure is linear in the range $3{,}63.10^{-8}$- $2{,}9.10^{-6}$ M of Sodium Dodecylsulfate, with correlation coefficient $r = 0{,}9989$.

The precision is estimated by determining the relative standard deviation (RSD %). The results obtained show that the RSD is less than 6% for $7{,}2.10^{-8}$ M and about 1,8% for $1{,}81.10^{-6}$ M of Sodium Dodecylsulfate.The limit of detection obtained for 10 replicates of the reagent blank is found to be $3{,}98.10^{-8}$ M.

References

1- Bubio-Barroso S.; Gomez –Rodriguez M.; Polo-Diez L.M., Microchem. Journal, 37, 1988, 93-98.
2- Argauer R.J.; White C.E., Anal. Chim. Acta, 32, 1965, 596-599.
3- White C.E., Fluorescence and phosphorescence analysis, Chapter 7, D.M Hercules ed. , 1966

P20- DETERMINATION OF OIL POLLUTION IN SEDIMENT USING FT- IR IN MAHSHAHR REGION, PERSIAN GULF

K. Karimzadeh[1], A. Zahmatkesh[2]

[1] Marine biology department, Islamic Azad University Lahijan Branch, 1616, Lahijan (Iran)
[2] Aquaculture Dep., MirzaKochak Khan Higher Education Center for Fishery Science and Technology, Rasht (Iran)

Persian Gulf is one of the most sensitive regions to sustain an injury with oil excavation and oil tanker. So it is susceptible for oil and petroleum pollution.

This research consists of measuring oil pollution in surficial sediments in Mahshahr region in Iran. The study has been conducted by monthly sampling from Augus through March in four stations. Samples were collected by van veen grab from surficial sediments. They stored in glass container according ROPME method at 4º C temperature. In laboratory, samples were freeze dried and homogenated by mixer. Extraction was performed with three chlrothree fluroetan. So, total oil in samples was measured by ft-IR according reference oil as standard curve. Oil concentration varied between 934µg g-1 dry wet to 7970 µg g-1 dry wet. The highest concentration was recorded in the first station (Khore-Ghzaleh) and the lowest in the third station (Khore Bihad).

[1] Phillips, D.J.H., Mar. Pollu.bull.32 (1), 65-69,(1996)
[2] ROPME. Manual of oceanography observation and pollutant analysis method, (1989)

P21- PHENOL AND PENTACHLOROPHENOL BIODEGRADATION DURING MESOPHILIC AND THERMOPHILIC MUNICIPAL SOLID WASTE ANAEROBIC DIGESTION: TEMPERATURE EFFECT AND METABOLITES IDENTIFICATION USING A STABLE ISOTOPIC APPROACH

M. R. Driss[1], J. Epissard[2], A. Guenne[2], I. Limam[1,2,3] and L. Mazeas[2]

[1] Unité de recherche Chimie analytique appliquée 05/UR/12-03, Faculté des Sciences de Bizerte, 7021 Jarzouna (Tunisia)
[2] Unité de recherche Hydrosystèmes et bioprocédés, Cemagref, Parc de Tourvoie, BP 44, 92163 Antony (France)
[3] Laboratoire des Méthodes et techniques d'analyse, Institut National de Recherche et d'Analyse physico-chimiques, 2020 Sidi Thabet (Tunisia)

Phenolic compounds are ubiquitous in the environment. Phenol and pentachlorophenol (PCP) belong to this variety of compounds. The primary use of phenol is in the production of phenolic resins. Other uses of phenol include as a disinfectant and in medicinal products. Phenol is known to have high acute toxicity [1-3]. PCP is used as a wood-protection product with fungicide and bactericide properties. It has been designated as a priority pollutant and is a probable human carcinogen [3]. Little is known about the fate of phenol and chlorinated phenols during the anaerobic digestion of municipal solid waste (MSW). In this study isotopic tracing using ^{13}C labelled PCP and Phenol is proposed as a tool to distinguish the loss of PCP and Phenol due to biodegradation from other physico-chemical processes. This isotopic approach was applied to accurately assess PCP and Phenol degradation under methanogenic conditions in several microcosms made up of household waste. These microcosms were anaerobically incubated at 35 °C (mesophilic conditions) and 55 °C (thermophilic conditions) without agitation. A follow-up of the biogas production (CH_4 and CO_2), was carried out during 130 days until the establishment of stable methanogenesis. Then, $^{13}C_6$-PCP and $^{13}C_6$-Phenol were injected in microcosms and its degradation follow-up at the two temperatures 35 °C and 55 °C was carried out simultaneously by isotopic (GC-IRMS) and molecular (GC-MS) analysis. This study proved the almost total dechlorination of PCP into 4-CP at 35 °C. In contrast, no dechlorination was observed at 55 °C. Concerning Phenol a total mineralisation into CH_4 and CO_2 occurred at 35 °C and 55 °C. Those results illustrate the potentialites of this new istopic approach to study the fate of micro pollutants in complex ecosystems.

References

[1] Agency for Toxic Substances and Disease Registry (ATSDR), U.S. Department of Health and Human Services, Atlanta, GA. (1998).
[2] Calabrese E.J. and Kenyon E.M. Air Toxics and Risk Assessment. Lewis Publishers, Chelsea, MI. (1991).
[3] U.S. Department of Health and Human Services. Hazardous Substances Data Bank (HSDB, online database), National Library of Medicine, Bethesda, MD. (1993).

P22- OPTIMIZATION OF A MATRIX SOLID-PHASE EXTRACTION METHOD FOR THE DETERMINATION OF PYRETHROID, ORGANOPHOSPHORUS AND CARBAMATE PESTICIDES IN EDDIBLE SEAWEED SAMPLES

A. M. Carro, R. Cela, D. García-Rodríguez, R. A. Lorenzo

Departamento de Química Analítica, Nutrición y Bromatología. Facultad de Química. Universidad de Santiago de Compostela. Avda. de las Ciencias s/n. 15782 Santiago de Compostela (Spain)

Historically, seaweeds have been used as food in Asian countries. Actually, world seaweed production is estimated to be around 7.5 million metric tones per year [1]. The interest of seaweeds as a healthy food in western countries has led to an increase on their presence in markets and also to the development of seaweed-based industries [2].

The main way of pest and disease control in aquaculture industry is the use of chemotherapeutants as organophosphate (OP), carbamate (CAR) and pyrethroid (PYR) pesticides. In addition, marine environment also receives fluxes of pesticides mainly from agricultural origin, due to their widespread use in this field. In recent years, many innovations have been developed in the analytical processes applied to prepare food samples for the extraction and determination of pesticide residues [3]. MSPD involves the dispersion of the sample in a solid support, followed by preliminary purification and the elution of the analytes with low amounts of solvent [4]. The advantages of MSPD include its simplicity, efficacy, low cost, and the possibility of simultaneous extraction and cleanup.

In this work we present the optimization of a MSPD method using anhydrous sodium sulphate as solid support for the determination of OPs (chlorpyrifos-methyl and chlorpyrifos-ethyl); PYRs (permethrin, cypermethrin, empenthrin, bioallethrin, resmethrin, tetramethrin, cyhalothrin, cyfluthrin, flucythrinate, fenvalerate and deltamethrin); and CARs (carbaryl and propoxur) in eddible seaweed samples. Also, piperonyl butoxide (a synergist commonly used in pyrethroid formulations) and 2-phenylphenol (a disinfectant widely used in food processing plants) are analyzed.

Separation and determination of these compounds was achieved by gas chromatography coupled to mass spectrometry and large-volumes of sample extracts were injected using a programmed-temperature vaporizer (PTV-LVI). Different dispersants (C18, Florisil® and anhydrous sodium sulfate) and clean-up sorbents (Florisil® and GCB) where evaluated and optimized by means of an experimental Box-Behnken design. The results suggest that the operational MSPD conditions are elution with 15 mL (40:60 ethyl acetate: hexane), Florisil (3.6 g) and graphitized carbon black 0.4 g as sorbents; and Na_2SO_4 anhydrous (4 g) as sample dispersant.

The method showed excellent linearity ($R^2 > 0.9985$) and precision (RSD $\leq$ 10.5%) for all compounds, with detection limits ranging from 0.3 pg g^{-1} for chlorpiryfos-ethyl, to 23.1 pg g^{-1} for deltamethrin. Recoveries in real seaweed samples were within the range 84-106 %. The method was satisfactory validated for the analysis of wild and cultivated edible seaweeds.

Acknowledgments

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[1] Dhargalkar, V.K., Verlecar, X.N., Aquaculture 287, 229-242 (2009).

[2] López-López, I., Cofrades, S., Ruiz-Capillas, C., Jiménez-Colmenero, F., Meat Sci. 83 255-262 (2009).

[3] Martinez-Vidal, J.L., Plaza-Bolanos, P., Romero-Gonzalez, R., Garrido-Frenich, A., J. Chromatogr. A 1216, 6767-6788 (2009).

[4] García-López, M., Canosa, P., Rodríguez, I., Anal. Bioanal. Chem. 391, 963-974 (2008).

P23- SULFATE (PFOS) ON ZrO_2 / DDAB ACTIVE NANO-ORDER FILM

SY Cheng, TF Kang, LP Lu, LH Xu

College of Enviromental and Energy Engineering, Beijing University of Technology,
Beijing 100022 (P.R. China)

In recent years, much attention has focused on understanding the toxicology of the most widely known perfluorinated chemicals(PFCs), perfluorooctanoic acid (PFOA), and perfluorooctant sulfate(PFOS). The high-energy C-F covalent bonds in PFCs are strong enough to resist hydrolysis, photolysis, biodegradation, and metabolism and thus result in a high degree of environmental persistence and bioaccummulation of PFCs and their derivatives. Many studies have been on the general toxicology of PFOS by biochemistry, however, there has been little substantial progress in understanding the action mode in detail. Here, we present a biomimetic surface and bind-strong DNA immobilization strategy that provides a well recogition interface. PFOS of the DNA damage was detected by electrochemical method with the electroactive methylene blue(MB) as an indicator.

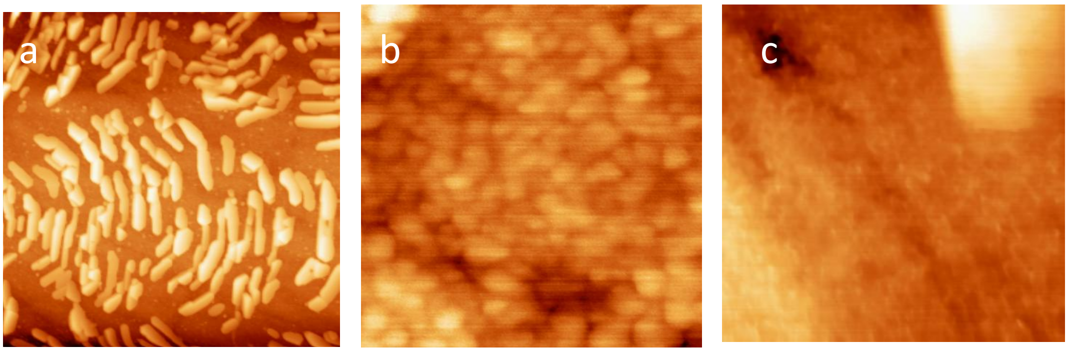

Fig. 1. AFM image , a: ct-DNA on the ZrO_2/DDAB/GCS; b: nano-ZrO_2 on the DDAB/GCS; c: DDAB layer on the GCS.

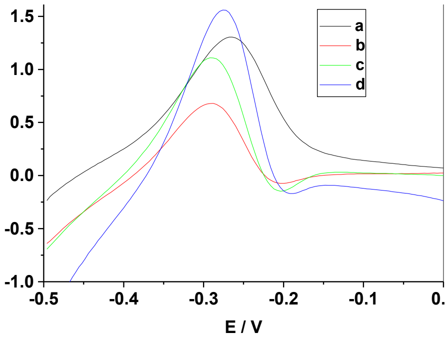

Fig. 2. Differential pulse voltammograms using 2.0×10^{-5} mol/L MB as the redox indicator at the dsDNA ZrO_2/DDAB/GCE incubated in PFOS for 1min(a), 2mins(b),3mins(c),and 10mins(d).

[1] Christopher, L., Katherine, A., Colette,H., David,L., Andrea P.H., Jennifer,S., Toxicological Sciences, 99,366-394(2007).
[2] Wei,Z., Tao, Y., Chen,J., Kui, J., Applied Surface Science, 254,4750-4756(2008).

P24- NEW TRENDS IN CHEMICAL CHARACTERIZATION OF *PHLOMIS PURPUREA* ROOT EXTRACTS BY ION TRAP HPLC-PDA-ESI/MS/MS

A. Cravador[1,3], M. C. Mateus[1,2], D. Neves[1], O. Wójcik[1]

[1]Faculdade de Ciências e Tecnologia, Universidade do Algarve, Campus de Gambelas,
8000-135 Faro (Portugal)
[2] CIQA - Universidade do Algarve, Campus de Gambelas, 8000-135 Faro (Portugal)
[3]IBB/CGB - Universidade do Algarve, Campus de Gambelas, 8000-135 Faro (Portugal)

Purple phlomis (*Phlomis purpurea*) a member of the family Lamiaceae is a spontaneous evergreen shrub, autochthonous to southern Iberian Peninsula and Morocco and is present in cork oak (*Quercus suber*) and holm oak (*Querkus ilex* subsp. *rotundifolia*) forest habitats in Portugal, especially in the Algarve region. A survey of the infested habitats led to the finding that purple phlomis was not infected with *Phytophthora cinnamomi*, a highly aggressive *wide-range host* root pathogen, the main biotic agent involved in cork and holm oak decline in Iberian Peninsula. This observation prompted us to study the potential use of this plant to control *P. cinnamomi* and the potential of root extracts to contain antimicrobial compounds.

In a first step, the effect of ethanol root extracts of *P. purpurea* was evaluated, *in vitro*, on mycelial growth, sporangial production, zoospore release and germination and chlamydospore production and viability. For all the cases significant inhibition was observed by inoculation.

In a second step, ethanolic crude extract of *P. purpurea* roots was analyzed by HPLC coupled to photodiode array detection and tandem mass spectrometry and compared with seven phenolic standards identified in root exudates from other plants. The selected compounds comprise flavonoids as rutin and quercetin, cafeic acid and their related aromatic acid compounds such as chlorogenic, vanillic, coumarinic and rosmarinic acids. Analysis by HPLC-ESI/MS/MS led to the identification of cafeic acid, chlorogenic acid and vanillic acid, based on their MS^2 mass spectrometric fragmentation patterns, for all the root extracts. The presence of caffeic acid instead of coumarinic acid is not in agreement with previous results [1] obtained for *P. purpurea* leaves extracts, suggesting that p-coumaroyl derivates were not present in the root extracts.

Additionally attempts were made to identify the main peak obtained for the full scan MS mode chromatogram. The observed m/z value for the $(M–H^+)$ molecular ion is 473. *P. purpurea* is very rich in saponins─amphipathic glycosides of steroids or triterpenes characterized by their detergent-like properties. The corresponding aglycones are oleanolic acid (OA), hederagenin (Hed), phytolaccadenic acid (PA), and serjanic acid (SA), all of them deriving from β-amyrin. Sugars can be linked to the aglycone at the C-3 and C-28. Fragmentation of saponin compounds produce product ions specific for the aglycones, namely m/z 473 (Hed)[2]. The MS^2 and MS^3 fragmentation spectrum of m/z 473 chromatographic peak isolated from the crude extracts are consistent with the fragmentation pattern of hederagenin [2].

[1] Francisco A. T-Barberán, *et all,* Phytochemistry, 31, 3097-3102 (1992).
[2] Tobias Madl*, et all*, J. Am. Soc. Mass Spectrom., 17, 795-806 (2006)

P25- DETERMINATION OF HEAVY METALS IN LEACHATES FROM MUNICIPAL LANDFILL IN NOVI SAD

M. Djogo, A. Dvornić, D. Milovanović, J. Radonić, M. Turk Sekulić,
M. Vojinović Miloradov, G. Vujić

University of Novi Sad, Faculty of Technical Sciences, Department of Environmental Engineering,
Trg Dositeja Obradovića 6, 21000 Novi Sad (Serbia)

Leachate water is generated by dissolvement of solid organic and inorganic compounds and water filtrated through landfill body. Landfill leachates might contain, among many other constituents, heavy metals in considerable concentrations. The heavy metals may constitute an environmental problem, if the leachate migrates into surface water or groundwater, or a treatment issue where the leachate is collected and treated prior to discharge. The existence of heavy metals in aquatic environments has led to much concern over their influence on plant and animal life in these environments and indeed on man's need for wholesome water. The accumulation of these elements, many of which are highly toxic, can have direct consequences for man and animal life in the aquatic ecosystem. Municipal landfills containing a mixture of household waste, commercial waste, industrial waste and treatment sludges usually produce leachate with heavy metal concentrations in the microgram per litre to low milligram per litre level. In aquatic environments the metals will exist as free metal ions, inorganic complexes, organic complexes, and associated with colloids, where colloids generally are defined as small particles from around 1 nm up to 1–10 µm. Sampling of leachate water was conducted in winter and spring period from 5 piezometers on the municipal landfill in Novi Sad. The metal analysis (Cr, Zn, Cd and Ni) were done by the digestion of 50 mL of the water sample using concentrated nitric acid to release metals bound organic matter or adsorbed on solid particulates. The digested samples were analyzed by the atomic emission spectroscopy S2Series+VP 100 Thermo Scientific. All chemical were of p.a. quality. Using obtained results leachate water was classified according to the Serbian legislation. Concentration levels of cadmium in winter period mostly exceeded limit values, and were much higher than in spring, while concentration levels of zinc were significantly higher in spring. According to measured levels of chromium and nickel in both spring and winter period leachates were classified as category I water. This type of field investigation of the quality of water in piezometers in the municipal solid waste landfill in Novi Sad was conducted for the first time. The results of concentraton levels of heavy metals gained in this study are not homogenous and authors could not compare obtained results with previously published data in Serbia. The quality of the water in the piezometers is very important for the good ecological status of environment in general and, according to the newly systematic campaign which is planned, the part of these activities is in progress.

[1] Baun D.L., Christensen T.H., Speciation of heavy metals in landfill leachate: a review, Waste Management & Research, 22, 3-23 (2004)

[2] Ogundiran OO, Afolabi TA, Assessment of the physicochemical parameters and heavy metals toxicity of leachates from municipal solid waste open dumpsite. Int. J. Environ. Sci. Tech. 5 (2), 243-250 (2008)

P26- TRACE MERCURY IN THE ENVIRONMENT

I. G. Dakova, I. B. Karadjova and E. K. Mladenova

Department of Analytical Chemistry, Faculty of Chemistry, Sofia University,
James Bourchier Blvd. 1, 1164 Sofia (Bulgaria)

Mercury is a global priority pollutant with very high toxicity. Permissible levels in all life areas (environment, biological materials, pharmaceutical products, foods) are extremely low. Directive 2008/105/EU set up 0.05 μg L^{-1} as maximum permissible concentration for Hg(II) in surface waters. This concentration level is below the detection limit of direct CV-AAS instrumental determination and even more sensitive ICP-MS could not be applied for surface waters with high salinity. Consequently, separation and preconcentration procedure by solid phase extraction is often required before instrumental determination of Hg(II). Solid phase extraction procedures are widely applied and their efficiency depends mostly of properties of sorbent used. The aim of the present work is to characterize and to compare two sorbents for Hg(II) separation and preconcentration from surface water samples - cysteine modified silicagel (Si-CYS) and cross-linked chitosan membranes. The purpose is to achieve quantitative sorption of Hg(II) from acidic solutions thus separating it from interference matrix and elements, ensuring interference free instrumental measurement. The effect of chitosan cross-linking reagent (glutaraldechyde or epichlorohydrin) over the sorption process is investigated. The sorption was examined at various pH values and chloride concentration. Sorbent amount, flow rate and sorption time were parameters which were also varied in order to achieve the optimal conditions for quantitative sorption. Several eluents were tested and their influence on the next CV-AAS determination was considered. The extraction efficiency of both types of sorbents is compared from the view point of fast sorption process, ease of operation, possibilities for field application. Analytical procedures for laboratory and field determination of Hg in surface waters were developed and characterized. The accuracy of the results obtained was confirmed by direct ICP-MS measurements of Hg in relatively soft waters. Application of analytical methods developed for monitoring studies in Bulgaria is presented.

P27- ASSESSMENT OF CORROSION RESISTANCE OF MILLED RESTORATIVE MATERIALS

T. Paryjczak[1], D. Rylska[2], J. Sokołowski[3], K. Sokołowski[3], M. I. Szynkowska[1]

[1]Institute of General and Ecological Chemistry, Technical University of Lodz, Zeromskiego 116, 90-924 Łódź (Poland)
[2] Institute of Material Engineering, Technical University of Lodz, Stefanowskiego 1/15, 90-924 Łódź (Poland)
[3]Department of General Dentistry, Medical University of Lodz, Pomorska 251, 92-213 Łódź (Poland)

Conditions present in the human oral cavity conduce the fact that non dental alloys can stay completely resistant to all forms of corrosion. Oral cavity is extremely aggressive environment for dental materials and their degradation is caused by mechanical, chemical or mechanical and chemical influences. These factors are thought to be inseparable from each other. Constantly changing pH of saliva depending on the food intake, amount of the plaque present, composition of saliva, and stomach acidity and e.g. physical and chemical properties of foods and applied alloy contributes to corrosion process. Numerous performed studied proved that type of dental material employed, the surface area of exposed restoration, the technical fabrication and polishing procedures as well as other used metallic fillings are also responsible for corrosion activity. Created corrosion products in the oral environment are taken up by saliva, tissues and food. It is possible to some extent that they are able to enter the body fluids and then being transported throughout the body and as a result accumulated in various organs [1]. During last few years we are witnessing the promotion of milling technique of metallic elements of restorative materials forming instead of frequently used casting technology. Few papers, which have been published on that subject suggest that metal prosthodontic restorations produced by milling technique possess excellence properties. However, till now there is lack of comprehensive information concerning the assessement of their physic-chemical, mechanical and biological characteristics. Application of milling process eliminates unfavorable effects, which are typically connected with metal melting and cast formation, and in consequence affecting directly the improvement of mechanical features, corrosion resistance a thus their biological tolerance.

The aim of the present work was to compare some surface properties of casted WIROBOND C elements and profile-milled elements made from ZENOTEC™ NP (Co-Cr alloys). Studied samples were formed by two techniques: inductive casting with rotary method in Formax foundry and system of milling of ceramic and metallic elements of dental materials. The investigation included the evaluation of profile's surface, microstructure and chemical composition. The OCP versus time measurements and potentiodynamic polarization technique in 0.9% NaCl solution were used to determine the corrosion resistance of both kinds of samples. Moreover, the surfaces of dental materials were analyzed by scanning electron microscope Hitachi S-3000. The obtained results revealed that aqueous corrosion resistance is better in case of alloy manufactured by profile-milling method.

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[1] Jakovac, M., Živko-Babić, J., Ćurković, L., Aurer, A., J. Europ. Ceram. Soc. 26 1695-1700 (2006).

P28- BEHAVIOR OF A NUMBER OF METAL SPECIES IN A CONTAMINATED ESTUARINE SYSTEM

A. Kindness and L. Pillay

School of Chemistry, University of KwaZulu-Natal University of KwaZulu-Natal,
University Road, Westville, Private Bag X 54001, Durban 4000 (South Africa)

The Isipingo estuarine system located in Durban, South Africa has undergone a number of radical changes over the past twenty years. This region is characterised by a mixture of industrial and residential areas. Changes have been implemented to prevent the Isipingo River flooding into the industrialised section. These changes include reclamation of the wetland area to facilitate the construction of a number of large industries, diversion of the main river and canalisation to control the water inflow into the industrial sector.[1] The changes have resulted in inadequate inflow into the estuary creating conditions under which the estuary is unable to function naturally.

Sediment and water samples have been collected over a two year period from a contaminated estuarine system and the heavy metal content analysed. A number of metal contaminants have been identified in the system, most notably zinc, which is present at levels higher than 9000 mg/kg at some areas of the system. XPS data shows that ZnO is the predominant species.

The behaviour of metals in estuarine systems is complex. Factors other than pH and redox affect the mobilisation of metals under estuarine conditions *viz.* flow of water into and out of the system, industrial discharge and biogeochemical processes. In addition, the properties of water are in continual change as the river and seawater mix creating a salinity gradient. Non-conservative behaviour of metals occurs along the salinity gradient and depending on the pH, redox potential, temperature and organic matter of the system, mobilisation of metals occurs.

The behaviour of a number of heavy metals with respect to mobility, salinity, pH and redox has been investigated to determine the potential environmental problems this estuarine system may face.

[1] S. Kalicharran in *Proposals for the Rehabilitation and Management of the Isipingo Lagoon and Estuary*, *Vol. MSc* Universiy of Natal, Durban, p. 95 (1990).

P29- EVALUATION OF AIR CONTAMINATION GENERATED BY NON-AGRICULTURAL PESTICIDES: A FIELD CALIBRATION OF TENAX PASSIVE SAMPLERS

B. M. R. Appenzeller[1], O. Briand[2], M. Millet[3], C. Raeppel[1,3], L. Tuduri[4]

[1] CRP Santé, LNS, Laboratoire de Toxicologie, Université du Luxembourg, Campus Limpertsberg, 162A av. de la Faïencerie, 1511 (Luxembourg) – e-mail: claude.schummer@gmail.com
[2] AFSSET, 253 avenue du Général Leclerc, 94701 Maisons-Alfort Cedex (France)
[3] LMSPC, Equipe de Physico-Chimie de l'Atmosphère, (UMR 7515 CNRS - Université de Strasbourg), 1 rue Blessig, 67084 Strasbourg Cedex (France)
[4] Institut des Sciences Moléculaires (UMR-5255 CNRS-Université Bordeaux 4), LPTC, Site Universitaire, 24019 Périgueux cedex (France)

If the influence of agricultural activities on atmospheric contamination processes is now well documented, few studies are available about the impact of non-agricultural pesticides use on indoor and outdoor air quality. As part of a study conducted to evaluate the influence of these activities on air contamination, the passive air sampling technique is applied. This simple method, easy to carry out and low expensive, is a way to reply to the question of making large scale sampling campaigns necessary to a specific description of spatial and temporal contamination levels.

Passive samplers developed by our laboratory are fit out with a Tenax resin tube. This sampling support presents the advantage to be coupled with automatic thermal desorption (ATD). The extraction is then followed by a GC/MS analysis. This method is fast and do not need many steps before analyses. A time, sensibility and cleanness benefit is therefore guaranteed.

In order to calibrate the Tenax passive samplers, a field calibration has taken place in an open space midtown garden in Strasbourg. Two passives samplers and a low volume active sampler have been deployed in parallel during the same stretch of time. A Partisol Model 2300 Speciation Sampler equipped with a ChemComb Speciation Sampling Cartridge was used as active sampler. Cartridges were filled with glass fibber filters and XAD-2 resin. Passives samplers were exposed for 1 or 2 weeks and the ChemCom cartridge was changed every week. The Partisol was set on a constant volumetric flow rate of 16,7 L/min. Active samples were extracted in two steps by Accelerated Solvent Extraction (ASE) and Solid Phase Micro Extraction (SPME) and straight afterwards analysed by GC/MS. After the determination of the samples concentrations obtained by these both systems, the sampling rate could be calculated.

This value will be used latter during filed experiments for air concentration calculations.

P30- POLLUTION ASSESSMENT AND SOURCE IDENTIFICATIONS OF POLYCYCLIC AROMATIC HYDROCARBONS IN THE COASTAL SEDIMENTS OF KISH ISLAND

S. Rahmanpour, H. Rezaie, M. S. Hashtroudi

Department of Marine Living Resources, Iranian National Center for Oceanography (INCO),
Tehran (Iran)

Determination and measurement of Polycyclic Aromatic Hydrocarbons (PAHs) which is one of the main groups of persistent organic pollutants (POPs) has always been of great interest. [1] Kish Island is of growing importance in the region due to the urban growth, tourism and different economical activities. So, the sustainable development of this island requires great emphasis on environmental considerations. Regular environmental monitoring enables us to attain this goal.

In this regard, the levels and possible sources of 16 EPA priority polycyclic aromatic carbons (PAHs) in the sediments from 10 stations in the coastal area of Kish Island were investigated. The PAHs was analyzed using HPLC with UV and Fluorescence detectors. [2,3]. The total PAH concentrations ranged from 3.5 to 97.6 μg kg^{-1} with a mean value of 32.0 μg kg^{-1} indicating low levels compared to reported values of other coastal regions in Iran and other countries [3,4]. Naphthalene, Anthracen, Phenantherene, pyrene, Benzo(a)anthracene and Chrysene have the dominant concentrations among the others. The PAH compositions presumed the petrogenic source of pollution.

References:
[1] UNEP report, Inventory of Information Sources on Chemicals: 3-66(1999)
[2] Wolska L.Miniaturised, Journal of Chromatography A, 959, 1-2, 173-180(2002)
[3] Seyed Hashtroudi M., et al; INCO Report (2007)
[4] Eghtesadi P., G. Riazi, M. Taghikhani and S. O. Ranaei Siadat, 69, 5, 704-711(2002)

P31- ENVIRONMENTAL PROBLEMS OF THERMAL PROCESSING OF WASTE AND ANALYTICAL MAINTENANCE OF THE CONTROL POLLUTION

[1]A. Z. Razyapov, [2]S. S.Voronich, [1]A. P. Skibarko, [2]A. G. Yudin, [1]L. A. Shults

[1]National University of Science and Technology "MISIS", Leninsky prospect 4,
119049 Moscow (Russia)
[2]Department of Nature Use and Environmental Protection of Moscow,
Novy Arbat 11/1, 121019 Moscow (Russia)

Problems of the control technological processes of thermal processing of waste demand use complex modern analytical methods, different high sensitivity and selectivity with possibility of definition of a wide class of pollution substances. Necessity of a complex of methods is caused by complexity of the technology thermal processing, together with that a waste represents a difficult mix of organic and inorganic substances of various concentration.

In the report it is noticed that in Russia till now removal of the majority of kinds of a waste is carried out mainly on burial place ranges. According to authors much more effective way of the decision of a problem is controllable burning on the installations equipped with multistage systems of clearing of emissions. However and in this case there are problems of maintenance of ecological safety which demand use of high-grade systems of monitoring of emissions of pollution practically at all stages of technology of processing of a waste.

In the basic part of the report the estimation of possibilities of various designs of furnaces for processing of an industrial and household waste is given. The basic attention is given the small-sized two-chamber furnace of a design of authors providing highly effective burning in a combination to the minimum values of emissions of polluting substances.

Hardware-methodical maintenance of the control of multiphase technological process with use of a complex of modern analytical methods is in detail described. Results of experimental researches of emissions of dangerous and especially dangerous pollution which number the firm weighed particles, chlorides, fluorides, connections of heavy metals, dioxins concern are resulted. The data is presented also according to efficiency of various systems of clearing of pollution.

It is noticed also that from among analytical methods chromatography, spectroscopic and mass spectrometric methods of definition pollution continue to play an appreciable role. At the same time devices of the express control of thermo-physical, aerodynamic and other parameters of process processing of waste are necessary.

P32- DEVELOPMENT OF CHIRAL HPLC METHOD FOR MONITORING ENANTIOSELECTIVE BIODEGRADATION STUDIES OF PROPRANOLOL AND ATENOLOL

A. R. Ribeiro[1,2], P. M. L Castro [2] and M. E. Tiritan [1,3]

[1] Centro de Investigação em Ciências da Saúde (CICS), ISCS-N; R. Central de Gandra 1317, 4585-116 Gandra (Portugal)
[2] Centro de Biotecnologia e Química Fina (CBQF), Escola Superior de Biotecnologia, Universidade Católica Portuguesa; Rua Dr. António Bernardino de Almeida, 4200-072 Porto (Portugal)
[3] Centro de Química Medicinal da Universidade do Porto (CEQUIMED-UP), Faculdade de Farmácia; Rua Aníbal Cunha 164, 4050-047 Porto (Portugal)

Pollution from pharmaceuticals in the aquatic environment is nowadays a subject of major concern with a huge number of publications [1]. Pharmaceuticals reach the environment mainly due to inefficient removal in wastewater treatment plants (WWTP) and by improper disposal of unused medicines. In aquatic environments they reach concentrations in the ng/L to µg/L range, and many of them are resistant to degradation.

Despite the numerous on-going research of pharmaceutical in the environment, the fate and effects of enantiomers in chiral pharmaceuticals in the environment are still largely unknown [2]. In spite of the similar physical chemistry properties, enantiomers have different interactions with enzymes, receptors or other chiral molecules leading to different biological activities and so they can affect the organisms in the environment in a different manner. Thus, biodegradation tends to be enantioselective in contrast to abiotic degradation. It is urgent to develop methodologies to determinate the enantiomeric fraction of chiral compounds in the environment and to study their biodegradation. This work describes the investigation on the resolution of propranolol and atenolol on three CSPs: *tris* 3,5-dimetylphenylcarmate of cellulose and amylose e one macrocyclic antibiotics (ASTEC Chirobiotic V 5µm) under different elution modes (normal, reversed and polar organic). The results were compared in order to establish the best choice to validate the method.

The 3,5 dimethyl carbamate of cellulose was able to resolve both atenolol and propanolol under normal phase (hexane:ethanol:diethyamine) in a single chromatographic run. The best parameters obtained has shown the separation factor of 1.4 and 1.2; resolution of 2.13 and 1.2 for propranolol and atenolol respectively.

[1] Kümmerer, K., J Environ Manage 90, 2354-2366 (2009).
[2] Stanley, J. K and Brooks, B. W., Integr Environ Assess Manag 5: 3, 364–373 (2009).

P33- METABOLITES OF NERVE AGENTS DETERMINATION BY CAPILLARY ELECTROPHORESIS

I. Ribalchenko [1], I. Rodin [2], O. Shpigun [2], R. Smirnov [2]

[1] Lumex Ltd., Suschevsky val 47-1, 127018, Moscow (Russia)
[2] Department of Analytical Chemistry, Chemical Faculty, M.V. Lomonosov Moscow State University, Lenin hills 1-3, 119991 Moscow (Russia)

V-gases are a group of a nerve chemical warfare agents (CWA, weapons of mass destruction), developed in the 50-70-ies of the XX-th century. According to the Convention on the Prohibition of the Development, Production, Stockpiling and Use of Chemical Weapons and on Their Destruction (CWC), V-gases are not allowed to use and their stockpiles are gradually destroyed. However, the potential danger of the use and impact of these substances still remains actual and is associated primarily with countries that have or develop chemical weapons and not ratifying the CWC; the terrorist groups and the productions aimed at the destruction of existing stocks of CWA. For example in Russia the total production of VR (R-33, the Russian analogue of the U.S. VX) was more than 15,000 tons. Thus, the problems of establishing the facts of impact of V-gases, their determination in the environment objects and the development of appropriate analytical techniques are still actual.

V-gases are few-volatile compounds with high boiling point and relatively high resistance to destruction. From a chemical point of view, most of them are from the class of S-dialkylaminoethyl-, O-alkyl- ethers of alkylphosphonic acid (VX, VR (R-33), VG and also VE, VM and VS offered as a perspective). When released into the environment and impacting animals and human, these compounds gradually decompose with the formation of the corresponding N,N-dialkylaminoethanesulfonic acids and esters of alkylphosphonic acids, which are much more stable than the initial compounds. These compounds are specific and not found in nature, and therefore may serve as markers, indicating the fact of use of V-gases.

In this work, several approaches to the determination of N,N-dialkylethanesulfonic acids in waters by capillary electrophoresis with spectrophotometric detection were proposed. N,N-dialkylethanesulfonic acids, represent the derivatives of taurine - aminoethanesulfonic acid. The developed approaches allowed to create and validate a technique for screening and quantitative determination of four N,N-dialkylethanesulfonic acids (where alkyl = methyl, ethyl, n-propyl and iso-propyl) in the mode of direct (200 nm) and indirect (254 nm) detection at the concentration level of 5-10 ppm. The optimization of separation conditions and the detection of the analyzed components were carried out. Lack of interference from the matrix (water from central water supply system, water from wells, melting snow, melting snow from the gas station with high oil content, water from the Moscow river) and good accuracy and precision were shown.

P34- ORGANOCHLORINE PESTICIDES AND POLYCHLORINATED BIPHENYLS IN ATMOSPHERIC FINE PARTICLES COLLECTED IN ZAGREB OVER TEN YEARS

I. Bešlić, V. Drevenkar, R. Godec, M. Sambolec, K. Šega, and Ž. Vasilić

Institute for Medical Research and Occupational Health, Ksaverska c. 2,
HR-10000 Zagreb (Croatia)

Organochlorine (OC) pesticides and polychlorinated biphenyls (PCBs) belong to a group of widespread, highly persistent, lipophilic, and semivolatile environmental micropollutants. They can be transported over long distances by circulation of air masses, precipitation of particles onto which pollutants are sorbed, and by wet depositions washing them out from the atmosphere. Their sorption to airborne inhalable particles with an equivalent aerodynamic diameter of <10 μm (PM_{10}) and respirable particles with an equivalent aerodynamic diameter of <2.5 μm ($PM_{2.5}$) is of special concern because particle toxicity varies not only with size but also with chemical composition. We studied the occurrence and levels of OC pesticides (hexachlorobenzene, α-, β-, and γ-hexachlorocyclohexane, 4,4'-DDT, 4,4'-DDE, 4,4'-DDD) and 20 PCB congeners (six indicator congeners: PCB-28, PCB-52, PCB-101, PCB-138, PCB-153, and PCB-180, and fourteen other toxicologically significant congeners: PCB-60, PCB-74, PCB-77, PCB-105, PCB-114, PCB-118, PCB-123, PCB-126, PCB-156, PCB-157, PCB-167, PCB-169, PCB-170, and PCB-189) in PM_{10} and/or $PM_{2.5}$ samples collected daily from October 2000 to December 2003, from January to March 2010, and from June to July 2010 at a site in the northern residential part of Zagreb. Twenty-four-hour samples of particle fractions were collected on one or two glass or quartz microfibre filters in parallel, from approximately 100 m^3 of ambient air per filter at the average air flow rate of 70 L min^{-1}. Filters with particle samples collected over seven consecutive days were combined for chemical analysis. The collection and analysis of seven-day air samples instead of seven combined 24-hour samples failed because of considerable volatilisation losses leading to an underestimation of particle-bound micropollutants. OC compounds associated with particles were accumulated by ultrasonic extraction with 1:1 acetone:*n*-hexane mixture. The extracts were purified with sulphuric acid and analysed using high resolution gas chromatography with electron capture detection. In the monitored ten-year period, mass concentrations of OC compounds in fine particles in air (pg m^{-3}) were characteristic of global environmental pollution. Their abundance and concentrations in $PM_{2.5}$ and $PM_{10.5}$ particle fractions did not significantly differ, which suggests that they were mainly sorbed in the respirable $PM_{2.5}$ fraction. A local input was observed only for γ-HCH, but a decrease in its environmental levels might be expected, since lindane has been banned for use in agriculture and forestry in Croatia since 2005. This study showed no pronounced seasonal variations in the concentrations of particles carrying any OC compound. A decreasing trend in the mass concentrations of β-HCH, 4,4'-DDE, 4,4'-DDT, PCB-138, PCB-153, and PCB-180 with increasing air temperature may be related to lower fine particles mass concentrations at higher temperatures, and, consequently, to less OC particle-bound compounds in the atmosphere.

P35- PHOTOELECTROCHEMICAL PROPERTIES OF NANOSTRUCTURED ELECTRODE WITH TITANIA NANOTUBE ARRAYS

L. Sang and Z. Zhang

Key Laboratory of Enhanced Heat Transfer and Energy Conservation, Ministry of Education and
Key Laboratory of Heat Transfer and Energy Conversion, Beijing Municipality,
College of Environmental and Energy Engineering, Beijing University of Technology, No.100
Pingleyuan, Chaoyang District, 100124, Beijing (China)

TiO_2 is one of the most promising candidates for a commercial photoelectrode for photoelectrochemical cell(PEC) for production of solar-hydrogen. TiO_2 nanotube arrays were fabricated by sonoelectrochemical anodic oxidation and calcined in nitrogen (TNT-N), air (TNT-A), and 5% hydrogen/ nitrogen (TNT-H). X-ray diffraction (XRD) and field emission scanning electron microscopy (FESEM) were used to characterize the crystal phase and surface morphology of the resulting oxide films. UV–vis diffuse reflectance spectra, voltammetry curves, Mott-Schottky plots and electrochemical impedance spectroscopy (EIS) were applied to investigate their photoelectrical properties and the charge transfer behaviors. It is found that TiO_2 nanotube arrays annealed in different gases exhibited similar surface morphology. But the photocurrent densities of the TNT-A, TNT-N and TNT-H under UV illumination (365±15nm) were about $0.27mA/cm^2$, $0.45mA/cm^2$ and $0.60mA/cm^2$, respectively. Because of the reduction of Ti^{4+} and the formation of oxygen vacancies, the charge transfer resistance showed in this order: TNT-A> TNT-N> TNT-H. It also affects the separation rate of photogenerate electron-hole pairs. TNT-H obtained the greatest charge carrier density of $9.86\times10^{20}cm^{-3}$, TNT-N and TNT-A possessed the less charge carrier density of $1.38\times10^{20}cm^{-3}$ and $1.06\times10^{20}cm^{-3}$, respectively.

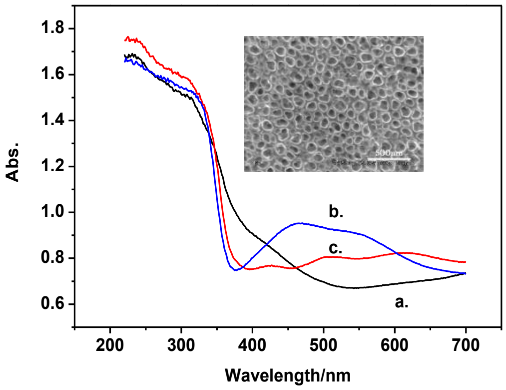

Fig 1 DRUV-vis spectra of as-prepared TiO_2 nanotubes annealed in (a) Air ,(b) N_2 and (c) 5% H_2/N_2 Inset is the FESEM image of the TiO_2 nanotubes

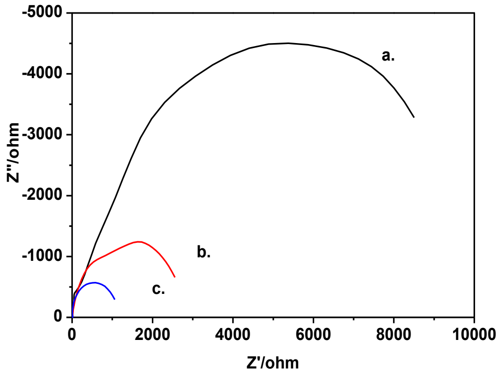

Fig 2 Electrochemical impedance spectroscopy plots of TiO_2 nanotubes annealed in (a) Air , (b) N_2 and (c) 5% H_2/N_2

[1] A. Fujishima, X.T. Zhang, D.A. Tryk. Surf. Sci. Rep. 63, 515-582(2008).
[2] H.F. Zhuang, C.J. Lin, Y.K. Lai, L. Sun, J. Li. Environ. Sci. Technol. 41, 4735-4740(2007).

P36- THE INFLUENCE OF NANOSILVER ADDITION ON METAL IONS RELEASE FORM LIGHT-CURED COMPOSITE AND COMPOMER RESTORATIVE MATERIALS INTO 0,9% NaCl

J. Sokołowski[1], K. Sokołowski[1], M. I. Szynkowska[2]

[1]Department of General Dentistry, Medical University of Lodz, Pomorska 251,
92-213 Łódź (Poland)
[2]Institute of General and Ecological Chemistry, Technical University of Lodz, Zeromskiego 116,
90-924 Łódź (Poland)

Nowadays, a wide spectrum of dental materials is available, material properties depend on the basic material type e.g. metals, ceramics or polymers. In fact, a detailed understanding of the key concept for each of them gives an insight into how each class of material can behave as a restorative dental material, as well as an idea of the potential of these materials if some of their limitations can be overcome. There is no surprise that only certain specific material properties determine their selection for application in restorative dentistry. Basing on that knowledge, it is possible to make a proper selection of the material being the best compromise of desired properties versus inherent limitations. Due to the fact that any class of basic type of presented materials possesses all the desired properties, in many cases they are used in combination limiting their usefulness [1]. The main objective of this study was to assess the release of ions by dental fillings into 0.9% NaCl solution in different time intervals. The investigated dental materials were samples of X Flow composite material with nanosilver and Dyract Flow compomer material with nanosilver, both being a light-cured dental restorative material with flow characteristics, which make it ideal for small cavities in anterior and posterior teeth. Composite restorations seem to represent excellent aesthetics properties, but due to the fact that they undergo polymerization shrinkage on setting, they are associated with marginal leakage, which causes bacterial penetration and, in consequence, the potential damage to the tooth. Notwithstanding, fluoride-releasing materials in combination with silver ions can influence the surrounding micro-environment, involving bacteria. Each of the samples was first washed with ethanol and then placed in a test-tube in 10 mL 0.9% NaCl solution. A number of counts of metal ions released into NaCl solution from the dental materials were determined using Optimass 8000 ICP-TOF-MS spectrometer (GBC Scientific Equipment, Australia) after a week, a month and three months time of storage. The results confirmed the significant increase in the number of counts of metal ions originating form the main components of studied dental material with the time of storage. The gathered spectra were also compared with some previous outcomes obtained for other restorative materials not containing silver in their composition.

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[1] O'Brien, W.J., “Dental materials and their selection”, 3rd Edition, Quintessence Publishing Co, Inc, Hanover Park (2002).
[2] Gjorgievska, E., Nicholson, J.W., Iljovska, S., Slipper, I., Contributions, Sec. Biol. Med. Sci. XXX/1 191-203 (2009).

P37- ENVIRONMENTAL "LIFE COURSE" OF A REPRESENTATIVE LIST OF PHARMACEUTICAL POLLUTANTS AND RESULTING TRANSFORMATION PRODUCTS: A PORTUGUESE CASE STUDY

M. F.Alpendurada, E. Cunha,C. Gonçalves and M. A. Sousa

Laboratory of Hydrology, Faculty of Pharmacy, University of Porto, Rua Aníbal Cunha,
164 / 4050-047 PORTO (Portugal); IAREN – Water Institute of the Northern Region,
Rua Dr. Eduardo Torres, 229 / 4450-113 Matosinhos (Portugal)

The concern over environmental pollution by pharmaceuticals and their by-products has been escalating over the past few years, propelling both scientific research as well as legal efforts, to protect and restore clean water and ensure its long-term, sustainable use. Among the various sources of pollution by pharmaceuticals, we can identify poorly (or un)treated effluents of hospitals and, clearly, wastewater treatment plants (WWTPs).

Accordingly, one purpose of this work was to properly characterise the pharmaceutical clean-up efficiency of a WWTP, built upon the riverside of a small tributary of Douro River (southern bank), located in the north region of Portugal. Furthermore, we aimed to assess the influence of the sampling methodology and its contribution to samples representativeness. In addition, the impact of the effluent discharges on the water quality of this small tributary was also evaluated.

The 23 pharmaceutical parent compounds included in the study are among the most consumed in Portugal over the last couple of years and belong to distinct therapeutic groups, comprising antibiotics, analgesic and antipyretic drugs, anti-inflammatories, lipid regulators, anxiolytics, antidepressives, diuretics, cardiotonics and anti-ulcer agents. The analytical method applied to wastewaters encompassed one single step of simultaneous clean-up and extraction, achieved with Oasis MAX adsorbent, while river waters followed a previous clean-up with Bakerbond spe 1º,2º-Amino (NH_2/NH) columns and were subsequently enriched on Bakerbond H_2O-philic cartridges. Both pursued LC-ion trap-MS/MS detection and the criteria set for positive identification included a fitting probability against a created MS^3-spectrum library >70%.

The monitoring results for influents showed that paracetamol highlights in concentrations above 10 $\mu g.L^{-1}$, followed by hydrochlorothiazide, furosemide, naproxen, ibuprofen, diclofenac and bezafibrate, with concentrations in the low $\mu g.L^{-1}$ range. Gemfibrozil and simvastatin occurred, on average, on several $ng.L^{-1}$ levels (>500), whereas ketoprofen was quantified in lower concentrations. Apart from the mentioned pharmaceutical groups, also azithromycin, bisoprolol and paroxetine were detected, though still in very significant concentrations. Regarding effluents, a similar scenario was found, apart from paracetamol and hydrochlorothiazide (now below the quantification limit). As to Douro's tributary waters, downstream the WWTP, they significantly increased their content in bisoprolol (> twice) and furosemide (more than 6 times), whereas hydrochlorothiazide, azythromycin, diclofenac, gemfibrozil and simvastatin became quantifiable in concentrations ranging from 40 to 360 $ng.L^{-1}$.

Finally, some by-products' structure predictions were attempted through a stepwise procedure, employing bioinformatic tools (namely the "University of Minnesota Pathway Prediction System (UM-PPS)"). Some transformation products were subsequently searched in different stages of the pathway.

P38- USE OF TiO_2 IN DIFFUSIVE GRADIENTS IN THIN FILMS TECHNIQUE (DGT) FOR MERCURY DETERMINATION IN AQUATIC ENVIRONMENT

P. Diviš[1], H. Dočekalová[2], M. Kadlecová[1], R. Szkandera[1] and J. Trávníčková[1]

[1]Brno University of Technology, Faculty of Chemistry, Purkyňova 118,
612 00 Brno (Czech Republic)
[2]Mendel University in Brno, Zemědělská 1/1665, 613 00 Brno (Czech Republic)

Titanium dioxide (TiO_2), recently used for determination of dissolved reactive phosphorus [1] and for speciation of inorganic arsenic and selenium [2] by diffusive gradients in thin films technique, was tested as a new binding agent for labile mercury species. Validation experiments have confirmed linear accumulation of mercury in TiO_2 adsorbent gel. The performance of TiO_2 was verified over environmentally relevant pH and ionic strength ranges. Results obtained by new DGT units with TiO_2 deployed into river sediment were similar to those obtained by previously verified Duolite GT 73 with thiol groups. Concentrations of mercury measured by commonly used Chelex-100 were lower compared to the above mentioned Duolite GT 73.

References:

[1] J. Panther, P. Teasdale, H. Zhao: Evaluation of DGT for accumulating dissolved reactive phosphorus in natural waters: a comparative study between ferrihydride and titanium dioxide adsorbents, Conference on DGT and the Environment, Santa Margherita di Pula, Italy, 2009
[2] W. Bennett, P. Teasdale, D. Welsh, D. Jolley: A novel diffusive gradients in a thin film (DGT) technique for the speciation of inorganic arsenic and selenium, Conference on DGT and the Environment, Santa Margherita di Pula, Italy, 2009

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P39- THE RELEASE STUDY OF THE METAL IONS FROM RESTORATIVE MATERIALS INTO 0,9 % NaCl SOLUTION

E. Leśniewska[1], T. Paryjczak[1], A. Pawlaczyk[1], J. Sokołowski[2],
K. Sokołowski[2], M. I. Szynkowska[1]

[1]Institute of General and Ecological Chemistry, Technical University of Lodz, Zeromskiego 116,
90-924 Łódź (Poland)
[2]Department of General Dentistry, Medical University of Lodz, Pomorska 251,
92-213 Łódź (Poland)

Dental materials belong to the group of the most used substitutes for biological tissue in the human body. It is assessed that in industrial countries even up to 50% of population receives new dental restorations annually. The negative effect of mercury containing amalgam and also esthetical factors have led to introduction of new materials on the dental market [1]. The restorative materials used nowadays are applied mainly in repairing frank cavities in teeth that have been damaged by caries, designed especially to be resistant to secondary caries and to micro-leakage at the edges. Resin-modified glass-ionomer cements and polyacid-modified composite resins called compomers seem to be the most important. It is postulated that by releasing fluoride, these materials offer protection to the hard dental tissues and the surrounding micro-environment [2]. Many patients who have received dental material in their early age leave it in their body for a large part of life. Their common use and longevity in the body extort a necessity of their low toxicity. Some papers suggest that many of the materials uses in stomatology can possess a potential hazard to human health. As a result, more detailed studies are needed to get information about dental fillings which are not sufficiently described in the literature and which in the future can present side effects unknown to both patients and dental personnel. It seems crucial to introduce more restricted regulation of dental materials, at least for substances that patients will be exposed to for decades [1].

The aim of the present work was to evaluate the release of ions by dental fillings into 0.9% NaCl solution in different periods of time. The investigated material consists of samples of composites X Flow Demi and compomer Dyract Flow Demi, both being a light-cured restorative material with flow characteristics which make it ideal for small cavities in anterior and posterior teeth. Dyract flow restorative is assumed to represent more restoration-protecting fluoride than conventional composite flowables. Each of the samples was first washed with ethanol and then placed in a test-tube in 10 mL 0.9% NaCl solution. A number of counts of metal ions released into NaCl solution from the alloys were determined using Optimass 8000 ICP-TOF-MS spectrometer (GBC Scientific Equipment, Australia) after a week, a month and three months of storage. The obtained spectra showed a significant increase in the number of counts of metal ions originating form the dental material composition with the time of storage.

The financial support of this work by the Polish Scientific Research Council (grant N N205 1806 33) is gratefully acknowledged.

[1] Tillberg, A., Järvholm, B., Berglund, A., Dental Materials 24 940 (2008)
[2] Gjorgievska, E., Nicholson, J.W., Iljovska, S., Slipper, I., Contributions, Sec. Biol. Med. Sci. XXX/1 191-203 (2009)

P40- USING LIQUID CHROMATOGRAPHY-TANDEM MASS SPECTROMETRY TO MONITOR ACCIDENTAL OR DELIBERATE PESTICIDE POSIONING OF VERTEBRATE WILDLIFE AND DOMESTIC ANIMALS IN SCOTLAND

G. A. Keenan, L. M. Melton, E. A. Sharp, M. J. Taylor and J. E. Watson

Chemistry Branch, Science and Advice for Scottish Agriculture (SASA),
Roddinglaw Road, Edinburgh, EH12 9FJ (Scotland)

The Wildlife Incident Investigation Scheme (WIIS) operated in Scotland by SASA investigates poisoning of vertebrate wildlife, pets, livestock and honeybees if it is suspected that pesticides or biocides may have been involved. The ‘active ingredients’ of the numerous plant protection and public hygiene products commercially available can be extremely toxic to aquatic species, birds, mammals and even humans particularly when they are used incorrectly.

There are hundreds of different ‘active ingredients’ possessing a wide range of physical and chemical properties and it is challenging to differentiate these extraordinary contaminants from many other natural chemicals and substances that exist in a test specimen. Consequently, we have been using Liquid Chromatography-Tandem Mass Spectrometry (LC/MS/MS) to separate, identify and quantify multiple-pesticide residues that may remain in or on the test specimen. This poster presents details of:

- The analytical strategy,
- Results obtained following analysis of various specimens involved in accidental or deliberate poisoning and
- How the results provide valuable feedback into the regulatory process and are used as evidence by the Scottish Government and police to identify violation of legislation relating to the safe use of pesticides and protection of the environment and animals.

P41- MICROBIAL DEGRADATION OF SEVERAL PHARMACEUTICALS MONITORING BY VALIDATED HPLC-DAD METHOD

C. Maranhão[2], M. T. Soares[2], A. R. Ribeiro[1,2], V. Gonçalves[2], A. Maia[2],
M. F. Carvalho[1], P. M. L Castro[1], and M. E.Tiritan[1,3]

[1] Centro de Investigação em Ciências da Saúde (CICS), ISCS-N; R. Central de Gandra 1317, 4585-116 Gandra (Portugal)
[2] Centro de Biotecnologia e Química Fina (CBQF), Escola Superior de Biotecnologia, Universidade Católica Portuguesa; Rua Dr. António Bernardino de Almeida, 4200-072 Porto (Portugal)
[3] Centro de Química Medicinal da Universidade do Porto (CEQUIMED-UP), Faculdade de Farmácia; Rua Aníbal Cunha 164, 4050-047 Porto (Portugal)

Pollution from pharmaceuticals and their metabolites in the environment is of great concern, therefore research studies on this area have been regularly reported [1]. Pharmaceuticals reach the environment mainly due to inefficient removal in wastewater treatment plants (WWTP) and by improper disposal of unused medicines. In aquatic environments they reach concentrations in the ng/L to µg/L range, and many of them are resistant to degradation [2].
This work describes a validated HPLC-DAD (High Performance Liquid Chromatography – Diode Array Detector) method for quantification of five pharmaceuticals [trimethoprim (TMP), sulfamethoxazole (SMX), ciprofloxacine (CPF), carbamazepine (CBZ), and diclofenac (DCL)], for monitoring their biodegradation.
The separation of the target pharmaceuticals was performed using an environmental friendly mobile phase composed by a gradient of 0.1% triethylamine (TEA) in water acidified at pH=2.23 with trifluoroacetic acid (TFA) and ethanol. The validated method demonstrated selectivity, linearity ($r2 > 0.99$) and precision ($1.85\% < RSD < 8.24\%$) in the range of 1.0 µg/mL – 30.0 µg/mL. The quantification limits were: TMP: 0.61 µg/mL; SMX: 0.81 µg/mL; CPF: 0.60 µg/mL; CBZ: 0.58 µg/mL and DCL: 0.63 µg/mL. Biodegradation studies were performed during 22 days using two microbial consortia: activated sludge (AS) and a consortium able to degrade aromatic compounds, namely fluorobenzene (FB).

[1] Kümmerer, K., J Environ Manage 90, 2354-2366 (2009).
[2] Loos, R., Gawlik B.M, Locoro, G., Rimaviciute E., Contini, S., Bidoglio, G., Environ. Pollut. 157, 561-568 (2009).

P42- NEW IMMUNOSENSORS FOR 2,4-D AND 2,3,5-T PESTICIDES DETERMINATION

L. Campanella, E. Martini, M. Tomassetti

Department of Chemistry, “Sapienza” University of Rome, P.le Aldo Moro 5,
00185 Rome (Italy)

Both 2,4-D and 2,3,5-T, dichloro- and trichloro-phenoxyacetic acid, respectively, are chlorinated herbicides, that is, synthetic compounds forming the active principle of the socalled “Agent Orange” known to have been used as a defoliant in recent conflicts.

Many herbicides are persistent and can remain active for several years in the environment [1], causing ecological damage. This has led to an increase in health risk due to chronic toxicity through continual, long-term low level exposure to pesticides. Typical examples of such herbicides are 2,4-D and 2,3,5-T, which are widely used for weed control in agriculture [2]. These chlorinated herbicides are in fact commonly used to restrict the growth of weeds in cultivated fields, together with other pesticides, i.e. atrazine, used for the disinfestation of cereals, maize and hay. Owing to their long-term persistence, their trace levels appear also in groundwater. The reference method for the determination of pesticides in water and in plants is generally chromatography, either GC and HPLC. However such methods are not suitable for on-site analysis as they are laborious and time consuming. Furthermore, sample pre-treatment is required and equipment costs are high. The various determination methods reviewed in the literature include enzyme inhibition biosensor methods. These are based on the degree of inhibition of enzymes, including tyrosinase. However, it has so far proved impossible to develop this type of inhibition biosensor to cater for chlorinated pesticides such as 2,4-D and 2,3,5-T.

Enzyme immunoassay is a powerful and flexible tool used in on-site environmental screening methods. In particular, electrochemical immunosensor methods allow more economic assays. Our team recently developed an immunosensor suitable for atrazine analysis [3]. However, the aim of the present research was to develop highly selective and sensitive amperometric immunosensors for 2,4-D and 2,3,5-T based on “competition” assay procedures. The two new immunosensors developed utilize non commercial antibodies, an amperometric electrode for hydrogen peroxide as transducer and the peroxidase enzyme as marker. The results show the full validity of these immunosensor methods, which were optimized by determining the best “competition” operating procedure. These immunosensors were also used to test pesticide recovery from common real matrices such as field samples of grass and other plant species, for which good results were obtained. The immunosensors developed demonstrated a high selectivity to different kinds of pesticides and may thus be considered as suitable devices for application to real matrices.

[1] J. Killard, L. Micheli, K. Grennan, M. Franek, V. Kolar, D. Moscone, I. Palchetti, R. Smyth, Anal. Chim. Acta 427, (2001) 173-180.

[2] R.W. Keay, C.J. McNeil, Biosens. Bioelectron. 13(9), (1998) 963-970.

[3] L. Campanella, D. Lelo, E. Martini, M. Tomassetti, in Sensors and Microsystems, Proceedings of the 13th Italian Conference, World Scientific Co, Singapore, 2009. Pp. 42-45.

P43- APPLICATION OF DGT TECHNIQUE IN ASSESMENT OF AVAILABILITY OF COPPER TO *RAPHANUS SATIVUS*

B. Dočekal[1], H. Dočekalová[2], J. Trávníčková[3]

[1]Institute of Analytical Chemistry, Academy of Science of the Czech Republic v.v.i., Veveří 97,
CZ-602 00 Brno (Czech Republic)
[2]Faculty of Agronomy, Mendel University in Brno, Zemědělská 1/1665,
CZ-613 00 Brno (Czech Republic)
[3]Department of Environmental Chemistry and Technology, Faculty of Chemistry, Brno
University of Technology, Purkyňova 118, CZ-612 00 Brno (Czech Republic)

The content of heavy metals in agricultural soils is gradually increasing from various processes such as utilization of fertilizers, atmospheric fall-out etc. These metals may transfer from contaminated soils into growing plants. Therefore, it is essential to assess the biological relevance of heavy metals in soils. Various leaching procedures are applied for this purpose. Total mineral analysis procedures can not provide information on biochemical activity of heavy metals. Sequential extraction procedures are adopted for determination of heavy metals distribution in different forms and phases. Diffusive gradient in thin films technique (DGT) can be applied for characterization of soils. DGT probe, when deployed in the soil disturbs soil/pore water equilibrium and simultaneously measures the response of the soil, re-supply fluxes of labile metal species from the soil solid phase to soil solution.

The results of DGT experiments under specified conditions and results of extraction techniques by common leaching procedures are presented and compared with respect to copper uptake in various parts of an experimental plant (*Raphanus sativus*) cultivated in pot experiments on a tested non-treated and gradually spiked soil.

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P44- HEADSPACE SINGLE-DROP MICROEXTRACTION OF COMMON PESTICIDE CONTAMINANTS IN HONEY

E. G. Amvrazi[1], M. A. Martini[1,2] and N. G. Tsiropoulos[1,2]

[1]Department of Agriculture, Crop Production and Rural Environment, University of Thessaly, Fytokou Str., 38446, Nea Ionia Magnissias (Greece)
[2]Applied Public Health and Environmental Hygiene Program, Medical School, University of Thessaly, Larissa (Greece)

The analysis of pesticide contaminants in honey demands extremely sensitive and selective analytical methods to meet the ultratrace levels of pesticides occurrence in honey and overcome the analytical problems derive from complex matrices as is honey [1]. Microextraction techniques are much promising techniques with lots of advantages as compared with classic analytical techniques for this type of analyses whereas headspace microextraction techniques could have the additional advantage to eliminate sample matrix induced interferences because disturbing matrix components remain in the sample solution. In the present work the headspace single-drop microextraction (HS-SDME) of common pesticide contaminants (diazinon, lindane, chlorpyrifos ethyl, DDE 4-4, and endosulfan) in honey was studied experimentally and an analytical protocol was further developed by the use of a multivariate optimization. The HS-SDME analytical method developed and two more analytical protocols for the determination of pesticides in honey by direct SDME [2] and liquid liquid extraction [3] were validated in parallel for the determination of target pesticides in honey and the three methods were further applied in the same real honey samples. The most favourable analytical characteristics from the later comparative study were achieved by direct SDME (by direct SDME LODs ranged from 0.04 μg/kg for β-endosulfan to 2.40 μg/kg for diazinon and repeatability expressed as %RSD from 3 for lindane to 15 for diazinon and chlorpyrifos methyl, by HS-SDME LODs ranged from 0.07 μg/kg for DDE 4-4 to 12.54 μg/kg for chlorpyrifos methyl and repeatability expressed as %RSD from 11 for chlorpyrifos methyl to 19 for DDE 4-4, and by LLE LODs ranged from 0.09 μg/kg for β-endosulfan to 19.31 μg/kg for diazinon and repeatability expressed as %RSD from 6 for DDE 4-4 to 11 for lindane) for all target pesticides but DDE 4-4 that did not recovered by direct SDME, whereas the proposed HS-SDME optimized in this study was shown to be the method of choice for the determination of diazinon in honey.

In conclusion, in the present study it was demonstrated that HS-SDME could be applied with success for the determination of pesticide contaminants in honey. Since, pesticides are semivolatile compounds and honey a complex analytical matrix the HS-SDME application may comprise several difficulties to be overcome by the use of different extraction conditions that should be optimized carefully and/or demand extra steps in the whole analytical protocol.

[1] Kujawski, M.W., Namieśnik, J., Trends in Anal. Chem. 27 (9), 785-793 (2008).
[2] Tsiropoulos, N.G. and Amvrazi, E.G., J. AOAC Int. *In Press*
[3] Blasco, C., Lino, C.M., Pico, Y., Pena, A., Font, G. and Silveira, M.I.N. J. Chromatogr. A, 1049, 155-160 (2004).

P45- DETERMINATION OF PESTICIDES BY SPE AND HPTLC: APPLICATION IN REUSE RAINWATER

M. Tanguy[1,2], C. Vialle[1,2], C. Sablayrolles[1,2], M. Montrejaud-Vignoles[1,2]

[1]Université de Toulouse; INP; LCA - Laboratoire de Chimie Agro-Industrielle;
ENSIACET, 4 Allées Emile Monso, F-31029 Toulouse (France)
[2]INRA; LCA - Laboratoire de Chimie Agro-Industrielle; F-31029 Toulouse (France)

Reuse of rainwater collected downstream of roofs is currently booming for outdoor uses, like garden watering, or domestic uses, such as WC flushing supply. In fact, this practice is said to be an interesting way to preserve the water resources, while allowing consumers to save money. However rainwater washes down the atmosphere and roofs before being stocked in an underground tank. Thus, it contains, in addition to dust, all the particles and urban pollution from industries and car fumes, notably pesticides sometimes in large concentrations. As a result, it is now necessary to detect and quantify pesticides in rainwater, with a specific and applicable routine technique, to ensure a water quality high enough for the development of such systems. In this study, 14 pesticides likely present in the Midi-Pyrenees (France) rainwater were selected: atrazine, simazine, metolachlor, endosulfan, lindane, trifluralin, alachlor, diuron, desethylatrazine, epoxiconazole, glyphosate, tebuconazole, bentazone and iodosulfuronmethyl-sodium. The selection was made according to specific criteria, such as their use in regional cultures and their detection in the wastewater treatment plants. Solid phase extraction (SPE) on Licrolut® RP-18 cartridges was carried out. Different volumes of drinking water samples, the impact of their acidification and three elution solvents were tested with benzanilid as internal standard. Then, analysis was performed by high-performance thin-layer chromatography (HPTLC) from CAMAG coupled with UV detection. Extracts were deposited on precoated HPTLC plates silica gel MERCK 60 F254 (20 x 10 cm) with an Automatic TLC Sampler III (ATS). A universal gradient based on dichloromethane was optimized using automated multiple development (AMD) to separate a mix of pesticides. The screening and quantification was then performed using a TLC Scanner IV. At the same time, rainwater samples were weekly collected in two roof run-off harvesting systems installed in the south-west of France. The first one is located in an individual house in a rural zone and the second one in a building in an urban area. The developed method was first validated on spiked drinking water and then used to analyze rainwater before and after run-off.

[1] Butz, S. and Stan, H. J., Anal. Chem. 67, 620-630 (1995) [2 Mc Ginnis S. C.and Sherma, J. Liq. Chromatogr., 17(1), 151-156 (1994) [3 CAMAG, Application notes Instrumental thin layer chromatography, A.28-7

P46- METAL-ENHANCED FLUORESCENCE BASED DETECTION OF BISPHENOL A

Dr. C. D. Geddes, S. A. Young

Institute of Fluorescence and Department of Chemistry and Biochemistry,
The University of Maryland, Baltimore County,
701 East Pratt Street Baltimore, Maryland 21202 (USA)

Bisphenol A (BPA) is a widely used monomer, commonly used as an intermediate in the production of polycarbonate plastics. It is found in many household products such as baby bottles, reusable plastic containers, food cans, dental sealants, occupational protective gear, automation equipment, and electrical appliances to name but just a few uses. The BPA epoxy resin is thought to leach from these products into food and drinking water during consumption, and is proven to be detrimental to aquatic organisms and human life. Bisphenol A is thought to be an endocrine disruptor, where it disrupts physiological function by acting like a hormone in the endocrine system. The goal of this research is to develop a sensor technology for the rapid detection of Bisphenol A in water and other aqueous based fluids, at very low levels.

Fluorescence spectroscopy is a widely used technique for the detection and quantitative analysis of many analytes and biomolecules of interest and is ideally suited for the direct detection of Bisphenol A. Current work employs the Metal-Enhanced Fluorescence (MEF) technology, a new near-field fluorescence nanotechnology which can provide for substantially enhanced intrinsic fluorescence signatures, much improved fluorophore photostabilities and is therefore ideal for Bisphenol A sensing. In the current paper, Aluminum nanoparticulate substrates of varying film thicknesses are examined to determine both the optimal theoretical and experimental particle size for signal enhancement in the ultraviolet-blue spectral region. Future work will include determining the most effective metallic substrate and sensing configuration, and ultimately using this novel sensor for contaminant detection of Bisphenol A in environmental samples.

[1] Vandenberg et al., Human Exposure to Bisphenol A, Reproductive Toxicology, 24, 139-177 (2007).
[2] Geddes et al., Metal-Enhanced Fluorescence, Journal of Fluorescence, 12, 2, 121-129 (2002).
[3] Chowdhury et al., Use of Aluminum Films as Substrates for Enhanced Fluorescence in the Ultraviolet-Blue Spectral Region, Plasmonics in Biology and Medicine, 6869, 68690E1-12 (2008).

P47- SPECIATION METHOD FOR Cr^{3+}, Cr^{6+}, As^{3+} / As^{5+} DETERMINATION BY SOLID PHASE EXTRACTION AND INDUCTIVELY COUPLED PLASMA ATOMIC EMISSION SPECTROMETRY

G. A. Zachariadis*, E. Trikas

Laboratory of Analytical Chemistry, Department of Chemistry, Aristotle University,
GR 54124, Thessaloniki (Greece)
*zacharia@chem.auth.gr

Humans are exposed to chromium and arsenic by food consumption or drinking water that may contain traces of these elements. Inorganic forms of arsenic are very toxic. The major inorganic chromium species are the trivalent chromium Cr(III) and the hexavalent chromium Cr(VI). These two forms of chromium differ in their toxicity. Cr(VI) is highly toxic and is a known carcinogen. That's why total Cr measurement is not suitable for the evaluation of water toxicity. Therefore, speciation of Cr(III) and Cr(VI) is important and the simultaneous determination of these toxic analytes of As and Cr is required in water quality control procedures [1-4]. In this context, an inductively coupled plasma atomic emission spectrometric (ICP-AES) method was developed for simultaneous determination of Cr^{3+}, Cr^{6+}, As^{3+} and/or As^{5+} species, since these species are toxic and their speciation is of special interest for drinking and natural water quality. The objective of this research was to study the speciation of Cr and As using solid phase extraction and ICP-AES (SPE-ICP-AES). Single- and multi-species solutions were analyzed in order to evaluate the developed method, examining four different spectral lines for each element. Finally with the use of a cation-exchange column filled with benzosulfonic acid and elution with acidic solution of HCl, the potential of speciation of mixture solutions containing (Cr^{3+}- Cr^{6+} - As^{5+}) or (Cr^{3+} - Cr^{6+} - As^{3+}) was examined. It was shown that the separation of the two chromium species is almost quantitative therefore the simultaneous determination of chromium species and arsenic is possible, with rather good performance characteristics. The estimated limits of detection for Cr^{3+}, Cr^{6+}, As^{3+} or As^{5+} were calculated in the low μg L^{-1} level and the calculated RSDs were ranged between 3.8-5.2 % correspondingly.

[1] Posta, J., Alimonti, A., Petrucci, F., Caroli, S., Anal. Chim. Acta 325, 185-193 (1996).
[2] Motomizu, S., Jitmanee, K., Oshima, M., Anal. Chim. Acta 499, 149-155 (2003).
[3] Sumida, T., Ikenoue, T., Hamada, K., Sabarudin, A., Oshima, M., Motomizu, S., Talanta 68, 388-393 (2005).
[4] Karthikeyan, S., Hirata, S., Anal. Bioanal. Chem. 375, 139-144 (2003).

P48- SCREEN PRINTED BIOSENSORS BASED ON NITRATE REDUCTASE FROM ASPERGILLUS NIGER AND ESCHERICHIA COLI

D. Albanese, M. Di Matteo and A. Crescitelli

Dipartimento di Ingegneria Chimica Alimentare Università di Salerno,
Via Ponte Don Melillo, 84084, Fisciano (Salerno) (Italy)

Nitrate pollution represents one of the most important environmental problems on worldwide scale. Intensive industrialization and the high use of chemical fertilizers are the prime reasons for the excessive amount of nitrates in water and soil. The excess nitrate in environmental water systems causes algal blooms, a depletion of dissolved oxygen, and possibly eutrophication [1]. With reference to human health, an high intake of nitrate through drinking water and food has been cited as a risk factor in developing ‘‘blue baby’’ syndrome and gastric cancer. In order to control nitrate pollution, European Union issued two directives (91/676/EEC; 98/83/EC) concerning the protection of waters against pollution caused by nitrates from agricultural sources and the quality of water intended for human consumption. Both directives define 50 mg/l as the maximum allowable concentration for nitrate in soil and water. The use of electrochemical biosensors as analytical devices for monitoring of nitrate pollution in aquifers is an attractive topic of research because of their high sensitivity, selectivity, ease and rapidity of use. The nitrate biosensor reported in literature [2,3,4] are electrochemical biosensors based on the immobilization of the Nitrate Reductase (NaR) enzyme, on glassy electrode. A shortcoming in the use of nitrate biosensors as analytical devices for monitoring of nitrate pollution is linked to their short lifetime, lower than two days [5]. The possibility to increase the stability of nitrate reductase biosensors represents a very important goal in nitrate biosensors development. Because the performance of nitrate biosensor in terms of stability and sensitivity depend on the immobilization procedure and on the enzymatic source, in this paper the effects of two microbial NaR enzymes were studied. In particular, NaR from Aspergillus niger and Escherichia coli were immobilized on screen printed electrodes through two different immobilization procedure based on cross linking between BSA and glutaraldehyde. The electron transfer mediator used for the development of two nitrate biosensors was methyl viologen. The characterization (sensitivity, detection limit and life time) of the two nitrate biosensors was carried out by Flow Injection Analysis in anaerobic conditions.

[1] Taylor, C. J.; Bain, L. A.; Richardson, D. J.; Spiro, and S., Russell, D. A., Anal. Biochem. 328, 60. 2004,
[2] Ramsay, G. and Wolpert, SM., Anal. Chem., 71, 504-506 (1999).
[3] Da Silva, S., Cosnier, S., Almeida, M. G., and Jos Moura, J.G., Electrochem Comm, 6, 404–408 (2004).
[4] Quan, D., Shim, J H., Kim, JD., Park, H S., Cha, GS. and Nam H., Anal. Chem. 77, 4467-4473 (2005).
[5] Kirstein, D., Kirstein, L., Scheller, F., Borcherding, H., Ronnenberg, J., Diekmann, S. and Steinrucke, P., J. Electroanal Chem, 474, 43-51(1999).

P49- MONITORING SULFAMETHOXAZOLE IN AQUACULTURE WATER

S. A.A. Almeida [1,2,3], A. M. Heitor[2], M. C. B.S.M. Montenegro[3], M. G.F. Sales[1]

[1]REQUIMTE/ISEP, Instituto Superior de Engenharia do Porto R. Dr. António Bernardino de Almeida, 431, 4200-072 Porto (Portugal)
[2]INSA-Porto, Instituto Nacional de Saúde Dr. Ricardo Jorge, 321,
4000-055 Porto (Portugal)
[3]REQUIMTE/Serviço de Química-Física, Faculdade de Farmácia da Universidade do Porto 164,
4057-047 Porto (Portugal)

Aquaculture is the farming of aquatic organisms, using interventions (e.g., feed, medications, controlled breeding, containment) that enhance production. Among the many chemical substances used in aquaculture, particular attention should be given to the use of antibiotics since a certain amount of such compounds are commonly used in aquaculture, for both prophylactic reasons and to treat disease [1].

Sulfamethoxazole (SMX) is a member of the sulfonamide family of antibiotics used in aquaculture. Like other sulfonamides, this drug competitively inhibits the utilization of *para*-aminobenzoic acid by bacteria in the synthesis of folic acid, this being a stage in the progressive synthesis of purines and ultimately of deoxyribonucleic acid [2].

The analytical control of SMX in aquaculture may be carried out by several methods, including microbiologal and chromatographic ones. They are either time consuming or too expensive to be employed in a routine basis. New simple methods that offer quick and selective readings are thus required.

Potentiometric determinations of ionic species by means of Ion-selective electrodes (ISEs) have found vast applications in diverse fields of analysis [3]. ISEs offer high precision and rapidity, low cost of analysis, enhanced selectivity and sensitivity over a wide range of concentrations [4]. In addition, they are easy to construct and manipulate and no sample pretreatment is needed before the analysis itself. Short response times, in the order of seconds, make ISEs appropriate devices for process control.

Hence, the present work describes new SMX selective electrodes for the potentiometric determination of this sulphonamide in water. The selective membranes were made of PVC with Mn^{III}TPPCl or cyclodextrin acting as ionophores. *o*NFOE was used as plasticizer and TOABr, DDABr or KTpClPB as additive. The best analytical performance was reported for ISEs of Mn^{III}TPPCl with 50 % of KTPClPb. Nerstian behaviour was observed after $4.0x10^{-5}$ mol/L, and the limit of detection was $1.2x10^{-5}$ mol/L. The electrodes displayed good selectivity for several anionic species. The analytical application to contaminated waters showed recoveries from 96 to 106 %.

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[1] Bjørklund, H.V., Raberg, C.M.I. and Bylund, G., Aquaculture 97, 85–96 (1991).
[2] Galán MJG, Cruz MSD and Barceló D, Trends Anal. Chem. 27:1008–1022 (2008).
[3] Cosofret, V.V., Buck, R.P, CRC Press, Boca Raton, FL, p. 448 (1992).
[4] Cosofret VV, Buck RP, "Recent advances in pharmaceutical analysis with potentiometric membrane sensors", Crit. Rev. Anal. Chem. 24, 1–58 (1993).

P50- FIELD SAMPLING, SPECIATION AND DETERMINATION OF DISSOLVED IRON(II) AND IRON(III) IN WATERS

S. Arpadjan[1], J. Knutsson[2], P. Petrova[2], K. Tsekova[3]

[1]Faculty of Chemistry, University of Sofia, 1164 Sofia, bld. J. Bourchier 1
[2]Chalmers University, Fysikgränd 3, 41296 Gothenburg (Sweden)
[3]Institute of Microbiology, Microbial Ecology Dept., Bulgarian Academy of Sciences "Acad. G. Bonchev" Str., bl. 26, 1113 Sofia (Bulgaria)

A simple and rapid field sampling procedure has been developed for the speciation of dissolved Fe(II) and Fe(III) in waters. The determination of iron species was possible by selective batch solid phase extraction of Fe(III) using chelating resin Chelex-100 in H^+ form, sample acidity range of pH 1.5 – 2.8, elution with 0.03 mol/l NH_4-EDTA, and detection by flame or electrothermal atomic absorption spectrometry (ETAAS). The sum of Fe(II) and Fe(III) could be determined without the need for preoxidation of Fe(II) to Fe(III) over a sample acidity range of pH 5 – 8. The concentration of Fe(II) was obtained as the difference between that of total iron and Fe(III), or by direct measurement of the concentration of Fe(II) remained in the water solution above the resin after sorption of Fe(III). Water samples were collected in situ and filtered by passing them through a syringe filter (0.45 µm). The batch procedure was performed at the field and then, the tubes containing the resins with the loaded analytes were returned to the laboratory where the iron species were eluted and determined. Field sampling prevents changes in the oxidation state of iron. The effect of humic acid was also investigated. The results obtained indicated that the method was not affected by the presence of up to 0.01% humic acid. A preconcentration factor of 14 was achieved and the limit of detection (3*s*) was 3 µg/l (ETAAS detection). The relative standard deviation (n=10) was 8% at the 10 µg/l Fe(III) level. Recoveries of spiked Fe(II) and Fe(III) in river, lake, sea, tap, mineral, spring, well, waste and groundwater samples ranged from 92 to 104%. The concentrations of Fe(II) and Fe(III) in synthetic aqueous mixtures obtained by the proposed procedure were in good agreement with the spiked values. The results for total iron concentration in the river water reference material SLRS-5, sea water CRM CASS-2 and in the mineral water sample from national proficiency testing experiment were in good agreement with the certified and the accepted values.

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P51- ELECTROCHEMICAL PREPARATION OF NANO-STRUCTURED COPOLYMER OF ANILINE AND m-AMINO BENZOIC ACID COATING AND ITS APPLICATION IN THE HEADSPACE SOLID-PHASE MICROEXTRACTION OF FATTY ACIDS IN ZOOPLANKTONS

M. Asiabi[1], A. Jabbari[1] and A. Mehdinia [2]

[1]Department of Chemistry, K.N. Toosi University of Technology, Tehran (Iran)
[2]Department of Marine Living Resources, Iranian National Center for Oceanography,
Tehran (Iran)

In this work, a novel nano-structured copolymer of aniline and m-amino benzoic acid film was used as solid-phase microextraction (SPME) coating for headspace (HS) extraction of unsaturated-fatty acids after derivatization and applied for the analysis of fatty acids in Zooplanktons by coupling to gas chromatography–mass spectrometry (GC-MS) [1]. The nanostructures were immobilized on a platinum wire by a simple electrodeposition method using co-polymerization of m-aminobenzoic acid (m-ABA) and aniline[2]. Improved temperature resistance (up to 350 ^{o}C), improved life time (more than 50 times) and satisfactory extraction efficiency were obtained by insertion of carboxylate groups into the framework of polyaniline respect to the polyaniline. Effect of different parameters influencing the extraction efficiency such as extraction temperature, extraction time, ionic strength, stirring rate and sample volume were investigated and optimized. In order to improve the separation efficiency of fatty acids all the analytes were derivatized prior to extraction using BF_3-MeOH. Under optimized conditions, the relative standard deviations (RSD, n = 5) for all analytes were below 5% and the limits of detection varied from 0.01 (C14:0) to 1.4 µg ml^{-1} (C20:0). Correlation coefficients (r^2) of the obtained calibration curves ranged from 0.9918 to 0.9982 showing an acceptable linearity within this interval of concentration.

[1] Dongmei Cha, Mingming Liu, Zhaorui Zeng, Dong'e Chengc, Guoqing Zhan. Analytica Chimica Acta 572, 47-54 (2006)
[2] Carolin Thiemann, Christopher M.A. Brett. Synthetic Metals 123, 1-9 (2001)

P52- COMPARISON OF DIFFERENT CAPILLARY COLUMNS IN THE OPTIMIZATION OF IN-TUBE SPME EXTRACTION OF ENDOCRINE DISRUPTORS IN ENVIRONMENTAL LIQUID SAMPLES

J. Aufartova[1], L. Novákova[1], J. J. Santana-Rodríguez[2], P.Solich[1],
Z. Sosa-Ferrera[2], M. E. Torres-Padrón[2]

[1]Department of Analytical Chemistry, Faculty of Pharmacy, Charles University, Heyrovského 1203,
500 05 Hradec Králové (Czech Republic)
[2]Department of Chemistry, Faculty of Marine Sciences, University of Las Palmas de Gran Canaria,
35017 Las Palmas de Gran Canaria (Spain)

Endocrine disrupting compounds (EDCs), such as bisphenol A, ethynylestradiol, levonorgestrel, norethisterone and estriol, are a class of emerging contaminants that are extensively and increasingly used in human medicine. They have become a major issue in the field of environmental science due to their ability to interfere with endocrine system in animal and humans. Trace level concentrations and their wide diversity are some of their characteristics for that their identification and quantification are necessary to understand their behaviour in the environment. Due to low concentration levels of these compounds in environmental waters, is necessary to apply an extraction and preconcentration process to improve their determination. In-tube solid phase microextraction has proved to be an appropriate method of extraction and preconcentration of different types of pollutants.

In this work we present the optimization of the chromatographic separation with two different analytical columns (phenyl and C18) and different capillary columns CP-SIL 19CB, Supel-Q porous layer open tubular (PLOT) and Carboxen 1006 PLOT for optimizing in-tube solid-phase microextraction of endocrine disruptors in environmental liquid samples coupled to high performance liquid chromatography with DAD detection (in-tube SPME-HPLC) [1-3].

Results obtained were evaluated and compared in function of different chromatographic parameters: time, peak shape and resolution for different extraction sorbents.

[1] Ouyang, G., Pawliszyn, J., TrAC, 25, 692-703 (2006)
[2] Mitani, K., Narimatsu, S., Izushi, F., Kataoka, H., J. Cromatogr. A 32, 469-478 (2003)
[3] Kataoka, H., Ishizaki, A., Nonaka, Y., Saito, K., Anal Chim.Acta, 1-2, 8-29 (2009)

P53- DISPERSIVE LIQUID PHASE MICROEXTRACTION COMBINED WITH FLAME ATOMIC ABSORPTION SPECTROMETRY FOR DETERMINATION OF Fe IN ENVIRONMENTAL WATER SAMPLES

R. Zakerian, S. Bahar

Department of Chemistry, Science Faculty, University of Kurdistan,
P. O. Box 66177-416, Sanandaj (Iran)

Dispersive liquid phase microextraction (DLPME) is a mode of LPME [1-3], which is based on ternary component solvent system such as cloudy point extraction and homogeneous liquid-liquid extraction [4]. This method uses an extracting solvent dissolved in a dispersive solvent, which is miscible with both extraction solvent and water. In this work a simple method for the determination of iron in environmental water samples was developed by DLPME preconcentration and flame atomic absorption spectrometry (FAAS) detection. In the proposed approach, 8-hydroxy quinoline was used as a chelating agent and chloroform and methanol were selected as extraction and dispersive solvent. After phase separation, the sedimented phase containing enriched analyte was allowed to evaporate at room temperature, then residue dissolved into 0.5 mL 1.5 mol L^{-1} nitric acid and determined by FAAS. The effect of various experimental parameters on the extraction was investigated. Under the optimum conditions the calibration graph was liner over the range 50-2000 µg L^{-1} with detection limit of 8 µg L^{-1}. The relative standard deviation to five replicate measurements of 100 µg L^{-1} was 4.1%.

[1] Berijani, S., Assadi, Y., Anbia, M., Millani-Hosseini, M.R., Agaee, E. J.chromatogr. A 1, 1123 (2006).
[2] Rezaee, M., Assadi, Y., Millani-Hosseini, M.R., Agaee, E., Ahmadi, F., Berijani, S. J.chromatogr. A 1, 1126 (2006).
[3] Farajzadeh, M.A., Bahram, M., Ghorbani-Mehr, B., Jonsson, J.A. Talanta 75, 832-840 (2008).
[4] Igarashi, S., Takahashi, A., Ueki, Y., Yamaguchi, H. Analyst 797, 2000 (2000).

P54- A KINETIC STUDY ON THE BIODEGRADATION OF TEXTILE EFFLUENT USING UV-VIS SPECTROSCOPY AND PLS

N. D. Bernardino, R. Afonso, S. R. G. Barreto, S. M. Obara Doi and W. J. Barreto

Department of Chemistry, Universidade Estadual de Londrina, Campus Universitário,
86051-980, Londrina, Paraná (Brazil)

A large amount of dye is released in textile processing effluent due to incomplete fixation of the dye on the fibers causing the contamination and degradation of water bodies. Many studies have shown that in particular azo-dyes and their byproducts can be toxic or carcinogenic and there is thus a need to develop technologies that minimize the volume and toxicity of industrial effluents. The mechanism of decolorization of polymeric dyes by white rot fungi is complex and involves the enzymes lignin peroxidase (LIP), manganese peroxidase and laccases, which act as biological catalysts and decrease the activation energy of reactions [1]. The objective was to study the kinetics of the biodegradation of textile dyes, in a mixture of three dyes, by the fungus *Ganoderma spp*, applying UV-Vis spectrophotometry, HPLC and regression by Partial Least Squares (PLS). The data were analyzed using 4 principal components (PC) that explained 99.98% of the total variance without loss of information. The spectra of the effluents showed a decrease in absorbance of the dyes Remazol Brilliant Orange 3R, Remazol Blue RR and Remazol Blue R ESP in the mixture with increasing incubation period. Using the concentrations calculated by the PLS a kinetic study of the biodegradation process by the fungus was performed obtaining the order and the rate constants by fitting the best straight line for the zero-, first- and second-order equations. Plots of the dye concentration over time showed a plateau at around 140 hours indicating a sharp decline in the rate of the reaction. This decrease in the biodegradation process can be explained by a decrease in the amount of laccase enzyme released by the fungus *ganoderma spp* in the medium, indicating that the reaction is dependent only on the enzyme, following the rate law $dx/dt = k[A]$. The rate constants (k) obtained were: $k = 1.17\ 10^{-1}\ h^{-1}$ and $k=2.07\times10^{-1}\ h^{-1}$ at 25 ° C, and $k = 0.62\ 10^{-1}\ h^{-1}$ and $k = 1.81 \times 10^{-3}\ h^{-1}$ at 28 º C for the dye Remazol Brilliant Orange 3R and Remazol Blue RR, respectively. For Remazol Blue R ESP $k=5.59 \times 10^{-1}\ h^{-1}$ at 25 °C and $6.22 \times 10^{-3}\ h^{-1}$ at 28 ºC, but there was also degradation at 31 °C, with $k = 5.46 \times 10^{-3}\ h^{-1}$ at 31 °C, which was attributed to the action of another type of enzyme, such as lignin peroxidase (LIP) or manganese peroxidase. The activation energies (Ea) were 175.90 kJ mol^{-1} for the dye Remazol Brilliant Orange 3R, 37.17 kJ mol^{-1} for Remazol Blue RR and 29.58 kJ mol^{-1} for Remazol Blue R ESP. The dye Remazol Blue R ESP showed the highest percentage of biodegradation (95.4%) after 335 hours of incubation at 25 °C. The rate constants obtained for the dye Remazol Blue R ESP from the HPLC analysis were comparable with the results obtained with the PLS methodology. The results showed that the PLS methodology can be used for quantification of the dyes in effluents in order to find the kinetic parameters of the biodegradation reactions.

[1] Machado, K. M. G., Compart, L. C. A., Morais, R. O., Rosa, L. H., Santos, M. H., Brazilian Journal of Microbiology 37, 481-487 (2006).

P55- UV-VIS SPECTROSCOPY AND CHEMICAL PROPRIETIES APPLIED TO CHARACTERIZE WATERS OF A TROPICAL RESERVOIR

A. M. Freitas, D. N. Ishikawa, E. M. Deduch, K. P. S. Zanoni, M. C. Solci,
M. do C. S. Ribeiro, S. R. G. Barreto and W. J. Barreto

Department of Chemistry, Universidade Estadual de Londrina, Campus Universitário,
86051-980, Londrina, Paraná (Brazil)

The formation of a reservoir for the generation of hydroelectric energy requires the contribution of several rivers which may have different chemical compositions. Obtaining knowledge on the chemical composition of the water of each tributary and of the reservoir itself is a very complex task which is rarely carried out. An important and complex component of the natural waters is the organic matter (OM). The humic content of a water sample can be described by a parameter called specific ultraviolet absorbance (SUVA). The SUVA values are defined as the absorbance at a certain wavelength due to the concentration of DOC in units of milligrams per liter [1]. The objective of this study was to characterize the surface waters of the Capivara reservoir, Brazil, and to verify the possible influence of the towns located along their banks on its composition. Surface water samples were collected at 19 sites of the Capivara reservoir. The DOM was analyzed by UV-Vis spectroscopy and the concentrations of metals, anions, total S and total P dissolved and chlorophyll-*a*, and pH, redox potential, alkalinity, DOC and electrical conductivity in the water samples were determined. The surface waters samples were collected in triplicate with the aid of polyethylene flasks at a depth of 30 cm below the air-water interface.in February 2008, during the high-water period. The sites close to the city of Primeiro de Maio were a predominance of aromatic substances from autochthonous sources ($SUVA_{260}$ between 16 and 23 cm^{-1} L g^{-1}) and the remainders were of pedogenic origin. The site close to the Porecatu city had lower DOC concentrations and the highest values for $SUVA_{260}$ (43 and 49 cm^{-1} L $g^{-1)}$, indicating that the aromatic carbon content in the DOC composition is greater than at the other sites. $SUVA_{285}$ assumes values close to 20 cm^{-1} L g^{-1} in the water samples from all sites, characterizing the waters sampled as essentially formed by fulvic substances, that is, by pedogenic refractory organic carbon. The $SUVA_{254}$, with values lower than 30 $cm^{-1}L\ g^{-1}$ at sites close to the city of Primeiro de Maio, confirmed the predominance of fulvic substances in the waters sampled from these locations. Therefore, the distribution of the DOC in the natural waters of the Capivara reservoir is relatively homogenous and there was no clear differentiation between the organic matter collected from the tributaries, the waters close to the towns and the central body of the reservoir. The principal components analysis identified two clusters of sites using all variables: the tributary Tibagi River and the tributary Paranapanema River (I) and the central part of the lake (II). It was verified a little but worrying impact of urban activities in the water composition, more evident close to the city of Primeiro de Maio were the highest concentrations (mg L^{-1})of Cr $(6.96 \pm 1.30)\text{x}10^{-5}$, Cu $(2.10 \pm 0.10)\text{x}10^{-3}$ and Ni $(0.61 \pm 0.04)\text{x}10^{-3}$ were determined indicating anthropogenic interference.

[1] Weishaar, J. L., Aiken, G. R., Bergamaschi, B. A., Fram, M. S., Fujii, R., Mopper, K., Environ. Sci. Technol. 37, 4702–4708 (2003).

P56- PASSIVE SAMPLING OF Ni(II) USING A KELEX 100-CONTAINED HOLLOW FIBER SUPPORTED LIQUID MEMBRANE DEVICE

A. N. Bautista Flores[1], J. De Gyves M.[1], J. Å. Jönsson[2], E. R. De San Miguel G.[1]

[1]Departamento de Química Analítica, Facultad de Química, UNAM, Ciudad Universitaria,
04510, México, D.F. (México)
[2]Department of Organic/Analytical Chemistry, Lund University, P.O. Box 124,
SE-221 00 Lund (Sweden)

Heavy metals have been identified as the most dangerous pollutants in aquatic ecosystems, due to their persistence and high toxicity. Among them Hg, As, Cr, Pb, Cd, Ni and Zn are considered very significant from an ecotoxicological point of view. Nickel is an essential metal for plants and animals, as a component of the enzyme urease and other five [1]. Nickel is moderately toxic, can cause allergic reactions and certain compounds are carcinogenic. This metal is released into the aquatic environment through the dissolution of rocks and soil, precipitation and biological cycles. Also, the high consumption of nickel in industrial and sewage wastewater inevitably leads to environmental pollution. Natural water contains low concentrations of nickel (0.5-1.5µg /L, river water 0.3 mg /L, surface water 0.7 mg /L), which are increased due to water pollution [1,2,3]. The determination of this ion is still a challenge for analytical chemistry because very few techniques have low detection limits [4], and usually they need sample manipulation and transformation. For this reason passive sampling techniques for monitoring nickel concentrations in natural waters are required. Supported liquid membranes are one of the new tools that are useful for this purpose, since they have the virtue of preconcentrating the species as soon as the system is put in contact with the test solution through the facilitated transport that occurs in the membrane. Thus, it does not require more energy than it provides the co-or counter-transport of other species.

In this work, the performance of a hollow fiber supported liquid membrane passive sampling device used for nickel (II) determination from aqueous solutions is studied**.** A commercial available extractant (Kelex 100: 7-(4-ethyl-1-methylocty)-8-hydroxyquinoline) was incorporated as metal carrier. Different parameters involved in the functioning of the device were optimized using a Doehlert design for three variables (donor phase pH, acceptor phase pH and extractant concentration) under equilibrium conditions. Mechanical and geometric factors for operation of the device were evaluated. The influence of sampling conditions was analyzed considering several factors: nickel concentration, presence of anions capable of forming labile complexes (NO_2^-, SO_4^{-2}, Cl^-, NO_3^-, CO_3^{-2}, CN^-), and presence of dissolved organic matter (humic acids). Enrichment factors around 120 to 1600 times were observed depending on module operation and sampling conditions.

[1] A. Aouarram, M.D. Gallindo-Riaño, M. García-Vargas, Talanta 71, 165-170 (2007).
[2] Stéphane Bayen, Kevin J. Wilkinson and Jacques Buffle, Analyst 132, 262-267 (2007).
[3] Norma Oficial Mexicana NOM-001-ECOL.
[4] Daniel G. Strawn and Donald L. Sparks, Soil Science Soc. Am. J. 64, 144-156 (2000).

P57- ALLERGEN FRAGRANCES IN WATER FOR ULTRASOUND-ASSISTED EMULSIFICATION–MICROEXTRACTION

E. Becerril-Bravo[1,2], J. P. Lamas[1], L. Sanchez-Prado[1], M. Lores[1], C. Garcia-Jares[1],
B. Jimenez[2], and M. Llompart[1]

[1]Departamento de Quimica Analitica, Nutricion y Bromatologia, Facultad de Quimica.
Campus Vida. Universidad de Santiago de Compostela, E-15782, Santiago de Compostela (Spain)
[2]Instituto de Ingenieria, Universidad Nacional Autonoma de Mexico, Ciudad Universitaria, 04510
Mexico, D.F. (Mexico)

Fragrances are any basic substance used in the manufacture of fragrance materials for their odorous, odour enhancing or blending properties. Some of the substances are suspected to cause allergenic and the health problems. Although the main route of exposition to these cosmetic ingredients is, in general, the direct application of cosmetics on the skin, the contact with water containing these fragrances should be also considered.

The aim of the present work is to develop a method of ultrasound-assisted emulsification–microextraction (USAEME) with (GC-MS) for the analysis of 24 EU-regulated fragrance suspected allergens in water samples. This approach is based on the emulsification of a microvolume of organic extractant in an aqueous sample by ultrasound radiation and further separation of both liquid phases by centrifugation. Method linearity was tested by injecting chloroform standard solutions between 0.020 µg mL^{-1} and 10 µg mL^{-1}. Determination coefficients (R^2) between 0.9974 and 1.0000 were obtained for all compounds. Recoveries between 75 and 110 % were generally obtained, and precision was characterized by RSD values < 10 % in most cases. LODs (signal-to-noise ratio of 3) are also presented, and they were below 1 ng mL^{-1}.

USAEME is proposed as an efficient, simple, rapid, environmentally friendly, and non-expensive alternative to other extraction techniques such as solid phase extraction (SPE), SPME and LPME. Using the optimized conditions established after a multivariate study of the USAEME process, good recoveries were obtained for almost all compounds, even in complex samples. The proposed method was applied to the analysis of several real water samples including tap water, baby bathwater, recreational place water, public washing place water, and sewage water.

P58- TRACE LEVEL ANALYSIS OF TRIFLOXYXTROBIN AND ITS TRANSFORMATION PRODUCTS IN WATER BY HPLC/MS

A. Boudina[1,2*], R. Baudot[3], J.M. Chovelon[2]

[1]Laboratoire d'Analyse Organique Fonctionnelle, Faculté de Chimie, U.S.T.H.B., BP 32 El-Alia,
16111 Bab-Ezzouar, Alger (Algeria)
[2] Laboratoire d'Application de la Chimie à L'Environnement (L.A.C.E), UMR CNRS 5634,
Université Lyon I. 43, Boulevard du 11 novembre 1918, 69622 Villeurbanne Cedex (France)
[3] S.C.A.- Service Central d'Analyse, U.S.R.059 CNRS-Echangeur de Solaize,
B.P.22 69390 Vernaison (France)
[*]aboudina36@yahoo.com

Trifloxystrobin is a systemic fungicide, it provide a large broad fungicidal bioefficacy against a large variety of crop pests.

Here we describe the approach using solid phase extraction (a polymeric isolute ENV+ cartridge) for the pre-concentration of trifloxystrobin after simulated sunlight degradation in water.

High performance liquid chromatography with diode array detector (HPLC/DAD) and HPLC/MS, equipped with currently most popular electrospray (ESP) and atmospheric pressure ionization (APCI) are used to detect trifloxystrobin fungicide and its photo-transformation products in water.

References

* K. Banarjee, A. P. Ligon, M. Spitller; spectral elucidation of the acid metabolites of the four geometric isomers of trifloxystrobin. Anal. Bioanal. Chem. 388 (2006) 1831-1838.

* A. Boudina , C. Emmelin, A. Baaliouamer, O. Païssé, J.M. Chovelon; Photochemical transformation of azoxystrobin in aqueous solution. Chemosphere 50 (2007) 1280-1288.

* Deb, D., Engel, B.A., Harbor, J., Hahn, L., Lim, K.J., Zhai, T.: Water Air Soil Pollut. 207(2010) 273-288.

P59- *IN SITU* SYSTEM DEVELOPEMNT FOR MEASURING CHLORINATED HYDROCARBONS IN GROUNDWATER

X. Boutsiadou and D. Hunkeler

Centre for Hydrogeology and Geothermics, Laboratory of hydrochemistry and contaminants,
University of Neuchâtel, Emile - Argand 11, 2009 Neuchatel (Switzerland)

Volatile organic compound (VOC) contamination is a widespread problem at environmental sites. Compounds, such trichloroethylene (TCE) and tetrachloroethylene (PCE), are also referred as dense non-aqueous phase liquids (DNAPLs), were used extensively in degreasing and equipment cleaning operations in the past, with disposal practices that led to their release to the environment. VOCs are the most significant organic contaminants in groundwater associated with disposal sites.

The on-line determination of specific chlorinated hydrocarbons in groundwater is an important analytical problem. Water often contains more than one single pollutant and the most frequently applied methods for analysis include a separation step, especially gas chromatography. The approved method of collection and analysis of volatile organic pollutants involves obtaining water sample from the field, transporting it to the laboratory, and analysing it by a specific procedure. While those methods are extremely versatile, sensitive and selective, they are not real time (continuous) or inexpensive. *In situ* monitoring or screening methods that could be applied in the field would benefit of low cost alternative for the determination of chlorinated hydrocarbons.

The objective of this project is to develop an instrument capable of providing real time measurement of the subsurface VOCs in the aqueous phase. Given the high volatility of the compounds and the availability of sensitive gas detectors, the chosen approach consists of an interface that employs a membrane to extract volatile chlorinated hydrocarbon compounds from a water matrix to the gas phase for subsequent introduction to a gas sensor. This technique offers the advantage of continuous on line extraction of the analytes.

The initial phase of this study consists of testing the suitability of different polymers for the extraction of the compounds from the aqueous phase to the gas phase using a laboratory set up. The mass transfer of the compounds through the membranes was investigated and the permeability through the membrane was quantified. In the second part, the performance of different types of gas detectors was evaluated. The third step consists of extensive field testing of the instrument combining the membrane system and the detector.

P60- DETERMINATION OF THE PSYCHIATRIC DRUG CARBAMAZEPINE IN WASTE WATERS BY ELISA

A. Bahlmann[2], V. Calisto[1], V. I. Esteves[1], R. J. Schneider[2]

[1]Department of Chemistry, University of Aveiro, Campus Universitário de Santiago 3810-193 Aveiro (Portugal)
[2]BAM - Federal Institute for Materials Research and Testing, Richard-Willstätter-Str. 11, 12489 Berlin (Germany)

Carbamazepine, a commonly prescribed psychiatric pharmaceutical, is one of the most frequently detected pharmaceuticals in the environment [1]. In general, pharmaceutically active compounds are continuously being introduced into the environment by Wastewater Treatment Plants (WWTPs) effluents which are considered to be the major source of aquatic environmental contamination [2].

In this research, a previously developed enzyme-linked immuno-sorbent assay (ELISA) [3], based on a monoclonal antibody, was applied to the quantification of carbamazepine in samples collected from two main WWTPs in the North of Portugal. The analyzed samples consisted on waste waters collected from different stages of treatment (after primary treatment, after biological treatment and final effluent - ready for discharge in sea).

Waste water samples were analyzed after a filtration step (with 0.22 μm filters) without any other cleaning procedure or enrichment process. The applied ELISA methodology has proven to be adequate for the analysis of waste water samples without suffering significant interferences of organic matter. The assays achieved a detection limit of 0.04 ± 0.01 μg/L (based on 12 independent experiments). Carbamazepine was detected in all the analyzed samples with concentrations ranging from 0.66 to 1.04 μg/L with relative standard deviations below 10%. No significant differences were found between samples obtained from different treatment stages.

This study aims to be the first approach to quantifying psychiatric pharmaceuticals on samples of Portuguese WWTPs. The obtained results are in accordance with numerous studies that showed that carbamazepine is not successfully removed by the treatment methods applied to domestic waste waters.

[1] Zhang, Y., S.-U. Geißen, and C. Gal, Chemosphere 73, 1151-1161 (2008)
[2] Calisto, V. and V.I. Esteves, Chemosphere 77, 1257-1274 (2009)
[3] Bahlmann, A., et al., Anal. Bioanal. Chem. 395, 1809-1820 (2009)

P61- AMPEROMETRIC DETERMINATION OF ARSENIC(III) USING PLATINUM -MODIFIED SCREEN-PRINTED CARBON-BASED ELECTRODES

C. Cremisini, L. Della Seta, M. R. Montereali, W. Vastarella

ENEA, C.R. Casaccia, Via Anguillarese 301, 00123 S. Maria di Galeria, Rome (Italy)

Arsenic is a relatively common and toxic element, known as a carcinogen and found in different chemical species that can be readily transformed by events such as biological activity, changes in redox potential or pH [1]. This creates the possibility of a wide variety of unstable arsenic species that can transform with subtle changes in the environment. Arsenic is increasingly being found in drinking water in many parts of the developing world such as Bangladesh, India, but also in western countries such as England and US. Arsenic water contamination is due to both natural (As-bearing rocks weathering and input of deep As-rich thermal waters into aquifers) and anthropogenic causes (mine waters, industrial contamination). The World Health Organization (WHO) revised the guideline for arsenic concentration from 0.05 to 0.01 mg/L in 1993 [2] and as a result the arsenic standard level in the European Union, is now set to 10 μg L^{-1}. Laboratory assays are generally required to accurately measure arsenic in an environmental sample to parts per billion (ppb) concentrations. The most used laboratory method for As assessment in water is inductively coupled plasma-mass spectrometry reaching a sensibility of ng L^{-1}, but field assays, in which lower sensitivities may be acceptable for sample screening or site surveys, strive detection goals of at least 10 μg L^{-1}, are relatively inexpensive, and can produce a large number of screening results in a short period of time [3]. Electrochemical methods offer the possibility to determine arsenic and arsenic compounds at such concentrations with simple instrumentation and operation and excellent selectivity which allows diversifying the oxidation states of arsenic. Voltammetry and polarography are the most widely used techniques for the determination and speciation of arsenic, while stripping analysis is better suited for trace determination in real samples, as the substance of interest is pre-concentrated on the working electrode [4]. A simple method based on the amperometric detection of direct oxidation of As (III) to As (V) [5] has been developed for water samples. Carbon based disposable screen printed electrodes, modified with different metals (Au, Rh, Pt) both added directly into the pastes or deposed as nanostructures in template membranes printed on the surface of the working electrodes, have been tested. Voltammetric techniques were used to determine the optimal working potential (0.8 V vs Ag/AgCl). The platinum modified electrodes gave the best results in signal intensity and stability and were used for all further measurements both in batch and flow conditions obtaining results at the level of the acceptable concentration for drinking water (10 μg L^{-1}).

[1] Jain C. K., Ali I., Wat. Res., Vol. 34, No. 17, 4304-4312 (2000)
[2] World Health Organisation (WHO), Guidelines for Drinking Water Quality, (1993)
[3] Melamed D., Analytica Chimica Acta 532 ,1–13 (2005)
[4] Munoz E.,Palmero S.,Talanta 65, 613–620 (2005)
[5] Sanllorente-Mendez S et al, Electroanalysis, Vol 21, No. 3-5, 635 – 639 (2009)

P62- HIGH-PERFORMANCE LIQUID CHROMATOGRAPHY WATER ANALYSIS USING COMBINED UV-ELECTROCHEMICAL DETECTION OF SOME EXPLOSIVES, BY-PRODUCTS AND METABOLITES

L. Didaoui and A. Touabet

Laboratoire d'Analyse Organique Fonctionnelle, Faculté de Chimie, U.S.T.H.B.,
El Alia B.P. 32, Bab Ezzouar, Alger (Algeria)

Explosives analysis is important in different area: explosive manufacture (quality and wastewater control), forensic science and toxicology (investigation of explosions or of criminal actions) and environmental monitoring (soil and water nearby sites intensively used for military purposes) [1].

The objective of this work was the development of a robust HPLC isocratic separation method for the analysis of a group of 14 neutral (nitramines, nitroaromatics and aminonitroaromatics) and 6 acidic (nitrophenols) explosives and related compounds.

The identification of nitrophenolics pollutants in water samples collected around contamined areas is difficult due to the large number of components present in water extracts. Small changes in experimental conditions often result in confusing peak movements, especially with charged species as nitrophenols whose ionisation and retention change as function of pH [2].

The influence of the most important eluent parameters on the resolution of 20 explosives and related compounds as the mobile phase composition (% B) and the pH of the aqueous eluent was studied. On the other hand, we have examined the effect of the column temperature and the nature of the packing material of the column. Therefore, the retention behavior of the sets of the explosives was studied on five different chromatographic columns: Nucleosil-100 C_{18}, UltraSepESEX C_{18}, Spherisorb-ODS2 C_{18}, Eurospher C_{18} and Nucleosil C_8.

Electrochemical detection (ED) in oxidative mode combined with UV detection was applied to the analysis of nitramines, nitroaromatics, aminoaromatics and nitrophenols in groundwater samples from the surroundings of a former ammunition plant in Elsnig (Germany).

The procedure is based on a preseparation into two fractions by multi-step extraction at different pH values (neutral fraction at pH 9 and acidic fraction at pH 2) followed by an HPLC analysis with double detection (UV/EC).

The electrochemical detector (EC) allowed a selective and sensitive detection of the nitrophenols and especially of the diaminoaromatics and, therefore, provides some advantages in the analysis of complex samples.

[1] Jenkins, T. F., Leggett, D. C., Grant, C. L., Bauer, C. F., Anal.Chem. 58, 170 (1986).
[2] Lewin, U., Wennrich, L, Efer, J., Engewald, W., Chromatographia 45, 91 (1997).

P63- DETERMINATION OF POLLUTANT PARAMETERS USING AAS IN LANDFILL LEACHATE WATER OF VOJVODINA REGION

M. Djogo, A. Dvornić, D. Milovanović, J. Radonić, M. Turk Sekulić,
M. Vojinović Miloradov, G. Vujić

University of Novi Sad, Faculty of Technical Sciences, Department of Environmental Engineering,
Trg Dositeja Obradovića 6, 21000 Novi Sad (Serbia)

Leaching occurs when soluble components are dissolved out of a solid material by percolating water. Depending on the waste types further contaminants may be introduced as a result of biodegradation of wastes. The main objectives of this study were the characterization and identification of major pollutant parameters in leachate samples from municipal waste landfills in Vojvodina region. Leachate samples were regularly collected from four municipal solid waste landfills in Novi Sad, Subotica, Kikinda and Zrenjanin, in the winter period. Electrical conductivity, pH, dissolved oxygen and temperature measurements were performed *in situ* with a portable Multi 340i device. A fraction of each water sample was separated and acidified with nitric acid to prevent metal precipitation. The non acidified fraction of samples was used for determination of BOD_5, NO_3^-, NO_2^- which were determined using UV- visible spectrophotometer. The metal analysis (Cr, Zn, Cd and Ni) was done by the digestion of 100 mL of the water sample using concentrated sulphuric acid in order to determine total amount of metals in samples. The digested samples were analyzed with the atomic apsorption spectrometer using the flame technique. The average pH value of all samples was 8.13. Conductivity of leachate samples from sanitary landfill was in the range from 19540 to 20800 μS/cm while the conductivity in leachate samples from non sanitary landfills ranged from 472 to 8800 μS/cm. All water samples had low concentration levels of dissolved oxygen (from 0.03 to 0.21 mg/L), except water samples from non sanitary landfill in Zrenjanin (from 3.67 to 4.50 mg/L) which indicates high organic contamination of samples. High values of BOD_5 of the samples from sanitary landfill (784-1275 mg/L) show high pollution of leachate water with biodegradable organic matter. Better quality of some leachate samples from non sanitary landfills has shown signs of aerobic degradation and also there is dilution factor that highly affects quality of water samples. The residues of the metals which were determined in the samples from non sanitary landfills have shown that metal cations of nickel (Ni^{2+}) is the most predominant metal in the landfills (0.591-5.029 mg/L). $Zn^{2+}$was found as the most abundant at the sanitary solid waste landfill (1.444-1.517 mg/L). Concentration levels of the cadmium were under the limit of detection, 0.02 mg/L, in all samples. The obtained results indicate low water quality of samples collected from sanitary and non sanitary municipal waste landfills. A release of leachate to the groundwater may present several risks to human health and the environment.

[1] Faculty of Technical Sciences, Department of Environmental Engineering: Project - Preliminary qualitative and quantitative analysis of leachate water and gas from the waste landfills for establishment of continuous monitoring, Novi Sad, 2009.

P64- SOLID PHASE EXTRACTION OF Ni(II) ON NOVEL PYRIDINE-FUNCTIONALIZED MCM-41 AND MCM-48 MESOPOROUS SILICAS AND ITS SUBSEQUENT DETERMINATION BY FAAS

H. Ebrahimzadeh, M. M. Amini, N. Tavassoli

Department of Chemistry, Shahid Beheshti University, G.C. 1983963113, Evin, Tehran (Iran)

A rather straight forward and sensitive solid phase extraction using novel pyridine-functionalized MCM-41 and MCM-48 mesoporous silica was developed and its application in preconcentration and determination of nickel by flame atomic absorption spectrometry (FAAS) was studied. MCMs have proved to be suitable to be used as an adsorbent in prior studies [1, 2]. Factors such as type, concentration and volume of eluent, pH of the sample solution, flow rate of extraction and volume of the sample were appraised. The effect of a variety of ions on preconcentration and recovery was also investigated. Quantitative recovery of nickel ions was observed to adsorb nickel ions at pH=7 and elute with 3.0 mol L^{-1} HCl solution. Limit of detection (LOD), defined as three times the standard deviation of the blank, was found to be lower than 3.5 μg L^{-1}. Recovery and precision (RSD %) of the method were above 98.5% and below1.5%, respectively. To gauge its ability in terms of application to natural samples, the proposed method was applied to a number of natural samples and the amount of nickel was determined by spiking known concentrations of nickel into the solution.

[1] Alan, M. and Kara, D., Sep. Sci. Technol. 42, 879–895 (2007).
[2] Ramesh, A., Mohan, K.R., and Seshaiah, K. , Talanta 57, 243–252 (2002).

P65- OPTIMIZATION OF AN SPE PROCEDURE FOR ANALYSIS OF HORMONES IN WATER SAMPLES BY HPLC-UV

S. M. Cardoso[1], I. V. Esteves[2], A. P. Fonseca[3]

[1]Faculty of Medicine, University of Coimbra, Rua Larga 3004-504 Coimbra (Portugal)
[2]CESAM -Department of Chemistry, University of Aveiro, Campus de Santiago,
3810-193 Aveiro (Portugal)
[3]Department of Pharmacy, College of Health Technology of Coimbra, Rua 5 de Outubro S. Martinho do Bispo Apartado 7006, 3040 -854 Coimbra (Portugal)

A precise quantification of natural and synthetic estrogens in Waste Waters Treatment Plants (WWTPsL waters for human consumption, rivers, lakes, etc., is essential for a risk assessment regarding endocrine disrupting effects in the aquatic environment. An optimization of analytical method based on HPLC procedure with UV detection has been developed for the simultaneous determination of estrogens in water samples, in less than 9 minutes. The estrogens investigated were estrone, 17β-estradiol, 17αethinylestradiol and estriol and the detection limits of calibration curves were in the range of 0.34 mg/L for 17α-ethinylestradiol and 0.42 mg/L for estrone, using C18 analytical column with a correlation coefficients higher than 0.9995.For application to real water samples, an extraction was achieved using a SPE procedure with polymeric Strata-X cartridges. Average recoveries obtained from 1.0 L of surface water sample ranged between 80-100%. Application of whole SPE-HPLC method to water samples allows a low microgram-per-liter determination for all four hormones.

P66- SIZE DISTRIBUTION AND ENVIRONMENTAL FATE OF ENGINEERED NANOPARTICLES UNDER AQUATIC CONDITIONS

T. Davis, F. Gagné, C. Gagnon and P. Turcotte

Environment Canada, Aquatic Ecosystem Protection Research, 105 McGill st, 7th floor,
Montreal, Qc, H2Y 2E7 (Canada)

Physical characterization, such as size distribution, of engineered nanoparticles has a tremendous impact on the evaluation of their potentially effects, including environmental aspects such as their fate and exposure routes to aquatic organisms. To initiate environmental fate studies, Ag concentrations in different size fractions will be evaluated in both Milli-Q water and natural river water samples, including municipal wastewater effluent-impacted waters. Ultrafiltration techniques were used for size fractionation of the quantum dots cadmium telluride (CdTe QD) and nanosilver (nAg) in both laboratory water and natural water samples, including wastewater-impacted waters. Nanoparticles and transformation products were divided by sequential micro-filtrations and ultrafiltration using membranes of various pore sizes: suspended particles (>0.45 um), coarse colloids, fine colloids, and truly dissolved phase (permeable < 1kDa). For the relatively dispersible nanoparticle CdTe QD, particle size distributions changed significantly under different experimental conditions. Agglomeration alterations were observed where most of the studied particles had a size greater than 0.45 um, which are considered as insoluble in natural waters. Flocculation effect was significantly enhanced by the natural organic matter. The fate of nAg was observed to be similar in natural waters where most material was also found in the large aggregate fraction, with some (10–15 %) found as nano-sized particles. Naturally occurring dissolved organic matter (eg., humic material) likely influences the fate of this type of nanomaterial in maintaining it in colloidal forms and large aggregates. Further characterization and independent validation of the particle sizes (eg. by UV spectroscopy) of sample fractions were also performed. Additional tools for chemical characterization such as measurements of certain optical properties need to be explored to investigate potential changes in reactivity or particle surface activity.
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P67- OCCURRENCE AND BIODEGRADATION OF PARABENS AND THEIR MOST COMMON HALOGENATED BY-PRODUCTS IN WASTEWATER

R. Cela, I. González, J. B. Quintana and I. Rodríguez

Department of Analytical Chemistry, Nutrition and Food Sciences, IIAA-Institute for Food Analysis
and Research, University of Santiago de Compostela, Constantino Candeira S/N,
Campus Vida, 15782, Santiago de Compostela (Spain)

Parabens, esters of *p*-hydroxibenzoic acid, are extensively employed as bactericides and preservative agents in creams, bath gels, shampoos and toothpastes. As in the case of many personal care chemicals, they are continuously released in urban sewage at relatively high levels and, although their removal during conventional wastewater treatments is considerable, they have still been detected in river samples at low ng L^{-1} [1]. Besides this, they can easily react with free chlorine when mixed with chlorinated tap water, yielding mostly mono and dichlorinated derivatives that, in fact, have already been detected in raw sewage water [2]. Although this halogenation masks the apparent estrogenic activity of the parent compounds [3], the resulting chlorinated by-products show higher toxicity responses when working with *Daphnia magna* bioassays [4], so they should be included in any ecological or environmental study involving parabens. In this way, an assessment of the sewage occurrence and environmental biodegradability of parabens and halogenated derivatives of methyl paraben is presented. Several wastewater samples were collected at three different wastewater treatment plants during April and May 2010. They were processed following a solid phase extraction (SPE) method previously described [1] and analysed by liquid chromatography-electrospray ionisation-tandem mass spectrometry (LC-ESI-MS/MS). From these analyses it is worth mentioning the high levels of methyl (MeP) and *n*-propyl paraben (*n*-PrP) in raw wastewater (0.1-10 µg L^{-1} level) and the co-occurrence of the mono and dichlorinated derivatives of the former (0.01-0.1 µg L^{-1} level). Halogenated by-products of *n*-PrP could not be quantified since no standards were available in the laboratory; nevertheless, they could be identified in many of the samples, corroborating the data described by Canosa et al [2], from their accurate precursor and product ion spectra masses measured with a quadrupole-time of flight-mass spectrometer (Q-TOF-MS). Regarding the removal efficiencies, all compounds showed values higher than 90%. Finally, biodegradation studies were carried out according to the regulation ISO 7827:1994. Individual test solutions containing an initial concentration of 5 mg mL^{-1} of each specie were prepared, several aliquots were taken throughout 3 weeks and they were analysed by LC-ESI-MS/MS. Whereas non-halogenated parabens turned out to be completely degraded in less than 4 days, halogenated derivatives of MeP needed longer times, showing a higher persistence that may be taken into account in case they reach the aquatic environment.

[1] González-Mariño, I., Quintana, J.B., Rodríguez, I., Cela, R., Rapid Commun. Mass Spectrometry 23, 1756-1766 (2009)
[2] Canosa, P., Rodríguez, I., Rubí, E., Negreira, N., Cela, R., Anal. Chim. Acta 575, 106-113 (2006)
[3] Terasaki, M., Kamata, R., Shiraishi, F., Makino, M., Environ. Toxicol. Chem. 28 204-208 (2009)
[4] Terasaki, M., Makino, M., Tatarazako, N., J. Appl. Toxicol. 29 242-247 (2009)

P68- WASTE WATER POLYAROMATIC HYDROCARBONS POLLUTION CONTROL USING LIQUID CHROMATOGRAPHY WITH A NEW BONDED LIQUID CRYSTAL STATIONARY PHASE AND OFF-LINE SOLID PHASE EXTRACTION

M. H. Guermouche*

Faculté de Chimie, USTHB, B.P. n°32, El-Alia, Bab-Ezzouar, Alger (Algeria)
*hguermouche@gmail.com

γ-Benzyl -L-glutamate-N-carboxyanhydride with amino propyl-Lichrospher 100 NH_2 is a new bonded liquid crystal stationary phase for high performance liquid chromatography [1-6]. Its thermal and some analytical properties were studied in a precedent work [7]. For the first time, It was used to determine polycyclic aromatic hydrocarbons (PAHs) in waste water. PAHs were extracted from the water samples using solid phase extraction. The wastewater were collected in drive to a marsh near the sea in two spots at 1 m depth located I tne west of Algier City. During the year, the PAHs profiles varied in the same way showing a maximal values during the dry summer in Algeria. During winter, the lowest PAHs amounts were found. The PAHs found were anthracene, phenanthrene, fluoranthene, benzo(a)fluorene, pyrene, chrysene, benzo(a)anthracene, benzo(k)fluoranthene, benzo(a)pyrene, perylene, dibenzo(a,h)anthracene, benzo(g,h,i)perylene. The results were compared some found in the literature [8-9].

[1] A. Meddour, I. Canet, A. Loewenstein, J.M. Pechine, J. Courtieu, (1994) *J. Am. Chem. Soc*. **116**, 9652

[2] I. Canet, J. Courtieu, A. Loewenstein, A. Meddour, J.M. Pechine, (1995) *J. Am. Chem. Soc*. **117**, 6520

[3] A. Meddour, P.Berdague, A. Hedli, J. Courtieu, P. Lesot. (1997) *J. Am. Chem. Soc*. **119**, 4502.

[4] M. Jakubcova, A. Meddour, J.M. Pechine, A. Baklouti, J. Courtieu, (1997) *J. Fluorine Chemistry* **86**, 149

[5] M.L.C.M.Oosterling, E.Willems, A.J.Schouten, (1995) *Polymer* **36**, 4463

[6] E.Dietz, N.Fery, K.Hamman, (1974) *Angew.Makromol.Chem*. **35**, 115

[7]O.Ferroukhi, N.Atik, S.Guermouche, M.H.Guermouche, P.Berdagué, J.P.Bayle, (2000) *Chromatographia,* **52**, 564

[8] L.Liguori, K.Heggstad, H.T. Hove , K. Julshamn, (2006) *Anal. Chim. Acta* **573,** 181

[9] L.C.Sander, S.A.Wise, (1984) *Anal.Chem.* **56**, 504

P69- SEPARATION AND SPECTROPHOTOMETRIC DETERMINATION OF VERY LOW LEVELS OF Cr(VI) IN WASTEWATER ON NOVEL PYRIDINE-FUNCTIONALIZED MESOPOROUS SILICAS

A. Asgharinezha, H. Ebrahimzadeh, F. Kamarei, N. Tavassoli

Department of Chemistry, Shahid Beheshti University, G.C. 1983963113, Evin, Tehran (Iran)

A modified SBA-15 mesoporous silica was developed, as an adsorbent, for the removal of Cr(VI) ions from natural-water samples. MCMs have proved to be suitable to be used as an adsorbent in prior studies [1, 2]. The effects of experimental parameters, including pH of solution, sample and elution flow rate, eluent type, concentration and volume of eluent, and the effect of coexisting ions on the separation and determination of Cr (VI), were investigated. The pH was found to be critical for the separation of Cr(VI) from Cr(III) ions, as it was shown that Cr(VI) was selectively adsorbed from aqueous solution at pH 3. Conversely, Cr(III) could be adsorbed from solution at alkaline pH. The retained Cr(VI) was subsequently eluted with 0.5 mol L^{-1} KCl solution in 0.1 mol L^{-1} Na_2CO_3. Under the optimum conditions, the modified mesoporous silica (py-SBA-15) with a high pore diameter exhibited an adsorption capacity of 136 mg g^{-1} and a lower limit of detection of 2.3 μg L^{-1} for the extraction of Cr(VI) ions. A preconcentration factor as high as 200 was calculated for Cr(VI). The loaded py-SBA-15 can be regenerated for recovery of more than 98.5% over at least eight cycles. The relative standard deviation (RSD) for Cr ion recovery was less than 1.2% in these experiments. The proposed method was applied to the determination of Cr (VI) in natural-water samples with successful results.

[1] Hosseini, M.S., Bandegharaei, A. H., Raissi, H. and Belador, F., J. Hazard. Mater. 169, 52-57 (2009).

[2] Chen, M., Zou, A., Zhong, C. and Wang, J., Anal. Sci. 23, 627-630 (2007).

P70- TANDEM USE OF SOLID-PHASE EXTRACTION AND DISPERSIVE LIQUID-LIQUID MICROEXTRACTION FOR DETERMINATION OF SOME PHTHALATE ESTERS IN WATER SAMPLES

A. Kashtiaray and H. R. Sobhi

Department of Chemistry, Tehran Payamenoor University, 1598686613 Tehran (Iran)

Solid-phase extraction (SPE) in tandem with dispersive liquid-liquid microextraction (DLLME) has been developed for determination of some phthalate esters in water samples using gas chromatography-flame ionization (GC-FID) detection system. In the hyphenated solid-phase extraction-dispersive liquid-liquid microextraction technique (SPE-DLLME), initially the analytes were adsorbed from a large volume of aqueous samples (100 mL) into a 500 mg octadecyl silane (C_{18}) sorbent. After the elution of analytes from the sorbent with acetonitril, the obtained solution was put under the DLLME procedure, so that the extra preconcentration factors could be achieved. The parameters influencing the extraction efficiency, such as breakthrough volume, type and volume of the elution solvent (disperser solvent) and extracting solvent, as well as the salt addition, were studied and optimized. The calibration curves were linear in the range of 0.2-200 µg L^{-1} and the limit of detection (LOD) for all analytes was found to be 0.05 µg L^{-1}. The relative standard deviations without internal standard varied from 6.0 to 11.4% ($n = 5$). The relative recoveries of the water samples were in the range of 83-118 %.

[1] Rezaee, M., Assadi, Y., Milani Hosseini, M.R., Aghaee, E., Ahmadi, F., Berijani, S., J. Chromatogr. A 1116, 1-9 (2006).
[2] Fattahi, N., Samadi, S., Assadi, Y., Milani Hosseini, M.R., J. Chromatogr. A 1169, 63-69 (2007).

P71- INVESTIGATING THE PHOTOCATALYTIC CAPABILITIES OF IRON OXIDE DOPED NANO TITANIUM OXIDE IN DEGRADATION OF FORMALDEHYDE

M. Khanmohammadi[1], A. Bagheri Garmarudi[1,2], H. Elmizadeh[1]

[1]Chemistry Department, Faculty of Science, IKIU, Qazvin (Iran)
[2]Department of Chemistry & Polymer Laboratories, Engineering Research Institute, Tehran (Iran)

The high rate increment in production and consumption of formaldehyde has caused harmful problems for both human and environment. It has already been known as a very toxic, mutant and carcinogen causing chemical which affects human eyes, membranes, and respiration systems. It is well-known that the condensation reaction between Fluoral P and formaldehyde produced a complex which is useful for spectrophotometric detection of formaldehyde. TiO_2 nano-crystalline is one of the most popular photocatalysts with versatile environmental and chemical capabilities. Nano sized TiO_2 so far has been prepared by hydrolysis of titanium precursors followed by annealing, flame synthesis, hydrothermal and sol–gel process. Nano TiO_2 particles provide high chemical stability, high resistance in acidic and alkali media, non-poisonous, safe and easy to prepare. It also facilitates the decomposition of organic pollutants by light, resulting in generating of non-toxic CO_2, H_2O and some inorganic products. Porous nano TiO_2 has been prepared by sol–gel route demonstrating high photocatalytic activity with high specific surface area. The titanium oxide – iron oxide hybrid nano composite was synthesized by sol-gel technique. Degrading effect of the hybrid nanostructure on formaldehyde - Fluoral P complex was investigated in presence of UV light by spectrophotometry. The probable influence of the nano photocatalyst on each constituent of the complex was also monitored.

P72- PREPARATION OF DIMETHYL(*E*)–2–(1-ACETYL)-2-OXO PROPYL-2-BUTENDIATE AS A NEW LIGAND FOR SOLID PHASE EXTRACTION AND SPECIATION OF Fe^{2+} AND Fe^{3+} IONS IN ENVIRONMENTAL WATER SAMPLES

S. Hassanpoor, G. Khayatian*, F. Nasiri, A. Zolali

Department of Chemistry, Faculty of Science, University of Kurdistan, 66177-15175,
Sanandaj (Iran)
*gkhayatian@yahoo.com

Iron is fourth in abundance of elements (after O, Si and Al) and second in abundance of metals on the earth's crust. It plays an outstanding role in chemical reactions, such as, in geological processes, in environmental and atmospheric chemistry, and in biochemistry[1]. Owing to the presence of iron in environmental and biological materials, and the lack of sufficient understanding of the role of the two oxidation states of this element, determination of both Fe(II) and Fe(III) is of the great importance[2]. In the present study, a solid phase extraction method was developed for the speciation and determination of iron in different water samples using the new ligand dimethyl (*E*)-2-(1-acetyl)-2-oxo propyl-2-butendioate (DAOPB) to retain the iron prior to detection by flame atomic absorption spectrometry (FAAS). Iron(III) reacts with DAOPB to form a red complex that absorb at $\lambda_{max} =$ 482 nm. Spectrophotometric and conductometric methods showed that a ML_3 complex is formed between ligand and Fe(III) ion that is responsible for extraction of metal ion on the disk. Various influencing factors on the separation and preconcentration of Fe(III), such as pH of aqueous solution, amount of ligand and sample flow rate have been investigated and the optimized operation condition were established. At pH 2.5 Fe(III) could be selectively retained by the disk but Fe(II) passed through it.

[1] Cornelis, R., Caruso, J., Crews, H..and Hramann, K., "Handbook of elemental speciation II, species in the environment, food, medicine and occupational health", John Wiley & Sons (2005).
[2] Aki, M. A. Microchem, J. 75,199 (2003) .

P73- PORTABLE ELECTROSPRAY IONIZATION MASS SPECTROMETRY (ESI-MS) FOR ANALYSIS OF CONTAMINANTS IN THE FIELD

C. Janfelt, R. Græsbøll and F. R. Lauritsen

Department of Pharmaceutics and Analytical Chemistry, University of Copenhagen,
Universitetsparken 2, 2100 Copenhagen (Denmark)

Hitherto analysis of chemicals in the field using mass spectrometry (MS) has been limited to analysis of volatile organic compounds using either a direct gas leak or a membrane inlet as MS interface. However, recently it was demonstrated that miniature mass spectrometers operating at elevated pressures ($> 1\cdot10^{-4}$ torr) can be combined with electrospray ionization (ESI) for analysis of non-volatile organic compounds [1]. This paper will present a simple miniaturized ESI unit for analysis of small liquid samples (20-30 µL). The ESI unit operates without pumps and supplementary sheet gases, which makes it very simple to handle in the field. 20-30 µL of sample solution is simply dropped into a small cavity in the ESI unit, where after the spray is initiated by applying high voltage to the unit. The ESI unit is well suited for combination with micro extraction systems for matrix removal and/or improved sensitivity. We present the first data obtained with the ESI unit in combination with a miniature mass spectrometer (the Mini-10 developed by Prof. R. Graham Cooks, Purdue University, IN [2]).

[1] Keil, A., Talaty, N., Janfelt, C., Noll, R.J., Gao, L., Ouyang, Z., Cooks, R.G., Anal. Chem. 79, 7734-7739 (2007).
[2] Gao, L., Song, Q.Y., Patterson, G.E., Cooks, R.G., Ouyang, Z., Anal. Chem. 78, 5994-6002 (2006).

P74- THE SELECTION OF AN UNIVERSAL CHEMICAL MODIFIER FOR VANADIUM DETERMINATION IN VARIOUS NATURAL WATERS BY ELECTROTHERMAL ATOMIC ABSORPTION SPECTROMETRY

L. Macháčková and M. Žemberyová

Department of Analytical Chemistry, Faculty of Natural Sciences, Comenius University in Bratislava,
Mlynska dolina CH 2, 842 15 Bratislava (Slovak Republic)

Vanadium is an essential element and is beneficial to normal cell growth. However, higher content of vanadium shows toxic properties. With the increasing industrial activities, the content of vanadium in the environment is increasing rapidly. Vanadium would enter and accumulate in human body through various ways, and natural water is one of the main routes. In aqueous solution, V(IV) and V(V) are the most commonly existing forms and they exhibit different nutritional and toxic properties. Vanadium (V) is a potentially dangerous chemical pollutant which coexists in environment with (IV) species. Determination of vanadium at trace levels is an important subject in analytical chemistry for understanding of its geochemical and biological effects as well as for a monitoring of environmental pollution.

The topic of this work is the comparison and the selection of universal modifier for the determination of vanadium in development of methodology for the direct determination of vanadium in several natural waters by electrothermal atomic absorption spectrometry (ETAAS) using transversely heated graphite tube. Some problems affect the analytical results by using this technique like the formation of thermally stable vanadium carbides enhanced by the ageing of the pyrolytic coating of the graphite tubes, where a decrease in the sensitivity is observed with increasing number of the firings; and the interferences in the presence of common chloride matrices, such as in sea water. The use of appropriate chemical modifier could prevent formation of carbides as well as interferences from the matrix. For this purpose, the various chemical modifiers (ascorbic acid, ammonium nitrate, EDTA and NH_4SCN) were tested. Because chloride salts, mainly NaCl, $CaCl_2$, $MgCl_2$ and $FeCl_3$ influenced the vanadium signal, the effects of increasing amounts of the mentioned salts as well as the nitrate salts of the elements for the comparison on the absorption signal of vanadium were studied. Tap water, mineral curing water, synthetic river and sea water were studied in this contribution. The best elimination of the matrix interferences was achieved by using ascorbic acid and ammonium nitrate. The applicability of this universal matrix modifiers for the determination of V(V) in the several types of waters by ETAAS have been confirmed by analyzing the certified reference material of drinking water (“Trace Metals in Drinking Water”) and standard reference material of fresh water (SRM 1643e “Trace Elements in Water”).

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P75- DETERMINATION OF HYDRAZINE IN BOILER WATERS BY COULOMETRIC TITRATION

E. Beinrohr, R. Hudec, A. Manova

Institute of Analytical Chemistry, Faculty of Chemical and Food Technology,
Slovak University of Technology,
Radlinského 9, 812 37 Bratislava (Slovakia)

Introduced work is focusing to possible study of determining hydrazine using methods of coulometry and chronopotentiometry to design a simple, effective method and choose appropriate conditions for its determination. Aim of the work is to specification selected validation parameters for determination of hydrazine by suggested method, validation of the method itself, to automatization the electrochemical system
of for unattended monitoring and to apply this procedure to analyses of real samples of water from power stations.

The flow-through chronopotentiometry is method which allow determination hydrazine from 23 $\mu g.dm^{-3}$ higher due to used electrode and stripping current. Furthermore it was important to optimize parameters, which rapidly influence the measurement, mostly to deal with a choice of appropriate current. Here we decided for 200 µA for microporous electrode E-53C and 10 µA for macroporous electrode E-104C because of length of stripping time, which should be the shortest for application in technical practice.

We found out the limit of detection (LOD) for hydrazine to be 7.8 $\mu g.dm^{-3}$ working with system EcaFlow and macroporous electrode E-104C with limit of quantification (LOQ) of 23.4 $\mu g.dm^{-3}$ or empiric found out 0.2 $mg.dm^{-3}$ (LOD) and 0.7 $mg.dm^{-3}$ (LOQ) and for microporous electrode E-53C, respectively. Testing of interferences of compounds typical for boiler water from power stations showed that determination was mainly influenced cuprous Cu(II), ferrous Fe(II) and ferric Fe(III) cations because of precipitates creation with hydrogenphosphosphate and ammonia, which increased the background. Flow-through chronopotentiometry is simple, relatively fast, well reproducible and repeatable method. This method gives accurate and correct results at microporous electrode. However the results obtained at the macroporous electrode are accurate only in the case of stabilized sample.

It is suitable for hydrazine determination in boiler waters from power stations together with industrial waste waters released into surface water from energetic industry (heating plants and power stations).

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P76- DEVELOPMENT OF A IONIC LIQUID BASED DISPERSIVE LIQUID-LIQUID MICROEXTRACTION METHOD FOR BENZOTRIAZOLES AND BENZOTHIAZOLES DETERMINATION IN WATER SAMPLES

C. Casais, R. Cela, C. Mejuto, T. Pena, X. Vecino

Departamento de Química Analítica, Nutrición y Bromatología, Facultad de Química,
Instituto de Investigación y Análisis Alimentario, Universidad de Santiago de Compostela,
15782 Santiago de Compostela (Spain)

Benzotriazoles and benzothiazoles are polar high production volume chemicals that find broad application in various industrial processes as well as in households. Benzotriazoles are used as corrosion inhibitors, industrial cooling systems and silver protection in household dishwashing agents, whereas benzothiazoles are used as vulcanization accelerators in rubber production, biocides in paper and leather manufacturing and anticorrosives. Due to their high solubility in water and resistance to biodegradation, these emerging contaminants have been detected in the aquatic environment [1-2].

The actual tendency in Analytical Chemistry is focussed to miniaturisation by using microextraction techniques. One of the emerging techniques in this area is dispersive liquid-liquid microextraction (DLLME), which offers several important advantages such as faster operation, no need to large amounts of solvent and low time and cost. On the other hand, within the last decade, ionic liquid have also attracted much attention due to their special feature like low-vapour pressure, high viscosity and good thermal stability [3].

The aim of this study was to develop and validate an ionic liquid based dispersive liquid-liquid microextraction method, for the extraction and concentration of benzotriazoles (1H-benzotriazole, 4-methyl-1H-benzotriazole, 5-methyl-1H-benzotriazole, 5,6-dimethyl-1H-benzotriazole, 5-chloro-1H-benzotriazole, 4-hydroxybenzotriazole, benzotriazole-5-carboxylic acid) and benzothiazoles (benzothiazole, 2-aminobenzothiazole, 2-hydroxibenzothiazole, 2-(methyltio)-benzothiazole, 2-mercaptobenzothiazole) from water samples. The influence of several variables (e.g. type and volume of dispersant and extraction solvents, pH, ionic strength, etc.) on the performance of the sample preparation step was carefully evaluated. Analytical determinations were carried out by high performance liquid chromatography with UV and fluorescence detection. The developed procedure exhibits good concentration factors as well as low quantification limits for all studied compounds.

[1] De Weber, H., Verachtert, H., Wat. Res. 31, 2673-2684 (1997).
[2] Giger, W., Schaffner, C., Kohler, H.-P.E., Environ. Sci. Technol. 40, 7186-7192 (2006).
[3] Baker, G.A., Baker, S.N., Pandey, S., Bright, F.V., Analyst 130, 800-808 (2005).

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P77- ECOTOXICOLOGY ASSESSMENT AND CHEMICAL CHARACTERISTICS OF WATER SAMPLES AFTER MINING AND PROCESSING OF URANIUM

M. Moos, Z. Holubova, L. Sommer

Brno University of Technology, Chemistry and Technology of Environmental Protection,
Purkyňova 118, 612 00 Brno (Czech Republic)

An ICP-MS spectrometer Agilent 7500ce, with a plasma generator of 27.12 MHz, power output 1500 W and concentric nebulizer MicroMist™ with a cooled Scott chamber was used. Linear calibration plots for 1-50 ppb Uranium are in solutions containing 0,5% HNO_3 for ^{238}U. Internal standard ^{209}Bi was successfully used for the suppression of signal of interfering elements (K^+, Na^+, NH_4^+, Fe^{2+}, Ca^{2+}, Mg^{2+}, Al^{3+}, NO_3^-, NO_2^-, SO_4^{2-}, Cl^-, HCO_3^-). The silica-based non-polar sorbent (C18) was conditioned with the cationic surfactant. The different organic reagents such as 4-(2-pyridylazo) resorcinol, Ammonium pyrrolidinedithiocarbamate, 8-Hydroxyquinoline-5-sulphonic acid and Alizarine S were used as complexing agents for preconcentration of U at pH 5-9. The mixture of acetone and ethanol (1:1) in presence of 1 $mol \cdot l^{-1}$ HCl was used for elution of uranium. Organic solvents and the excess of acid were removed by evaporation prior to the determination by ICP-MS. The *Thamnocephalus platyurus* as THAMNOTOXKIT F ™ was used for ecotoxicology assessment of water samples after mining and processing of uranium.

P78- CONTAMINATION OF LAKE ATITLÁN, GUATEMALA

E. Hernández[1], F. Martínez[1], B. E. Oliva-Hernández[1], J. F. Pérez-Sabino[1],
B. S. Valladares-Jovel[2]

[1]Escuela de Química, Edificio T-12, Universidad de San Carlos de Guatemala zona 12,
01012 Guatemala city, (Guatemala)
[2]Escuela de Biología, Edificio T-10, Universidad de San Carlos de Guatemala zona 12,
01012 Guatemala city, (Guatemala)

Levels of nutrients, bacteria, physicochemical parameters and toxic metals were analyzed in samples of water, superficial sediments, fish and aquatic plants in Lake Atitlán, during 2009. Lake Atitlán known in the region as “the most beautiful lake in the world” is a lake of 100km^2 and of volcanic origin, located at 1800 m above sea level in the highlands of Guatemala. The lake has been classified as oligotrophic in previous studies, but the human population growth, direct wastewater discharges, deforestation, non adequate use of fertilizers in the basin and the tropical storm “Stan” in 2005 have increased the levels of nitrogen and phosphorus in the water.

Levels of total nitrogen up to 0.28 mg/L and of total phosphorus up to 0.21 mg/L were found in the lake water in this study, which are tenfold higher than levels found in the 1970’s, and changing the lake to be nitrogen-limited. The levels of nitrate-N (up to 0.12 mg/L), ammonia-N (up to 0.13 mg/L which is higher than recommended limits) and phosphate-P (up to 0.06 mg/L) have also increased notably. A bloom of the cyanobacteria *Lyngbya sp*. which has covered nearly 90% of the lake surface has occurred in octuber 2008 and 2009, revealing the change in the composition of the phytoplankton population due mainly to the increase in the contamination levels. Some species of Lyngbya cyanobacteria are known to produce cyanotoxins [1], however to date is unknown if the cyanobacteria in Lake Atitlán produces cyanotoxins, so this is one of the main objectives to continue the study in the short term.

Zn, Cd, Pb, Cu and As were determined by polarography in fish muscle of different species consumed in the region *(Lepomis macrochirus, Micropterus salmoides, Pomoxis nigromaculatus)*, aquatic plants (*Thypa dominguensis, Eichornia crassipes, Utricularia gilbba, y Potomogeton pectinatus*) and phytoplankton, showing bioaccumulation.

Different proposals to remediate the problem have been made by emergency committees, including the installation of water treatment plants, the use of sonication to destroy the cyanobacteria, to change the agricultural practices, but no agreement has been reached.

[1] Smith, J.L., Boyer, G.L., Zimba, P.V. A review of cyanobacterial odorous and bioactive metabolites: Impacts and management alternatives in aquaculture. Aquaculture 280, 5-20 (2008).

P79- FAST DETERMINATION OF ARSENIC INORGANIC SPECIES IN GROUNDWATER BY SPE-ETAAS

L. Achene, M. Ottaviani, P. Pettine*, E. Veschetti

Istituto Superiore di Sanità, Dep. of Environment and Primary Prevention,
Viale Regina Elena 299, 00161 Rome (Italy)

The application of the Drinking Water Directive 98/83/EC have had a great impact on drinking water supply in Italy due to the introduction of few parametric values significantly lower than previous water quality standards. This caused cases of non-compliancy for a number of parameters, such as As, which is a frequent naturally-occurring contaminant of Italian groundwater. On account of this, a monitoring activity was carried out between 2007 and 2009 in a large volcanic aquifer of central Italy, where high levels of arsenic were reported. Analytical results from 239 samples showed that the concentration of the target element was in the range 2.0-5.0 µg/L for 40% of the concentration values, but was greater than 10 µg/L in about 40% of the analysed samples and greater than 3 times the legal limit in 20% of the sites (in the south-east area of Vico lake). In the latter zone water treatment is currently the only possible strategy to reduce arsenic level within the limit of acceptability as no further water supply with low As contamination is sufficiently near to operate water dilution. Generally, the removal technologies are strongly affected by the oxidation state of the element. Therefore, arsenic speciation represents an essential activity that must precede the planning stage of the most suitable plant.

In this study we have worked out speciation analyses to evaluate the ratio between arsenite and arsenate in groundwater samples. Arsenic trichloride was selectively extracted into OASIS HLB cartridges (styrene-divinylbenzene polymer) from HCl solutions and then subsequently hydrolyzed and eluted with water for analysis. The concentration of As (III) as well as total arsenic content were then determinate by electrothermal atomic absorption spectrometry (ETAAS). Experimental conditions (HCl concentration, washing flow rate, eluent polarity and flow rate, ashing and atomization temperatures) were optimized to improve As(III) recovery and speciation selectivity. The effect of additives (no chemical addition, hydrochloric acid or ethylenediamine-tetracetic acid) was evaluated to inhibit species inter-conversion before the determination. Finally, the ratio between As(III) and As(V) was correlated with physico-chemical and chemical parameters (i.e. pH, redox potential, temperature, electrical conductance, as well as major and minor inorganic cations and anions) of aqueous samples.

P80- EXTRACTION OF AMITROLE FROM WATER SAMPLES BY SPME AND LPME PRIOR TO GC-MS ANALYSIS

R. Bernardino[2], J. P. Noronha[1], Ž. Petrovski[1], M. I. Pinto [1,2]

[1]REQUIMTE/CQFB, Chemistry Department, FCT, Universidade Nova de Lisboa,
2829-516 Caparica (Portugal)
[2]GIRM/ESTM, IPL, Campus 4, Santuário N.ª Senhora dos Remédios, Apt. 126,
2524-909 Peniche (Portugal)

Amitrole is a triazole herbicide that has been used to control weeds in vineyards and orchards and also in railroads and roadsides. The direct application of amitrole on food crops has already been cancelled in many countries since the compound has been classified as a probable human carcinogen. Although amitrole has found some applications as cotton defoliant and as photographic reagent, in the European Community, the compound can only be used as an herbicide. When applied to vegetation, the compound is absorbed through roots and leaves where chlorophyll formation is inhibited by its action. After application, it can persist in soil for several weeks and in water for more than 200 days [1]. Surface and groundwater contamination can occur as a consequence of leaching processes. In drinking waters, amitrole concentrations higher than of 100 ng/L are not allowed by European legislation which also states that the limit of detection (LOD) of the analytical methods used to quantify pesticides should be 25 ng/L [2]. As a consequence of its polarity and high water solubility, ion chromatography with electrochemical detection is the technique of choice for amitrole analysis, however, the difficulty to remove interferences such as the competitive ions and the high LOD, make the developed methods not very suitable for routine analysis. So far, few articles have been published concerning amitrole water analysis. The pre-concentration of the compound present at trace levels is a difficult step to carry on due to its high water affinity. Evaporation of aqueous samples and solid phase extraction (SPE) have been the techniques used to concentrate the compound [3]. Other new techniques like liquid phase microextraction (LPME) and solid-phase microextraction (SPME) have been applied to different class of pesticides but to the best of our knowledge there is no publication concerning the concentration of amitrole or its derivatized products by SPME or LPME. Moreover, gas chromatography-mass spectrometric detection (GC-MS) has never been applied. Thus, the aim of this study is to analyze amitrole in water samples by GC-MS using other recently extraction technique such as SPME after derivatization of amitrole diazonuim salt with β-naphthol.

[1] E. Commission, D.G.H.C. Protection, A.A.P.H. Directorate E - Public, in Unit E1 Legislation relating to crop products and animal nutrition (2001).
[2] Directive 98/83/EC of the Council of 3 of November on the quality of water intended for human consumption, Off. J. Eur. Comm., L330, 05.12.1998, p.32 (1998).
[3] Girod M., Delaurent C., Charles L., Rapid Commun. Mass Spectrom. 20 (2006) 892.

P81- TRIMETHROPIM - IMPRINTED MATERIALS FOR POTENTIOMETRIC DETERMINATION IN AQUACULTURE WATER

S. A.A. Almeida[1,2], T. S.C.R. Rebelo[1] and M. G. F. Sales[1]

[1]REQUIMTE/ISEP, Instituto Superior de Engenharia do Porto R., Dr. António Bernardino de Almeida, 431, 4200-072 Porto (Portugal)
[2]INSA-Porto, Instituto Nacional de Saúde Dr. Ricardo Jorge-Porto, 321, 4000-055 Porto (Portugal)

Trimethoprim is generally administered in large quantities to humans and animals to treat a variety of diseases. Often, a high percentage of them are excreted from animals without metabolism or in conjugated forms which readily convert back into the parent compounds [1]. A thorough search in the literature revealed that liquid chromatography (HPLC) is the analytical method currently available to detect this antibiotic in water and wastewater. These liquid chromatographic methods (HPLC) are usually coupled to mass spectrometry (MS) [2], tandem MS/MS [3], electrospray MS (ESI-MS) [4] and electrospray tandem MS (ESI-MS/MS) [5] detection.

Ion-selective sensors would be an alternative analytical tool because they offer high precision and rapidity, low cost of analysis, enhanced selectivity and sensitivity over a wide range of concentrations [6]. Ionophore molecules are responsible for the chemical sensing and signal generation in the electrochemical interface of a potentiometric sensor. These could be molecularly-imprinted materials to enable stereochemical recognition of the analyte and enhance the selectivity enhancement of sensor.

This work proposes a new biomimetic sensor material for Trimethoprim. It is prepared by means of radical polymerization, having trimethylolpropane trimethacrylate as cross-linkerm, benzoyl peroxide as radical initiator, chloroform as porogenic solvent, and methacrylic acid (MAA) and 2-vinyl pyridine (VPY) as monomers. In order to ascertain the amount of sensor that provides the best analytical, different percentages of sensor in a range between 1 and 6% were studied.

The presence of an additive in the sensing membrane can improve the sensitivity of the potentiometric sensor. Therefore, tetrakis(p-chlorophenyl)borate was used as additive, in concentrations between 0 and 2%.

The Trimethoprim sensors with 1% MAA showed the best response in terms of slope (59.7 mV/decade) and detection limit (4.01×10^{-7} mol/L). These electrodes displayed also a good selectivity towards nickel, manganese aluminium, ammonium, lead, potassium, sodium, iron, chromium, sulfadiazine and alanine, cysteine, tryptophan, valine, glycine. The sensors were not affected by pH changes ranging from 2 to 6. The sensors were successfully applied to the analysis of aquaculture water.

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[1] Daughton, C.G. and Ternes, T.A., Environm. Health Persp. 107, 907-938 (1999).
[2] Lindberg, R., Jarnheimer, P.A. and Olsen, B., Chemosphere 57, 1479-1488 (2004).
[3] Gros, M., Petrovic, M. and Barceló, D., Talanta 70, 678-690 (2006).
[4] Rao, R.N. and Narsimha, R., J. Chromatogr. A 1187, 151-164 (2008).
[5] Hilton, M.J. and Thomas, K.V., J. Chromatogr. A 1015, 129-141 (2003).
[6] Cosofret, V.V. and Buck, R.P., Anal. Chem. 24, 1-58 (1993).

P82- ANALYSIS OF ENDOCRINE DISRUPTORS IN WATER BY SOLID-PHASE EXTRACTION, LIQUID CHROMATOGRAPHY AND ELECTROSPRAY TANDEM MASS SPECTROMETRY – COMPARISON OF HPLC AND UPLC SYSTEM PERFORMANCE

A. M. Rodrigues, V. V. Cardoso, E. Ferreira, and M. J. Benoliel

EPAL, Laboratório Central, Rua do Alviela 12, 1170-012 Lisboa (Portugal)

Endocrine disrupting compounds (EDC) encompass a variety of chemical classes, including hormones, plant constituents, pesticides, compounds used in the plastics industry and in consumer products, other industrial by-products and pollutants. These compounds are pervasive and widely dispersed in the environment. Some are persistent organic pollutants (POP's), and can be transported long distances across national boundaries and have been found in virtually all regions of the world. After usage these compounds are released to the environment and may reach and contaminate water for human consumption. Health effects attributed to endocrine disrupting compounds include a range of reproductive problems, changes in hormone levels, early puberty, brain and behavior problem, impaired immune functions and various types of carcinomas.

In this work nine EDCs had been studied: estriol, bisphenol A, diethylstilbestrol, estrone, β-estradiol, ethinylestradiol, progesterone, 4-tert-octylphenol and mestranol.

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

The use of UPLC instead of HPLC leads to a significant increase of the analytical method performance. The high operation pressure of the UPLC binary pump, lead to a shorter chromatographic run time when compared with HPLC (6 min instead of 28 min). The high efficiency of UPLC columns allowed to achieve narrow and higher chromatographic peaks (width <0.177min and <0.580min for UPLC and HPLC, respectively) leading to an increase of the method sensitivity. The UPLC-ESI-MS/MS method showed excellent chromatographic linearity ranges for all EDCs (20-100 μg/L), with determination coefficients greater than 0.9987 (β-estradiol). Several statistical tests were performed to verify the linearity and working range. Recovery studies in several matrices with different fortification solution levels were performed using HLB solid phase extraction cartridges with recoveries between 50.2% (progesterone) and 100.5% (diethylstilbestrol) with RSD lower than 20.4% (ethinylestradiol). The method quantification limits (MQL) obtained for these compounds were between 0.020μg/L (diethylstilbestrol) and 0.060 μg/L (mestranol). Interlaboratory studies showed good performance for this method with z-score 0.93 for 4-tert-octylphenol and a relative error of -7.7% for bisphenol A.

P83- DETERMINATION OF 1,4-DIOXANE IN WATER SAMPLES BY SELF-DOPED POLYANILINE BASED SOLID-PHASE MICROEXTRACTION FIBER

A. Jabbari[1] A. Mehdinia [2] and F. Roohi[1]

[1] Department of Chemistry, K.N. Toosi University of Technology, Tehran (Iran)
[2] Department of Marine Living Resources, Iranian National Center for Oceanography, Tehran (Iran)

In this work, a novel solid-phase microextraction coating termed self-doped polyaniline (SPAN)-based fiber was coupled with selective gas chromatography–flame ionization detector (GC–FID) for the extraction of 1,4-dioxane in water samples. Nano-structured sulfonated polyaniline was coated onto a platinum wire and used as an adsorbent and that was placed in a stirred aqueous sample solution. The morphological study was done by scanning electron microscopy and the measured size of particles was obtained below 100 nm. The good environmental stability of the parent polyaniline is further improved by the presence of the $-SO_3^-$ group on the phenyl rings due to its strong electron-withdrawing properties [1]. It has also been shown that SPAN has better thermal stability than its parent [1-3]. These acidic anionic groups act as counter anions as well. So there is no need to use an external doping anion in the polymer structure that of the un-substituted polyaniline doped with an external dopant. The polymerization was performed by cyclic voltammetry method from -0.3 to 1.0 V vs. Ag/AgCl at scan rate of 10 mV s^{-1}. Higher thermal and mechanical stability was achieved for SPAN than pure polyaniline. The fibers were stable up to 350º C and could be used for extraction more than 50 times. Relative standard deviation ($n = 5$) were smaller than 6% and limit of detection ($S/N= 3$) were obtained 0.3ng ml^{-1}. The calibration curve was linear in the concentration range of 1-100 ng ml^{-1}. The new SPME coating was evaluated for the analysis of 1,4-dioxane in three water sample and good recoveries ranged from 98±1 to 120±1% was observed.

References

[1]Han,C. C.;Hong, S.P.;Yang, K.F.;Bai, M.Y.;Lu, C.H.;Huang, C.S.Macromolecules. 34, 587(2001)
[2]Titelman GI, Zilberman M, Siegmann A, Haba Y,Narkis M .J Appl Polym Sci.66,2199- 208 (1997)
[3] Narkis M, Zilberman M, Siegmann A. Polym Advan Technol . 8,525–89 (1997)

P84- FAITH OF POLYCHLOROBIPHENYLS DURING AN AQUEOUS BIOREMEDIATION ASSAY WITH PHANEROCHAETE CHRYSOSPORIUM. KINETICS OF DEGRADATION AND SORPTION ON MYCELIUM

M. Sangely[1,2,3], C. Sablayrolles[1], P. Strehaiano[2], L. Thannberger[3]
and M. Montrejaud-Vignoles[1]

[1]INRA, UMR 1010, F-31077 Toulouse (France)
Université de Toulouse; INPT, ENSIACET; LCA - Laboratoire de Chimie Agro-Industrielle;
118 Route de Narbonne ; F-31077 Toulouse
[2]Laboratoire de Génie Chimique, UMR CNRS 5503, 5 Rue Paulin Talabot, 31106 Toulouse (France)
Université de Toulouse, INPT, UMR 1010, F-Toulouse
[3]VALGO, 81 rue Jacques Babinet, 31100 Toulouse (France)

Polychlorinated biphenyls (PCBs) are known to be world wide spread persistent organic pollutants (POP) [1]. The white rot fungus Phanerochaete chrysosporium is able to degrade PCBs in water, and soil [2, 3]. As POP, PCBs can also be adsorbed onto organic matter, such as Phanerochaete chrysosporium mycelium. A previous study have estimated the fractioning of PCBs in water in an aqueous bioremediation assay in truly degraded PCBs, adsorbed PCBs and residual PCBs [4]. The objective of this work is to determine the kinetics of this fractioning. Six bioremediation assays of 500 mL have been performed. For each assay, a mineral solution is stained with PCBs (IUPACC numbers 28, 52, 101, 118, 138, 153 and 180) up to a concentration of 10 $\mu g.L^{-1}$ and inoculated with Phanerochaete chrysosporium grown on Malt extract broth. PCBs are analysed at t = 0 day, t = 1 d, t = 2 d, t = 3 d, t = 7 d and t = 14 d. For each point of the kinetic, a whole experiment is stopped and PCBs concentrations in aqueous phase and in mycelium are determined by high performance gas-chromatography coupled to low resolution mass spectrometry detection. Results show a quick sorption of PCBs on Phanerochaete chrysosporium mycelium during the 48 first hours corresponding with a decrease of PCBs in water. Then the quantity of PCB decreases both in water and mycelium. This fact gives a strong evidence of PCBs degradation by this white rot fungus.

1. UNEP, *Stockholm Convention on Persistent Organic Pollutants.* 2004.
2. Kamei, I., R. Kogura, and R. Kondo, *Metabolism of 4,4'-dichlorobiphenyl by white-rot fungi Phanerochaete chrysosporium and Phanerochaete sp. MZ142.* Applied microbial and cell physiology, 2006. **72**: p. 566–575.
3. Ruiz-Aguilar, G.M.L., et al., *Degradation by white-rot fungi of high concentrations of PCB extracted from a contaminated soil.* Advances in Environmental Research, 2002. **6**(4): p. 559-568.
4. Sangely, M., et al., *Polychlorinated biphenyls fractionning assessment in aqueous bioremediation assay with Phanerochaete chrysosporium.* International Journal of Environmental Analytical Chemistry, 2009. **89**(8): p. 849 - 856.

P85- THE EFFECT OF LOCAL INDUSTRY IN WROCLAW CITY ON THE CONTENT OF HEAVY METALS IN HUMAN SCALP HAIR

K. Chojnacka, I. Michalak and A. Zielińska

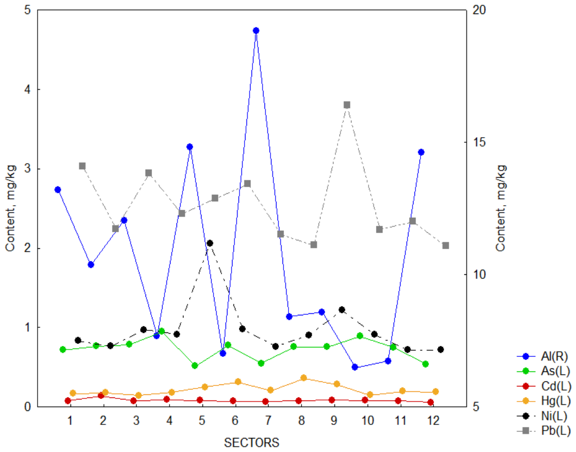
Institute of Inorganic Technology and Mineral Fertilizers, Wrocław University of Technology,
Smoluchowskiego 25, 50-372 WROCŁAW (Poland)

In the present work, hair mineral analysis of 142 individuals was carried out to determine environmental exposure based on the distance from a subject's residence to a pollutant source. The subjects were asked to fill a questionnaire concerning their place of living in Wrocław city (Poland, Lower Silesia Region), which was divided in 12 sectors. The residence location was related with local industry located in those sectors. The profile of companies and the type of released contaminates were presented in table 1.

Tab. 1 The names of companies in Wrocław city and released contamination

No.	Name of the company	Type of pollutant
1	Producer of non-ferrous metals	Al, Pb, Cd, Ca, Mg
2	Chemical Institute	Al, As, Pb
3	Heat and power generating plant	As, Cd, Cu, Cr, Hg, Ni, Pb, Zn
4	Chemical Institute	As, Cu, Hg, Pb, Zn
5	Producer of paints	As, Cd, Cu, Pb
6	Heating Institute ‘	As, Cd
7	Producer of domestic appliances	Pb, Hg
8	Producer of furniture	Al, Hg
9	Institute	As, Pb, Ni, Cr, Zn
10	Gas Company	Cd, Pb

Fig. 1 The content of heavy metala in twelve regions



The content of minerals in hair was determined by ICP-MS technique in the laboratory certified by Polish Centre for Accreditation and ILAC-MRA (nr AB 696). The results were elaborated statistically by Statistica ver. 9.0. Each person served as the experimental unit. Post-hoc comparisons were made by the Tukey's test and the Spjotvoll/Stolin test. Results were considered significantly different when $p < 0.1$. The content of Al, As, Cd, Hg, Ni and Pb in each considered sector was presented in fig.1. The differences in the content of As were statistically significant between IV - V region ($p = 0{,}0374$), IV - VII ($p = 0{,}0775$) and IV – XII ($p = 0{,}0633$). In the case of Cd the statistically significant differences were found between II and XII region ($p = 0{,}0377$). The highest content of As was noted for IV sector which is close to heat and power generating plant and producer of non-ferrous metals. The highest content in scalp hair was found in II sector which is placed near the heat and power generating plant.

The following statistically significant correlations between the element content were found: Al-As (-0.34), As-Cd (0.28) and As-Pb (0.21). Additionally, statistically significant differences between male and female of Ni ($p = 0.0591$) content in human scalp hair was found. These results showed that hair mineral content reflected exposure of elements from the environment.

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P86- THE CORRELATION BETWEEN MINERAL COMPOSITION OF HUMAN HAIR AND THE ILLNESSES

K. Chojnacka, I. Michalak, A. Zielińska

Institute of Inorganic Technology and Mineral Fertilizers, Wroclaw University of Technology,
Smoluchowskiego 25, 50-372 Wroclaw (Poland)

The aim of the present work was to find the correlations between mineral composition of human hair and the illnesses such as: infections of the respiratory system, asthma, vertigo, migraines, nervousness, hair loss, dandruff, brittle fingernails and white spots on fingernails. In the literature, there are several papers that examine the relation between mineral composition of hair and health, for example: Forte et al. (2005) assessed whether hair could be a reliable marker in Parkinson's disease [1], Lech (2002) examined hair as a tool in the diagnosis of diseases of the neurological system [2], Park et al. (2009) in the diagnosis of metabolic syndrome [3].

In the present study, the mineral content of human hair (N=155) was determined by the multielemental analysis by ICP-OES Vista-MPX instrument from Varian (Australia) and ICP-MS Thermo Fisher Scientific. The obtained data were elaborated statistically by *Statistica ver. 9.0*. The information about the health condition of the examined subjects came from the questionnaire.

It was found that subjects currently suffering from frequent infections of the respiratory system and asthma had higher Zr content in hair (three and four times, respectively), than healthy subjects. People, who suffered from vertigo in the past, had 53 % higher content of Ca, 54 % of La and two times more Sr in hair than people, who suffered from it at present. Subjects, who declared suffering from migraines currently, had 86 % higher content of W in hair than people, who did not have attacks. The content of K in hair of nervous people was three times higher than in hair of people, who never suffered from nervousness. It was found that statistically significant correlation (at $p<0.05$) was observed between the content of Cu in hair of a group of people, who complained of hair loss in the past and people, who did not declare this ailment. In the case of dandruff, brittle fingernails and white spots on fingernails, statistically significant correlations concerned the content of Ca and La in hair of the examined group. People, who had dandruff in the past, had 69 % higher content of Ca in hair and 72 % higher of La than people, who had it at present. Hair of subjects, who had brittle fingernails, contained higher content of Ca and La in comparison with subjects, who had healthy fingernails (41 % and 55 %, respectively). Similar correlation was also observed in the case of occurrence of white spots on fingernails.

On the basis of conducted experiments it can be concluded that mineral analysis of human hair can be recognized as a tool for the prediction of many illnesses, since it can detect the deficiencies and excesses of elements, which can lead to diseases.

References

[1] Forte, G., Alimonti, A., Violante, N., Di Gregorio, M., Senofonte, O., Petrucci, F., Sancesario, G., Bocca, B., J. Trace Elem. Med. Biol. 19, 195–201 (2005).
[2] Lech, T., Biol. Trace Elem. Res. 85, 111–126 (2002).
[3] Park, S.B., Choi, S.W., Nam, A.Y., Biol. Trace Elem. Res. 130, 218–228 (2009).

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P87- UNSYMMETRICAL DIMETHYLHYDRAZINE AND GLYOXAL DETERMINATION BY HPLC-UV BASED ON THE REACTION OF ALKYLHYDRAZINES WITH GLYOXAL

I. Rodin, O. Shpigun, R. Smirnov, A. Smolenkov

Department of Analytical Chemistry, Chemical Faculty, M.V. Lomonosov Moscow State University,
Lenin hills 1-3, 119991 Moscow (Russia)

Unsymmetrical dimethylhydrazine (UDMH) is a well known highly toxic component of high-energy propellants. Existing approaches to the determination of UDMH in contaminated soils are mainly limited to the establishment of its total contents, while UDMH in soil exists in various forms, taking an active part in the complex physical-chemical equilibrium processes between the products of its transformation, the components of soil and the remaining original substance. From the analytical and environmental points of view the problem of the objective determination of so called “free-form” (physically absorbed by soil particles and a part of mechanic soil solution) UDMH is very important.

There are a number of techniques for UDMH determination based on the derivatization of UDMH with different organic reagents, including carbonyl compounds. But many of these techniques are complex; the derivatization reagents are expensive and specific; the obtained products of the reactions are not stable enough. The reaction of aliphatic hydrazines with carbonyl compounds which leads to the formation of the corresponding alkylhydrazones is widely known. Alkylhydrazines don’t absorb neither in UV nor visible area, while corresponding alkylhydrazones usually have an absorption maximum in UV range of spectrum.

A new simple approach for the determination of UDMH in aqueous solutions and soil extracts using glyoxal as a highly active derivatization reagent was proposed. UDMH reacts with an excess of glyoxal forming N,N-dimethylhydrazone of glyoxal (mono-derivative) quantitatively without by-products. This reaction is characterized by high rate of formation of the derivative at a room temperature. The possibility of UDMH determination in aqueous solutions and soil extracts by reversed phase HPLC-UV at 310 nm was shown in a concentration range 0.002–10 ppm with good linearity, accuracy and precision. Glyoxal was also proposed as a reagent for the simultaneous extraction and determination of free UDMH in soil. Moreover, high stability and low reactivity of the resulting dimethylhydrazone of glyoxal allowed considering glyoxal as a promising agent for detoxification UDMH in contaminated soil.

Glyoxal is a highly active and a widely used chemical with a low toxic effect. It is interesting to understand behaviour of glyoxal in soil and to investigate possibility of UDMH detoxification by glyoxal.

As it was described above a new approach for the determination of glyoxal in aqueous solutions and soil extracts using an excess of tertbuthylhydrazine (more stable and less toxic than UDMH) as derivatization reagent was proposed. This reaction is similar to described above, and also has high rate of formation of mono-tertbuthylhydrazone of glyoxal at a room temperature. Glyoxal may be determined by reversed phase HPLC-UV at 310 nm in aqueous solution in a concentration range 0.002–10 ppm with good linearity, accuracy and precision. The presence of formaldehyde, acetaldehyde and glyoxylic acid were shown not to interfere the determination of glyoxal.

P88- REMOVAL AND ANALYSIS OF ORGANIC POLLUTANTS IN INDUSTRIAL WASTE WATER AND THERMAL WATER

I. Ábrahám, A. Dombi, M. Májer, K. Mogyorósi, E. Szabó, K. Vajda, G. Veréb

Department of Inorganic and Analytical Chemistry, University of Szeged,
Research Group of Environmental Chemistry, Dóm tér 7, Szeged, H-6720 (Hungary)
UNICHEM Kft., Tanya 461, Kistelek, H-6760 (Hungary)

One of the main challenges in environmental protection is the removal of toxic or hazardous organics from waste water. Industrial waste water contains different kind of organic pollutants including dye molecules that are used in large quantities by the textile industry. The increasing energy needs require the use of alternative energy resources. Although the utilization of geothermic energy from thermal water is already significant, its release to surface water could cause harm to the environment due to the presence of toxic aromatic compounds and other hydrocarbons.

The optimal conditions of the removal of different model pollutants, such as phenol and thymol and dyes (methylene blue, methylorange and indigo carmine), were determined in this study [1]. Our methods involve the formation of adsorbent composites containing organoclays that were prepared *in situ* with clay minerals, cationic surfactant (HTABr), polyaluminium chlorides and polyelectrolytes [2-3]. Raw clay minerals consisting mainly sodium montmorillonite (Süd-Chemie AG, Kunimine Industries) were used with different cation exchange capacity (0.8-1.2 mmol/g). Cation exchange capacity of sodium montmorillonite was covered in 40%, 60%, and 100% in order to maximize the adsorption of organic compounds from water.

Model waste water and thermal water samples were treated in Jar-test equipment. Aqueous suspension of sodium montmorillonite was added first to the treated water and subsequently the cationic surfactant was added in solution. In this *in situ* process the sodium cations are replaced by the surfactant causing the formation of an organoclay adsorbent. Polyaluminium chloride (Unichem Kft.) and polyelectrolytes (Cytec Industries Inc.) were used to improve the separation of the adsorbent.

The adsorption of the dye can be easily monitored spectrophotometrically measuring the spectra of the solution. In the case of aromatic substrates HPLC was used to determine the concentration change in solution phase. TOC analysis was applied to characterize the remaining organic carbon from the substrate and the added chemicals.

This method was found to be very efficient for methylene blue (cationic dye), methylorange and indigo carmine (anionic dyes) with 60-96 % of removal efficiency in the initial concentration range of 3-10 mg/L. In the case of phenol, even at very high applied organoclay concentration (10000 mg/L), only 22 % removal efficiency was achieved. Thymol has been removed with much better efficiency (50-60 %, c_{clay} = 200 mg/L). It was concluded that the chemical nature of the pollutant is the primary factor determining the removal efficiency of our method.

[1] Lizhong, Zhu; Jianfeng, Ma, Chemical Engineering Journal 139 (2008) 503-509.
[2] M.J. Sánchez-Martín, M.C. Dorado, C. del Hoyo, M. S. Rodríguez-Cruz Journal of Hazardous Materials 150 (2008) 115-123.
[3] G. Jock Churchman, Applied Clay Science 21 (2002) 177-189.

P89- REMOVAL OF ORGANIC POLLUTANTS FROM THERMAL WATER BY ADSORPTION-COAGULATION METHODS AND ADVANCED OXIDATION PROCESSES

I Ábrahám, A. Dombi, M. Májer, K. Mogyorósi, K. Gajda-Schrantz,
E. Szabó, K. Vajda, G. Veréb

Department of Inorganic and Analytical Chemistry, University of Szeged, Research Group of Environmental Chemistry, Dóm tér 7, Szeged, H-6720 (Hungary)
UNICHEM Kft., Tanya 461, Kistelek, H-6760 (Hungary)

Various types of natural organic matters are present in Hungarian water sources (both ground and thermal ones). Although many of these organics are non-toxic, but some of them are potentially hazardous or even toxic, such as aromatic compounds. Used thermal water could be released into surface water environmentally friendly only after the removal of phenol and its derivatives.

Our preliminary experiments indicated that phenol cannot be removed easily from water by traditional adsorption-coagulation methods. Therefore Advanced Oxidation Processes (AOPs) could be applied for the mineralization of aromatic compounds.

The aim of our present studies is to develop an effective method to eliminate the inert humic substances from thermal water in order to make oxidation technologies more economic for the mineralization of aromatics with significant toxicity.

The removal of sodium humate was investigated by the combination of coagulation-adsorption methods using polyaluminium chloride (PAC) coagulants and aluminium oxide adsorbents in model thermal water [1]. The concentration of sodium humate in the solution phase was determined by spectrophotometric measurements.

Optimization of different process parameters was carried out in Jar Test equipment; thus the optimal treatment time, concentration of added coagulant and flocculant were determined. High and medium basicity PAC coagulants (BOPAC, UNIPAC W2, UNICHEM Kft.) were used at different concentrations (40, 80 mg/L). BASF Al_2O_3 adsorbents (CPN, DD6; a^S_{BET} = 280-350 m^2/g) were also tested at significantly higher concentration (10000 mg/L). The influence of a non-ionic flocculant (UNIFLOC M20) was studied in the concentration range of 1-5 mg/L. The adsorption equilibrium has been approached within 2 hours. It was concluded from adsorption isoterms of humate (c_H = 2-100 mg/L) that high basicity coagulant is much more efficient than the Al_2O_3 adsorbents. The best performing coagulant BOPAC provided 88-100 % of removal efficiency (c_{BOPAC} = 80 mg/L, c_H = 2-100 mg/L).

Preliminary studies were carried out in a semi pilot scale reactor (200 L) with sodium humate solution in tap water (with and without H_2O_2) irradiated with low-pressure mercury vapour lamp [2]. Using high purity quartz sleeve surrounding the lamp, ozone is produced from the air flow that has been applied in the reactor. It was concluded that coagulants could provide most efficient, economic and rapid removal of humic substances from thermal water.

[1] Shi, B., Wei, Q., Wang, D., Zhu, Z., Tang, H., Colloid Surf. A 296, 141-148 (2007)
[2] Wang, G-S., Hsieh, S-T., Hong, C-S., Water Research 34, 3882-3887 (2000)

P90- ANALYSIS OF POLYCYCLIC AROMATIC HYDROCARBONS IN SEWAGE SLUDGE SAMPLES BY HIGH PERFORMANCE LIQUID CHROMATOGRAPHY AND FLUORESCENCE DETECTION. COMPARISON OF DIFFERENT SAMPLE PREPARATION PROCEDURES

C. Casais, R. Cela, C. Mejuto, T. Pena, X. Vecino

Departamento de Química Analítica, Nutrición y Bromatología, Facultad de Química,
Instituto de Investigación y Análisis Alimentario, Universidad de Santiago de Compostela,
15782 Santiago de Compostela (Spain)

Polycyclic aromatic hydrocarbons (PAHs) are well-known carcinogens and mutagens which are present in sludge [1]. In wastewater treatment plants, PAHs are almost completely removed from wastewater (up to 90%), being concentrated in sludge because of their poor solubility in water and high adsorption capacity on solid particles. This results in the formation of sewage sludge that typically contains between 0.02 and 25 mg kg^{-1} (dry mass basis, dm) of each of different PAHs. Since a way of recycling sludge is to spread them on agricultural lands as fertilizer, there is a risk of soil contamination, and therefore, a public health hazard. Consequently, maximum acceptable concentrations of several PAHs in sludge have been set in some countries. A 3rd draft of a European Union (EU) directive has regulated the total concentration (sum of 11 PAHs) in sewage sludge for agriculture use to 6 mg kg^{-1} (dm) [2]. Sewage sludge is often regarded as one of the worst environmental matrices to extract as it can contain a large variety of pollutants as well as amounts of organic matter especially lipidic substances. Sample preparation and especially extraction is a critical step in PAHs analysis because these hydrophobic compounds are strongly sorbed to the solid materials. Therefore, highly efficient extraction methods and cleanup procedures are required to allow accurate analytical determinations. In this work, three extraction methodologies (microwave assisted extraction (MAE), matrix solid-phase dispersion (MSPD) and pressurized liquid extraction (PLE)) were tested and compared to extract 17 PAHs from real sewage sludge samples. Analytical determinations were carried out by high performance liquid chromatography with fluorescence detection. Quantification limits obtained for all studied compounds (lower than 0.01 μg g^{-1}) were well below of the limits recommended in the EU. Excellent recoveries and reproducibility were obtained by using MAE, MSPD and PLE. A reference material (RTC-CNS312-04) and a certified reference material (BCR 088) were also processed by these sample preparation techniques, obtaining good agreement between the results and the certified and/or reference values.

[1] Harvey, R.G., Polycyclic aromatic hydrocarbons, Wiley-VCH, New York (1996).

[2] Council of the European Community, 27 April, 2000, Working document on Sludge, 3rd Draft, Brussels.

Acknowledgements

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P91- IN-SAMPLE ACETYLATION-NON-POROUS MEMBRANE-ASSISTED LIQUID-LIQUID EXTRATION FOR THE DETERMINATION OF PARABENS AND TRICLOSAN IN WATER SAMPLES

R. Cela, I. González-Mariño, J. B. Quintana, R. Rodil, I. Rodríguez, E. Villaverde-De-Sáa

Department of Analytical Chemistry, Chemical Faculty, Institute for Food Analysis and Reseach (IIAA),
University of Santiago de Compostela, Constantino Candeira s/n, 15782, Santiago de Compostela (Spain)

The aim of the study was to determinate the simultaneous presence of triclosan and seven parabens (esters of 4-hydroxybenzoic acid), including methyl, ethyl, i-propyl, n-propyl, i-butyl, n-butyl and benzyl groups in different kinds of waters. They are widely used as preservatives in cosmetics and pharmaceutical products, and approved as food additives. Analytes were extracted from the sample and isolated from interfering species using the in-sample acetylation-non-porous membrane-assisted liquid-liquid extraction technique (MALLE) and were determined by large volume injection-gas chromatography-ion trap-tandem mass spectrometry (LVI-GC-MS/MS). This technique is carried out by using a non-porous polyethylene membranes as interface between the sample (donor) and the organic solvent (acceptor).To introduce extracts on GC a sample derivatisation stage was needed, so three different derivatisantes were evaluated: N-methyl-N-(*tert*-butyldimethylsilyl)-tri-fluoro-acetamide (MTBSTFA) for post-extraction silylation and in situ acylation with acetic anhydride (Ac_2O) and isobutylchloroformate, which implicated also an investigation to choose a basic catalyser and an acceptor solvent for acylation reaction. In-situ derivatisation with Ac_2O and potassium hydrogenphosphate (as basic catalyser) was the best combination to obtain higher yields, lower toxicity and avoid bubble formation. Then, an experimental design was developed to select experimental variables which affect to derivatisation-extraction yield such as pre-stirring time, salt addition and volume of Ac_2O. Using a sample volume of 18 mL and optimised conditions, detection limits from 0.1 to 1.4 $ng.L^{-1}$ were achieved. Extraction efficiencies were estimated by comparison with liquid-liquid extraction; getting for methyl-and ethyl-parabens recoveries between 46% and 110%. A study of matrix effects was also developed and showed that there was not any effect on parabens' extraction but a reduction of 40% on triclosan results when wastewater samples were analysed; so internal and external calibration can be used for quantification of parabens, but internal standard calibration must be used for triclosan. The precision of the method expressed as relative standard deviation (RSD) was evaluated obtaining results in the 4-8% range. The calculated calibration curves using internal standards gave a high level of linearity for all target analytes with correlation coefficients ranging between 0.994 and 0.998. The application of the method to real samples showed the highs levels for triclosan with values of 423 ng L^{-1} and concentrations up to 26 ng L^{-1} for methyl paraben for raw wastewater; the prevalence of the linear isomer of propylparabens (*n*-PrP), and the coexistence of the two isomers of butylparaben (*i*-BuP and *n*-BuP) at similar levels.

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P92- ACCUMULATION OF MERCURY AND OTHER TRACE METALS IN LIVER AND MUSCLE OF MULLET AND KUTUM FISHES FROM THE CASPIAN SEA IN THE IRANIAN COASTLINE

H. Agah[1,2 *], P. Eghtesadi Eraghi[2], S. M. R. Fatemi[3] , F. Owfi[4]

[1] Department of Analytical and Environmental Chemistry (ANCH), Vrije Universiteit Brussel, Pleinlaan 2, 1050 Brussels (Belgium)
[2] Marine Living Science Department, Iranian national institute of Oceanography,
9 Etemadzadeh street, Western of Fatemi Ave. Tehran (Iran)
[3] Department of Marine Biology, Science and Research unit, Islamic Azad University, Tehran (Iran)
[4] Iranian Fishery Research Organization (IFRO), Marine Ecology Department, Tehran (Iran)
[*]hagah@inco.ac.ir, aaagah_hom@yahoo.com

In this study, concentrations of mercury and 16 other elements as well as mercury speciation were quantified in muscle and liver of two commercial fish species. It was also our intention to evaluate potential risks to human health associated with seafood consumption. The fish species, Mullet and Kutum (Caspian White fish) fishes, were obtained from Tonekabon at the Iranian waters of the Caspian Sea. In this investigation fish tissues (muscle and liver) were analyzed to determine Al, As, Be, Cd, Cr, Co, Cu, Fe, Hg, Pb, Mn, Mo, Ni, Sb, Tl, V, Zn and methylmercury. Total mercury concentration in the fish muscles and liver ranged from 0.02 to 0.13 and from 0.03 to 0.06 $\mu g\ g^{-1}$w.w, respectively. Almost all the elements were more accumulated in the muscle of Mullet than Kutum fish, except for Hg, Pb and Ni. Concentrations of all the elements in the muscle of both fishes were lower than the WHO maximum consumption limit in fish muscle. All elements were more accumulated in the fish liver than the muscle tissue, except for mercury in Kutum fish. This study identifies a statistical relationship between metal concentrations and fish sizes and also the relationship between element levels in the fish tissues.

P93- APPLICATION OF ULTRASONIC PROBE-ASSISTED DISPERSIVE LIQUID-LIQUID MICROEXTRACTION FOR QUANTITATION OF SOME POLYCYCLIC AROMATIC HYDROCARBONS IN SOIL SAMPLES

A. Kashtiaray [2], N. Oruji[1] and H. R. Sobhi [2]

[1] Medical University of Zabol, Jahad square, 9861615585 Zabol (Iran)
[2] Department of Chemistry, Tehran Payamenoor University, 1598686613 Tehran (Iran)

Ultrasonic probe-assisted dispersive liquid–liquid microextraction (DLLME) coupled with gas chromatography-flame ionization detection (GC-FID), was developed for the extraction and determination of some polycyclic aromatic hydrocarbons (PAHs) in soil samples [1,2]. In the developed method, Acetone was used for the extraction of PAHs from soil samples, assisted by probe-based ultrasonic system. Initially, microextraction efficiency factors were optimized and the optimum experimental conditions were as follows: tetrachloroethylene (15.0 µL) as extracting solvent, acetone (1.0 mL) as disperser solvent, 5 mL aqueous sample without salt addition. Under the selected conditions, the linearity was found to be in the range of 1-500 µg kg^{-1} and also the regression coefficients were greater than 0.9952. For all analytes, the limit of detection was 0.5 µg kg^{-1}. The relative recoveries varied in the range of 81.0 % to 116.0 % and, the relative standard deviations (RSDs, $n = 4$) were in the range of 7.2–11.8%.

[1] Hu, J., Fu, L., Zhao, X., Liu, X., Wang, H., Wang, X., Dai, L., Anal. Chim. Acta 640, 100-105 (2009).
[2] Rezaee, M., Assadi, Y., Milani Hosseini, M.R., Aghaee, E., Ahmadi, F., Berijani, S., J. Chromatogr. A 1116, 1-9 (2006).

P94- COMPARISON OF DRY ASH AND WET EXTRACTION METHODS TO DETERMINE TOTAL MERCURY IN ENVIRONMENTAL SAMPLES (CASE STUDY: THE PERSIAN GULF AND THE CASPIAN SEA)

H. Agah*[1,2] , S. M. R. Fatemi[3], A. Mehdinia[2], A. Savari [4]

[1] Department of Analytical and Environmental Chemistry (ANCH), Vrije Universiteit Brussel,
Pleinlaan 2, 1050 Brussels (Belgium)
[2] Iranian National center of oceanography. 9 Etemadzadeh Street, western of Fatemi Ave, Tehran (Iran)
[3] Department of Marine Biology, Science and Research unit, Islamic Azad University, Tehran (Iran)
[4] Marine Biology Dept. Khorramshahr, University of Marine Science and Technology (Iran)
*aaagah_hom@yahoo.com

Monitoring of mercury in the environmental samples with its proven toxicity on the food chain requires sensitive and accurate analytical techniques. In this study, two methods for identification and quantification of total mercury in biological and sediment samples are compared: i) Dry ash, Combustion Atomic Absorption spectrometry, (AMA 254) and, ii) Wet extraction consisted of classical and microwave oven digestion methods combined with cold Vapor Atomic Absorption (CV AAS) analyzing method.

In order to compare the accuracy of the methods for total mercury determination, eight biological and sediment certified materials and ten environmental samples were analyzed with six replications. The detection limits (DLs) based on three times standard deviation (3sd) of the procedural blanks in the combustion AAS (AMA) for biological and sediment samples was 0.28 ng g^{-1}dw, in CEM (MDS 2000, CEM Corporation) microwave oven CVAAS for biological and sediment samples were 48 ng g^{-1}dw and 20 ng g^{-1}dw respectively, in CEM (Mars 5, CEM Corporation) microwave oven CV AAS for biological samples was 12 ng g^{-1} and finally in normal oven for sediment samples was 3 ng g^{-1}dw. The AMA 254 with lower detection and quantification limits (even lower than the environmental quality target) is more sensitive analyzing method in comparing with the other methods. For rich sulfur sediments, especially in low mercury levels, the classical method (acid digestion in normal oven) is more practical.

P95- ORGANIC COMPOSITION OF AEROSOLS EMITTED FROM A WILDFIRE IN CENTRAL PORTUGAL

C. Alves, M. Evtyugina, C. Gonçalves, C. Monteiro, A. Vicente

Centre for Environmental and Marine Studies, Department of Environment,
University of Aveiro, 3810-193 Aveiro (Portugal)

On May 31st 2009, smoke particles from a wildfire in Sever do Vouga (~40°35'59"N and 8°22'10"W), central Portugal, were sampled. The vegetation in the region was composed mostly of eucalyptus (*Eucalyptus globulus*), and golden wattle (*Acacia longifolia).* Particulate matter with aerodynamic diameters below 2.5 µm ($PM_{2.5}$ – fine particles) and in the range 2.5-10 µm ($PM_{2.5-10}$ – coarse particles) was collected sequentially by impaction on quartz fibre filters with a high-volume sampler operating at 1.13 m^3 min^{-1}. A small portion of the filters was analysed by a thermal-optical transmission technique to determine the elemental and organic carbon (EC and OC) contents. The particulate organic matter was then solvent extracted and fractionated by vacuum flash chromatography into different classes of organic compounds. The detailed organic speciation was performed by gas chromatography-mass spectrometry. Particle concentrations were in the ranges 158-2592 µg m^{-3} and 113-956 µg m^{-3} for $PM_{2.5}$ and $PM_{2.5-10}$, respectively. Fine particles represented, on average, 77% of the PM_{10} mass. The OC-to-EC ratios ranged from a minimum of 5, obtained in a sample collected during the flaming phase of the wildfire, to a maximum of 713 for smouldering particles. The major organic compounds in smoke particles comprised triterpenic constituents, acids, sugars, aliphatics, alcohols, phenolics and sterols. The homologous series of *n*-alkanes, which represented around 30 µg g^{-1} OC for both fine and coarse particles, showed an odd carbon number predominance, maximising, in general, for in the C_{25}-C_{33} interval. The most abundant polyaromatic hydrocarbon was retene, with an average OC-normalised concentration of 190 µg g^{-1} OC for $PM_{2.5}$ and 237 µg g^{-1} OC for $PM_{2.5-10}$. The *n*-alkanoic acid homologous series ranged from C_8 to C_{24}, peaking at C_{14} and C_{16} for $PM_{2.5}$, and at C_{16} and C_{18} for $PM_{2.5-10}$. The carbon preference indices for these homologous compounds was always higher than 10, reflecting the strong biogenic input. Phenolic compounds, from lignin combustion, with the syringyl and vanillyl structures were also present in the smoke samples. One of the dominant phenolic constituents was the syringic acid with average concentrations of 4446 and 1782 µg g^{-1} OC in fine and coarse particles, respectively. Vanillin acid was present in all samples at concentrations of about 1500 µg g^{-1} OC. Coniferyl aldehyde was only detected in coarse particles (207 µg g^{-1} OC). Sinapic acid, a syringyl-type compound, averaged 26.7 and 4.39 µg g^{-1} OC, respectively, in fine and coarse particles. Fine particles were more enriched in coniferyl and sinapyl alcohols than $PM_{2.5-10}$. Stigmasterol reached concentrations of about 20 µg g^{-1} OC in all samples, while β-sitosterol averaged 62 µg g^{-1} OC ($PM_{2.5}$) and 174 µg g^{-1} OC ($PM_{2.5-10}$). The pyrolysis decomposition product of cellulose, levoglucosan, and its stereoisomers mannosan and galactosan were detected in fine particles at levels of 11.8, 6.72 and 4.60 µg g^{-1} OC, whereas in coarse particles the levels were 14.1, 7.20 and 3.18 µg g^{-1} OC, respectively. The comprehensive database obtained may be useful for numerical models to evaluate the impact of wildfires on the micro- to regional scale atmosphere in the Mediterranean region, which is particularly uncover by this type of studies. Since source apportionment models require detailed emission factors, this investigation may also contribute to estimate the input of wildfires to the atmospheric levels currently measured at monitoring sites.

P96- USE OF SOLID-PHASE EXTRACTION ON HYPERCROSSLINKED POLYSTYRENE FOR HPLC DETERMINATION OF METHYLXANTHINES

E. Y. Andreeva, S. G. Dmitrienko, J. Tang

Division of Analytical Chemistry, Chemical Department, Lomonosov Moscow State University,
Leninskie gory, 1/3, 119991 Moscow (Russia)

Methylxanthines are widespread pharmaceuticals: theophylline and theobromine have been used as a treatment for asthma and other diseases of the respiratory tract, pentoxifylline - for cerebral blood flow improvement, caffeine - for enhancement of mental and physical efficiency. In addition, methylxanthines enter the body through different soft drinks. On account of their large consumption, methylxanthines can be considered as contaminants, which has led to increasing concern about potential environmental risks. Indeed it is proposed that caffeine could be a good indicator for untreated wastewaters [1].

In the present work, sorption of theophylline, theobromine, caffeine and pentoxifylline on hypercrosslinked polystyrene MN-200 with their subsequent determination by high-performance liquid chromatography was studied, and the feasibility of its application for the determination of methylxanthines in urine and river water was assessed.

Hypercrosslinked polystyrene sorbents are distinguished by their high specific surface area, relatively small pore size, and pronounced affinity to polar organic compounds. Sorption was carried out in the dynamic mode, a 0.15-ml concentrating microcolumn (25 × 2.7 mm) packed with hypercrosslinked polystyrene sorbent (0.055 g) was used, along with a peristaltic pump. Using the peristaltic pump, 25 ml of the aqueous solution of methylxanthines was passed through it at the volume rate of 0.7 ml/min. The degrees of extraction of methylxanthines are 97 – 100%. Desorption was carried out at counterflow. Studies of the degree of desorption of the substances in question as dependent on the nature of the eluent was studied. Methanol was suggested to use as solvent for desorption and for subsequent separation and determination by HPLC.

Methylxanthines determination was performed in a liquid chromatograph equipped with a UV detector. The column was Luna 5u C18(2) (150×3.0 mm, 5 µm). Methylxanthines was separated with a mobile phase of 90% phosphate buffer with 10% acetonitrile, pH 3.5, at a flow-rate of 0.5 mL/min, at room temperature. Injection volume was 20 ml and detection was carried out at 270 nm. At this conditions total analysis time that include sorption on hypercrosslinked polystyrene, desorption and chromatographic determination is 55 min. The metrological performances of methylxanthines determination by HPLC with and without sorption are compared. Application of preliminary concentration made it possible to bring down the methylxanthines detection limits at 10 – 40 times. Accuracy and reproducibility of measurements are confirmed by the comparison of the introduced methylxanthines amounts and detected ones in water solution.

The proposed method was applied for the determination of methylxanthines in the human urine and river water. Urine was collected from a male subject abstaining from methylxanthines –containing foods and beverages for five days before the study. The samples of urine and water was centrifuged, filtered and diluted by water and then an aliquot of solution was assayed by the proposed method. The preliminary sample sorption on hypercrosslinked polystyrene makes it possible to bring down the methylxanthines detection limits, to reduce of the sample interfering components content and avoid the chromatographic column overloading.

[1] Moldovan, Z., Chira, R., Alder, A.C., Environ Science and Technology in Romania. 16, S46–S54 (2009).

P97- SILVER NANOPARTICLES IN POLYURETHANE FOAM: SYNTHESIS AND ANALYTICAL USING FOR DETERMINATION OF OXIDANTS AND REDUCTANTS

V. V. Apyari, S. G. Dmitrienko, P. A. Volkov, Y. A. Zolotov

Division of Analytical Chemistry, Chemical Department, Lomonosov Moscow State University,
Leninskie gory, 1/3, 119991 Moscow (Russia)

Applications of nanoparticles in chemical analysis is very diverse: to enhance a signal in Raman and fluorescence spectroscopy, voltammetry, when developing electrochemical, piezoquartz, immuno- and optical sensors, for increasing sorption ability of materials. In most cases, nanoparticles keep many of their valuable properties in immobilized on solid matrices state. As solid matrices for nanoparticles immobilization one often uses glass, different polymers such as polyvinylpyrrolidone, polyethylene, oligourethanemethacrylate et al. Practically unexplored in this role matrix is polyurethane foam (PUF). Meanwhile, chemical stability, mechanical durability, easiness of separation from a solution, relative cheapness and availability of this polymer could play an essential role while producing new nanocomposites for chemical analysis.

In this work the possibility of synthesis of PUF modified with silver nanoparticles (PUF/Ag) is investigated. The potentialities of using destruction/formation of silver nanoparticles processes in PUF matrix for determination of oxidants and reductants are demonstrated.

Two ways to obtain PUF/Ag have been suggested. First of them was based on sorption of previously synthesized in water solution silver nanoparticles by PUF. The second one included sorption of silver nitrate by PUF followed by reduction of the silver ions directly in PUF matrix. Due to silver nanoparticles, PUF/Ag had a surface plasmon resonance (SPR) band in diffuse reflectance spectra. Spectral characteristics and optimal conditions of the composite formation have been found.

It has been stated that when PUF/Ag getting in touch with hydrochloric acid solution of Fe(III) or dichromate ions, the SPR band disappeared and the colour of the samples was changed from yellow to white that seems to be connected with the oxidation of the nanoparticles. On the contrary, formation of the nanoparticles in PUF matrix by the reduction of sorbed silver nitrate with ascorbic acid resulted in appearing SPR band and changing colour from white to yellow.

These processes were shown can be used for determination of oxidants and reductants. Metrological performance of the determination of Fe(III), dichromate and ascorbic acid using such an approach has been evaluated. The possibility of decreasing the detection limits by varying volume of the solution and content of the nanoparticles or silver ions in PUF matrix has been demonstrated. The technique suggested has been tested for determination of Fe(III) in natural waters and ascorbic acid in vitamin samples.

Thus, such a composite material based on PUF and silver nanoparticles seems to be attractive for environmental analysis.

P98- CHARACTERIZATION OF PAHs IN ATMOSPHERIC PARTICULATE AT A REMOTE SITE IN THE MEDITERRANEAN

F. Artuso [1], S. Becagli [2], C. Bommarito [3], D. Cataldi [1], M. Mansueto [4], D. M. Sferlazzo [5],
P. Spezzano [3], R. Udisti [2]

[1] ENEA, Via Enrico Fermi 45, 00044 Frascati (RM) (Italy)
[2] Chemistry Department, University of Florence, Sesto Fiorentino (Italy)
[3] ENEA, Via Catania 2, Palermo (Italy)
[4] ENEA, Casaccia, Via Anguillarese 301, Rome (Italy)
[5] ENEA, Capo Grecale, 92010 Lampedusa (AG) (Italy)

Polycyclic aromatic hydrocarbons (PAHs) are mutagenic and carcinogenic organic pollutants [1] emitted by incomplete combustion processes. In atmosphere PAHs are partitioned between the gas and particle phase (PM). These species may have an atmospheric lifetime ranging from few hours to several weeks and for this reason are subject to long-range atmospheric transport. Due to their long lifetime and dangerous effect on human health PAH emissions are controlled under the United Nations Economic Commission for Europe (UNECE) protocol [2]. Many studies have been focused on the characterization of airborne PAHs in urban areas but atmospheric transport of PAHs to the marine remote environment has received little attention [3]. This work is aimed to investigate the influence of long and short-range transport on PAHs levels recorded in PM10 samples collected at the remote site of Lampedusa (35°31'N, 12°37'E), in the Mediterranean Sea, in the period May-August 2007. The objectives of this study are two: 1) to evaluate the PAH background levels resulting from the transport of pollutants emitted by anthropic and natural sources in the Mediterranean basin; 2) to characterize the PM origin and individuate the sources distribution by using PAHs as combustion process markers. Results have shown the following mean concentrations for each compound: 13.7±5.4 pg/m^3 for pyrene,11.1±5.2 pg/m^{3}for benzo(a)pyrene, 3.1±1.8 pg/m^3 for benz(a)anthracene, 9.8±5.1 pg/m^3 for crysene, 27.4±13.6 pg/m^3 for benzo (b+k) fluoranthene, 9.5±6.7 pg/m^3 for indeno(1,2,3-cd)pyrene, 12.4±8.1 pg/m^3 for benzo(g,h,i)perylene and 14.6±6.6 pg/m^3 for benzo(e)pyrene. PAH data have been correlated with several compounds contained in the same samples (elemental carbon (EC), organic carbon (OC), SO_4^{2-}, K^+, $HCOO^-$, $H(COO)_2^-$). A good correlation among the concentration patterns have been found for compounds with common aerosol origin. Influence of transport has been investigated through back-trajectory analysis. Measurements of PAH concentrations have been combined with the back-trajectories (Hybrid Single-Particle Lagrangian Integrated Trajectory model, HYSPLIT) run by the corresponding air-masses and with fire satellite data (MODerate-resolution Imaging Spectroradiometer-MODIS) in order to get information on the distribution of possible sources and to individuate the PM origin. PAH diagnostic ratios have also been calculated in order to distinguish emissions and understand the impact of different sources.

[1] ATSDR, Agency for Toxic Substances and Disease Registry. Toxicological Profile for PAHs. Atlanta, GA, USA (1995).
[2] United Nations Economic Commission for Europe (UN ECE). ECE/EB.Air/60 (1998).
[3] Crimmins, B.S., Dickerson, R.R., Doddridge, B.G., Baker, J. E., J. Geophys. Res. 109, D05308 (2004).

P99- EFFECT OF SOME POLLUTANTS ON THE ENVIRONMENTAL OF ERBIL CITY

P. I. Azez

Aljin School, Ministry of Education, Erbil (Iraq)

Decades of research have provided the scientific foundation for understanding the role of the environment in disease. For many pollutants, scientists know with some certainty that exposure to these pollutants, at sufficiently high concentrations; can cause a variety of health effects. For other pollutants, where scientific evidence is less conclusive, scientists can only establish an “association” between exposure and health problems. Some effects on health may be short-term and reversible, such as irritated eyes from smog. Other effects, such as emphysema, heart disease, and cancer are chronic or even fatal. Some effects may appear shortly after exposure. Others, such as cancer, may require a long lead time before the disease appears. In many cases, pollution likely is just one of several factors—including diet, exercise, alcohol consumption, and genetic make-up—that influence whether an exposed person will ever become sick. Further complicating the picture is the fact that several segments of the population may be at higher risk for damage or disease from environmental pollutants. Potentially sensitive groups include children; older Americans; people with existing health problems such as diabetes, respiratory disease, or heart disease; and persons with compromised immune systems, including those who have HIV/AIDS or are undergoing cancer chemotherapy. Many studies in people have demonstrated an association between environmental exposure and certain diseases or other health problems. Examples include radon and lung cancer; and cancer arsenic in several organs; lead and nervous system disorders; disease-causing bacteria such as *E. coli* O157: H7 (e.g., in contaminated meat and water) and gastrointestinal illness and death; and particulate matter and aggravation of heart and respiratory diseases. The effect of some pollutants is suggested to study their effects on the environment of Erbil City.

P100- MULTIRESIDUE ANALYSIS OF ORGANOCHLORINES IN SOIL: A COMPARISON BETWEEN ASE AND QUECHERS EXTRACTION

C. Arnaudguilhem, A. Bulete, F. Rouviere

Service Séparation et Spectrométrie de masse, CNRS Service Central d'Analyse, Echangeur de Solaize,
Chemin du Canal, 69360 Solaize (France)

This study is part of a program on soil and water's depollution. Due to persistent, bioaccumulative and toxic substances contamination in soil and water, a new process, based on plants use, is developing. One objective is to create an alternative method to replace the current and expensive treatments like adsorption on charcoal for water or excavation followed by incineration for soil.

The aim of this project is to develop a multiresidue method for the analysis of 30 aromatics organochlorines (belonging to different chemical families) in soils by GC-MS.

Several extraction techniques were reported in literature like soxlhet extraction [1], Microwave Assisted Solvent Extraction (MASE) [1], Ultrasonic solvent extraction [2] or Accelerated Solvent Extraction (ASE) [3]. Here, ASE was compared to a new method, called QuEChERs and based on a single extraction. Firstly developed for the analysis of pesticides in food, this method was applied to soil in our study.

After optimization of each method, dichloromethane was the best extraction solvent in terms of recovery. For ASE, recoveries between 60 and 87 % were obtained, but due to high temperature, all volatiles compounds were lost. The QuEChERs extraction allows the detection and the quantification of all compounds with recoveries between 70 and 110%. The linearity, within-day precision, inter-day variation and limits of detection and quantification were evaluated.

[1] Wang W., Analytica Chimica Acta 602, 211-222 (2007)
[2] Tor A., Analytica Chimica Acta 559, 173-180 (2006)
[3] Hubert A., Anal. Chem 72, 1294-1300 (2000)

P101- SOIL CHARACTERIZATION BY DIFFUSIVE GRADIENTS IN THIN FILMS TECHNIQUE

H. Dočekalová[1*], V. Kovaříková[2], B. Dočekal[3]

[1] Faculty of Agronomy, Mendel University in Brno, Zemědělská 1/1665, CZ-61300 Brno (Czech Republic)
[2] Faculty of Chemistry, Brno University of Technology, Purkyňova 118, CZ-61200 Brno (Czech Republic)
[3] Institute of Analytical Chemistry of the Academy of Sciences of the Czech Republic, v.v.i., Veveří 97, CZ-60200 Brno (Czech Republic)
[*]hana.docekalova@mendelu.cz

The diffusive gradient in thin films technique (DGT) [1-4] was used for characterization of homogenized and undisturbed soil samples of the South Moravian district (sampling sites Veverska Bityska – wild land and Ostrovacice - arable land). The concentration of Cd, Cu, Ni and Pb obtained by DGT technique was compared with those recovered by sodium nitrate and pure water extraction. The majority of DGT measured metals occurred in small inorganic forms as proved by using the diffusive gels with different pore size. Concentration of metals measured in soil solution was used for R-value calculation. The R-values (0.6 – 1.1) indicated high lability and mobility of Cd species at both sampling sites. Lead was labile and mobile only in Veverska Bityska soil (R: 0.45-0.75). This correlates very well with heavy traffic close to the sampling sites and with cultivation of the studied soils. It was also found, that drying, homogenization and subsequent soil slurry preparation changed metal fractionation in Ostrovacice sample. Concentration of all elements in a homogenized soil was 2-10 times higher compared to undisturbed soil. However, the measurement of kinetically labile and mobile metal species in the soil slurry can be used much easily for rough estimate of plant accessible metals.

[1] Davison, W., Zhang, H.: Nature, 367, 546-548 (1994).
[2] Zhang, H., Davison, W., Knight, B., McGrath, S.: Environ.Sci.Technol., 32, 704-710, (1998).
[3] Hooda, P.S.,.Zhang, H., Davison, W., Edwards, A.C.: European J.Soil Sci., 50, 285-294 (1999).
[4] Zhang, H., Davison, W., Miller, S., Tych, W.: Geochimica et Cosmochimica Acta, 59, 4181-4194 (1995).

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102- MODELING THE ANALYTICAL RESPONSE OF CHEMICAL OPTICAL FIBER SENSORS

A. C. Duarte[1], L. I. B. Silva[1], M. E. Pereira[1], M. Freitas[2], T. A. P. Rocha-Santos[1,2]

[1]CESAM & Department of Chemistry, University of Aveiro, Campus universitário de Santiago,
3810-193 Aveiro (Portugal)
[2]ISEIT/Viseu -Instituto Piaget, Estrada do Alto do Gaio, Galifonge, 3515-776 Lordosa, Viseu (Portugal)

The use of optical fiber (OF) sensors have gained increasing interest as highly competitive and suitable instrumentation for in-situ monitoring of chemical pollutants in a number analytical and environmental applications. The suitability of OF technology for chemical sensors can be highlighted in terms of some particular advantages, such as immunity to electromagnetic interference and electrically passive operation, portability, compact and versatile design, remote and real-time monitoring, over conventional electronic sensing techniques [1-4]. In spite of their notable analytical features these analyzers display a complex analytical response of logistic or sigmoidal shape. Therefore, a proper study of the analytical signal is required for the benefit of usefulness and applicability of these systems to chemical analysis. In the last few years, several signal processing methods have been applied for modelling the analytical response of OF devices, aimed at the optimization of the analytical measurements and complexity minimization of the non-linear analytical response. In this work, a calibration model based on a cumulative symmetric double sigmoidal (SDS) function has been investigated and applied to the fitting of the experimental points of the analytical signal of OF sensors for volatile organic compounds (i.e. benzene, toluene, ethylbenzene, *o-, m-*, *and p-*xylene) determination. The estimative of the figures of merit of these devices, particularly sensitivity and detection limits, has been performed using the SDS model. The proposed model describes the full working range of the OF sensor in which it can be observed an area of rapid change in the analytical signal, centred between areas of slightly pronounced changes. The SDS model allows establishing the lower and upper detection limit of analytical systems and includes a linear calibration zone from which it is possible to calculate the analytical sensitivity. The SDS calibration model can constitute the basis for accurate characterization of the analytical performance of different OF-based sensor architectures for the monitoring of different analytes of chemical/environmental interest; in alternative to linear calibration models, which promotes the loss of the full analytical information, also providing estimates of the figures of merit, with no practical significance.

[1] Wolfbeis, O.S., Anal. Chem. 80, 4269-4283 (2008).
[2] Elosua, C., Matias, I.R., Bariain, C., Arregui, F.J., Sensors 6, 1440-1465 (2006).
[3] Kuswandi, B., Andres, R., Narayanaswamy, R., Analyst 126, 1469-1491 (2001).
[4] Silva, L.I.B., Costa, A.M., Freitas, A.C., Rocha-Santos, T.A.P., Duarte, A.C., Intern. Environ. Anal. Chem. 89, 183-197 (2009).

P103- ORGANOCHLORINE CONTAMINANTS (PCBs AND OCPs) IN CAPTURED AND FARMED FISH FROM SPAIN

J. Fenoll, M. D. Hernández, J. Cava, M. Martínez, M. V. Molina, P. Hellín and P. Flores

Instituto Murciano de Investigación y Desarrollo Agrario y Alimentario (IMIDA),
C/Mayor s/n, La Alberca, 30150, MURCIA (Spain)

Organochlorine pesticides (OCPs) and polychlorinated byphenyls (PCBs) are among the most known and investigated persistent organic pollutants (POPs). OCPs are man-made organic chemicals that have been used to control pest and diseases that damage vegetables and fruit. PCBs are not pesticides but do have many of the same properties. They are by-products and constituents of a variety of industrial products, such as electrical transformers. Due to their persistence and their chronic toxicity in humans and animals, these organic chemicals were banned in the early 1970s in develop countries. Humans are exposed to OCPs and PCBs primarily through the ingestion of foods contaminated by these chemicals. The highest levels of theses pollutants have been mainly detected in fish and other seafood. For that reason, during 2009 we measured the levels of chemical contaminants (including OCPs and PCBs) in different species of captured and farmed fish from Spain. Extraction for organochlorine pesticides and polychlorinated byphenyls was carried out according to the method of Bordet et al. [1]. OCPs and PCBs were analyzed in captured and farmed fish samples by gas chromatography (GC) with electron-capture detection (ECD). Confirmation analysis of pesticides was carried out by capillary gas chromatography coupled with mass spectrometry in the selected ion monitoring (SIM) mode. In both captured and farmed fish samples five organochlorine pesticides were detected, p,p'-DDD, p,p'-DDE, p,p'-DDT, o,p'-DDE and hexachlorobenzene. Among analysed PCBs, PCB 101, 105, 118, 138, 153 and 180 were detected in both captured and farmed fish samples. The most toxic PCBs (PCB 77, 81, 126, 169) were not found in the samples.

References

[1] Bordet, F., Inthavong, D. and Fremy, J.M. . J AOAC Int. 85, 1398-409 (2002).

Acknowledgments

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P104- SORPTION BEHAVIOUR OF MUNITIONS CONSTITUENTS IN NATURAL SOILS

V. Drevenkar and S. Fingler

Institute for Medical Research and Occupational Health, Ksaverska cesta 2,
HR-10000 Zagreb (Croatia)

The environmental fate of organic micropollutants is strongly influenced by their sorption in natural sorbents. Understanding their sorption behaviour could help us predict their transport in the environmental compartments. In this study the sorption and desorption behaviour of high explosives hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX), 1,3,5,7-tetranitro-1,3,5,7-tetraazacyclooctane (HMX), and 2,4,6-trinitrotoluene (TNT) as well as propellants 2,4-dinitrotoluene (2,4-DNT), 2,6-dinitrotoluene (2,6-DNT), and trinitroglycerin (TNG) was analysed in two natural uncontaminated surface soils and two contaminated soils collected at a military training ground. Batch experiments were carried out in a wide range of initial mass concentrations of single compounds and their mixtures in aqueous solutions of different ionic strength. After achieving sorption/desorption equilibrium, mass concentrations of non-sorbed compounds were determined in aqueous phase using high-performance liquid chromatography with a UV diode-array detector. Corresponding mass fractions in soil were calculated as the difference between the initial and equilibrium mass concentrations in the aqueous phase. Experimental data sets were fitted to the Freundlich sorption/desorption isotherm curve. No competitive effects between multiple solutes were observed by comparison of Freundlich sorption/desorption coefficients calculated in experiments with single sorbates and with the sorbate mixtures. The results of batch experiments with sorbates dissolved in aqueous solution of calcium chloride or of a mixture of calcium chloride and sodium azide showed that ionic strength affected sorption/desorption intensity. Sodium azide should be added to all solutions to prevent biodegradation of sorbates. To see how sorbate and sorbent chemical-physical characteristics affect sorption/desorption intensities, the Freundlich sorption coefficients were correlated with hydrophobicity and water solubility of sorbates and organic matter content and pH values of sorbents. Desorption experiments showed apparent sorption-desorption hysteresis for most sorbate/sorbent pairs, which indicates a highly reversible sorption of compounds in both contaminated and uncontaminated soils. Easy desorption could facilitate the transport of investigated munitions constituents from contaminated soils to surface and ground waters used as public water supplies.

P105- ANALYSIS OF BIOGENIC VOLATILE ORGANIC COMPOUNDS EMITTED BY *JUNIPERUS COMMUNIS* USING HS-SPME/GC/MS AND A COMPARISON WITH ITS ESSENTIAL OIL

N. Boutarene[1], Y. Foudil-Cherif[1], B. Y. Meklati[1,2] N. Yassaa[1]

[1]Laboratoire d'Analyse Organique Fonctionnelle, Faculté de Chimie, Université des Sciences et de la Technologie Houari Boumediene, BP 32 El-Alia Bab-Ezzouar, 16111 Algiers (Algeria)
[2]Centre de Recherche Scientifique et Technique en Analyses Physico-Chimiques (CRAPC), BP 248, Alger RP, 16004, Algiers (Algeria)

The composition of monoterpenes and sesquiterpenes has been determined in the gaseous emission of *J. communis* needles and berries using headspace-solid phase microextraction (HS-SPME) and gas chromatography-mass spectrometry (GC-MS). The optimum sampling conditions have been obtained by employing a mixed phase divinylbenzene-polydimethylsiloxane (DVB-PDMS) fibre coating. For sake of comparison, the essential oils from the same plant species were also analysed by means of gas chromatography equipped with either flam ionization detector or mass spectrometer. Sabinene with circa 26 % was the major compound followed by β-caryophyllene (11 %) and α-pinene (10%) in the atmospheric emissions of the needles. However in the emissions of the berries, β-caryophyllene dominated by 22 % followed by α-pinene with 17 %. In the essential oils obtained from the needles of *J. communis,* sabinene was the dominant monoterpene species (circa 30 %) followed indeed by α-pinene (circa 20%).The results obtained are discussed in the context of plant-atmosphere interactions.

P106- PREPARATION AND VALIDATION OF DIFFUSIVE GRADIENTS IN THIN FILMS DEVICES (DGT) AND THEIR APPLICATION TO SOIL SOLUTIONS

T. Garrido R. and J. Mendoza C.

Departamento de Química Inorgánica y Analítica. Facultad de Cs. Químicas y Farmacéuticas,
Universidad de Chile, Santiago (Chile)

The use of devices to determine different elements and predict their bioavailability has become very important because it allows in situ measurements, quantifying different metals and describing the kinetics of the processes. The (DGT) technique uses an ion exchange resin (Chelex 100) impregnated in a hydrogel that is covered by another hydrogel permeable to the ions that is exposed to the soil. The element that is being studied is immobilized by the resin gel, and if the flow remains constant the metal flow can be calculated from Fick's law of diffusion [1].

The gels were prepared according to Zhang & Davison [1], with some modifications. Validation of the DGT was made according to the information described in DGT-Research [2]. These devices were used on soil solutions in soil:water ratios of 1:2 and 1:10, the metal concentration was determined in the DGT by atomic absorption spectroscopy, and the concentration of free Cu in the solution with an ion selective electrode (ISE). On the other hand, the amount of bioavailable metal was evaluated, and the metal absorbed by wheat plants cultivated in nutrient solution and at the same time the metal captured by DGT devices in 24 hours was determined, applying doses of 2 mg/L of Cu, Ni, Cd and mixtures of them. Once the experiments were finished, the fresh and dry weight, the metal concentration in the devices, and the metals in the aerial parts and the roots were determined.

The optimum amounts for the preparation of the diffusing gel and resin gel were 30 μL of ammonium persulfate and 10 μL of TEMED, considering the addition of Chelex for the resin gel, with a thickness of 0.3 mm, for which the differences between the concentration determined in the (C_{DGT}) device and the concentration of the final solution and that from the diffusion (C_{Final}) was less than 10%, with a C_{DGT}/C_{Final} quotient of less than 10%, and a good correlation between C_{DGT} and C_{Final} ($r = 0.998$).

The soil solution was obtained from a clay loam neutral soil with an organic matter content of 3.8% and a Cu content as total metal of 1,561 ppm, mainly of anthropic origin, of which 18% is available (extractable with DTPA). The concentrations determined in the DGT corresponded to 2% of free metal determined by ISE for both extracts and 1.3% of total metal. For the experiments in nutrient solution the amount of copper mass found in the DGT was significantly greater for the treatment that considers the mixture of the metals. This difference was not found for Ni and Cd. None of the treatments showed competitive effects for the metal between DGT and the plants.

It is concluded that the thickness of the resin gel is an important factor that must be controlled: the less the thickness, the greater the reproducibility and precision of the results of metal absorbed by DGT. The ability to extract Cu from the soil solution corresponds to 1.3% of the total metal in the soil. The wheat plants subjected to stress for 24 hours with Cu, Ni, Cd or their mixture did not present visible symptoms of toxicity.

Acknowledgments
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[1] Zhang, H., Davison, W., Millar, S. and Tych, W. Geochim. Cosmochim. Acta, 59, 4181-4192 (1995).
[2] http://www.dgtresearch.com/ (2010)

P107- OLIVE OIL ADULTERATION SENSING WITH LASER SPECTROSCOPY

S. Botti[1], L. Cantarini[1], M. Falconieri[2], G. Giubileo[1], A. Puiu[3], P. Stacchini[4]

[1]ENEA, Via Enrico Fermi 45, 00044 Frascati (Italy)
[2]ENEA, Via Anguillarese 301, 00123-Rome (Italy)
[3] Tor Vergata University, Via del Politecnico 1, 00133-Rome (Italy)
[4] Istituto Superiore di Sanità, Via R. Elena 299, 00161-Rome (Italy)

The adulteration of extra virgin olive oil with cheaper oils is a major problem in the olive oil market. In the present work, experimental determinations of lower cost vegetable oils content in extra virgin olive oils were performed by FTIR and the Raman spectrometry. To this purpose a set of pure oils and mixtures of extra-virgin oils and different vegetable oils were arranged and served as experimental material in the reported study. The reference spectra were collected in the ENEA Research Laboratories with a Perkin Elmer Spectrum 100 FTIR Spectrometer and with a Ocean Optics HR3000 Raman Spectrometer. The chemical analysis to certify the analyzed samples were performed by the National Reference Laboratory of the Istituto Superiore di Sanità, Public Health Department. A data treatment of the spectral results was performed to allow an easy and fast comparison of the samples. The classification of the different mixtures was based on the intensity ratio between selected bands. Sensors based on laser spectroscopy were confirmed to be specific, fast and non destructive in the oil analysis.

P108- LEVELS OF HEAVY METALS IN SOIL EXTRACTS AND PLANT TISSUES AT AROUND OF A FACTORY LANDS

E. E. Golia, N. G. Tsiropoulos, A. Dimirkou and S. Floras

University of Thessaly, Department of Agriculture, Crop Production and Rural Environment,
38 446 Fytokou Road-N.Ionia Magnisias (Greece)

The pollution of soil is a source of danger to the health of people. The anthropogenic pollution caused by heavy industries enters plants then goes through the food chain and ultimately endangers human health. In the context, the knowledge of the regional variability, the background values and anthropogenic vs. natural origin of potentially harmful elements in soils is of critical importance to assess human impact [1, 2].

The present study was undertaken on soil contamination in Almyros region, Central Greece. The vegetables studied were lettuce samples (Lactuca sativa L.). Sampling was done randomly with five replicates.

The aims of the study were: i) to determine extent and distribution of heavy metals (Cu, Cd, Zn and Pb) ii) to find out the large scale variability, iii) to delineate the source as geogenic or anthropogenic based on the distribution maps and correlation of metals in soils. Soil samples were collected from this industrial area

from top 30 cm layer of the soil. The soil samples had been analyzed for physicochemical parameters such as pH values, Electrical Conductivity (EC), Cation Exchange Capacity (CEC), buffering capacities and organic matter content.

Heavy metals were determined after division into four fractions by sequential extraction with (a) acetic acid (exchangeable and specifically adsorbed metals), (b) a reducing agent (bound to Fe/Mn hydroxides), (c) an oxidizing agent (bound to soil organic matter), and (d) aqua regia (bound to mineral structures, residual)[3]. The freshly harvest vegetables were washed, cut into small pieces before being oven dried at 75^{o} C to constant weight. The samples were then pulverized with a mortar and pestle and were subjected to wet digestion in a conical flask with HNO_3:$HClO_4$ (2:1) for 3h on sand bath.

Metal concentrations in the supernatant solution were determined with flame or Graphite furnace atomic absorption. For each extract, external standards, prepared in the corresponding extraction solution, were used for calibration. All extraction sequences were replicated four times.

Thematic maps were created, using Geographic Information Systems (GIS) techniques using geostatistical tools. Factor analysis was conducted in order to assess the possible sources of the pollution.

The levels Cu, Zn and Pb determined were lower than the maximum permitted, except for Cd, which concentration was, in some cases, higher than the critical limits for soils.

Statistics are in agreement with the distribution maps of contaminants.

[1] Krishna A. K. and Govil P. K. Environ. Monit. Assess. 124, 263–275(2007)

[2] Leveia, E., Frentiub, T., Pontab, M., Senilaa, M., Micleana, M., Romana, C. and Cordosab, E. Intern. J. Environ. Anal. Chem. 89, 635–649 (2009)

[3] Golia E.E., Tsiropoulos N.G., Dimirkou A. and Mitsios I. Intern. J. Environ. Anal. Chem. 87, 1053–1063 (2007)

P109- PASSIVE SAMPLING ON XAD-2 RESIN OF POLYCYCLIC AROMATIC HYDROCARBONS : FIELD CALIBRATION BY USING HIGH-VOLUME SAMPLING

F. Gueguen[1,2], J. J. Schwartz[1], M. Millet[1], C. Schummer[1,3], P. Stille[1,2]

[1] Laboratoire Matériaux, Surfaces et Procédés pour la Catalyse, Equipe de Physico-Chimie de l'Atmosphère, (UMR 7515 CNRS), Université de Strasbourg, 1 rue Blessig, 67084 Strasbourg Cedex (France)
[2] Laboratoire d'Hydrologie et de Géochimie de Strasbourg (LHyGeS) – (UMR 7517 CNRS-Université de Strasbourg) – 1, rue Blessig – 67084 Strasbourg cedex (France)
[3] CRP Santé, LNS, Laboratoire de Toxicologie, Université du Luxembourg, Campus Limpertsberg, 162A av. de la Faïencerie, 1511 (Luxembourg)

Passive air sampling has been shown to be a very interesting alternative to high-volume sampling as it allows to overcome the disadvantages linked to this latter technique, like bulkiness or the need of electric power supply often absent in field campaigns. Though, to date, only limited data are available about passive air sampling of PAHs and data concerns PUFs disks passive samplers. To increase knowledge about passive air sampling of these compounds, a new passive sampler based on XAD-2-resin were deployed on five locations (two urban, one semi-urban, and two rural sites) in southern Luxembourg for one year, with durations of exposure varying from 30 to 81 days. Samplers were extracted using accelerated solvent extraction (ASE), and analyses were done using GC-MS/MS. The collected data were used to study the spatial and temporal variations of the atmospheric concentrations of the studied compounds.

15 PAHs with two to five aromatic rings were detected at concentrations ranging from 2,5 ng/sampler (pyrene) to 9727 ng/sampler (naphthalene. PAHs were detected quite regularly throughout the entire year of sampling. Concentrations of naphthalene were highest from October to December; which is in accordance with most studies having used high-volume sampling, while for other PAHs (e.g. acenaphthene, fluorene), highest concentrations were measured from April to June and, in parallel to naphthalene, from October to December. This indicates that some PAHs have a second important emission source causing large emissions of PAHs in springtime, and that does not produces particularly high amounts of naphthalene. Significant spatial variations of atmospheric PAHs were detected for acenaphthylene ($p = 0.049$), with highest concentrations on the urban sites and lowest concentrations on the rural sites.

In order to calibrate these samplers, some consecutive sampling campaigns using XAD-2 based samplers and high volume samplers were undertaken near the centre of Strasbourg in winter 2009 and spring 2010. XAD-2 based passive samplers were exposed for two weeks and traps (filter and XAD-2 resin) of high volume samplers were changed each 3 days in order to avoid potential degradation and volatilisation from filters. The total amount of air which go through the active sampler was measured by using a debimeter. For Two weeks periods the amount of air was measured of about 1 000 m^3. Different seasons were chosen in order to evaluate a potential influence climatic condition on the sampling rate of PAHs. The particle phase, as for PCDs was considered in order to check the sampling rate

Discussion on the influence of these different parameters will be presented and discussed in the poster.

P110- OPTIMIZING SAMPLING STRATEGIES IN TERRESTRIAL COMPARTMENTS FOR HOTSPOT DISTRIBUTIONS

J. W. Einax, T. Hildebrandt and D. Pick

Department of Environmental Analysis, Institute of Inorganic and Analytical Chemistry,
Friedrich Schiller University of Jena, Lessingstraße 8, 07743 JENA (Germany)

Pollution of soil and environment as a result of human activity is a major problem [1]. Nowadays, the determination of locally isolated contaminations (hotspots) is of interest for environmental remediation. These hotspots can have various toxic effects on plants, animals, humans, and the whole ecological system. However, economical consequences are also possible, e.g. high costs for remediation measures. The investigation of optimizing and estimating sampling strategies for hotspot distributions is part of the Research and Development project “Assurance of success at environmental remediation” funded by the Federal Ministry of Economics and Technology.

In this study, a field of dimensions 30 m by 30 m was constructed for sampling experiments. This test field was divided into 900 segments each with an area of one square meter and spiked with a nitrogen fertilizer in a randomized hotspot distribution comprising 5% of the field (45 hotspots).

Three sampling strategies (simple random grid, stratified random grid, stratified systematic square grid [2]) were applied and hit rates of hotspots were the basis for the comparison of the efficiency of these sampling strategies. For each sampling grid 36 samples were collected from the field. The average number of hotspots found was two, representing the a priori given contamination of 5%. The obtained real datasets were used for the validation of a newly developed computerized simulation. Depending on various parameters such as shape and size of the area, number of hotspots and sample numbers, optimal sampling strategies were predicted by this simulation program. Furthermore, an estimation of biases arising from sampling methodology is possible.

The computerized simulation and the real test field data showed similar results for the three sampling strategies. In addition to the investigated ones, the computerized simulation contains further sampling strategies such as polar or cross-shaped grids. However, there is a relatively high variability of finding the real number of hotspots.

The developed computerized simulation is an innovative tool for optimizing sampling strategies in terrestrial compartments for hotspot distributions.

[1] Lombi, E., Wenzel, W.W., Adriano, D.C., “Soil contamination, risk reduction and remediation”, Land Contamination & Reclamation 6, 183-197 (1998)

[2] Barth, D.S., Mason, B.J., Starks, T.H. and Brown, K.W., “Soil Sampling Quality Assurance User’s Guide”, 2nd Edition, United States Environmental Protection Agency, EPA/600/8-69/046 (1989)

P111- Fe_2O_3 CORE-Co[Fe(CN)$_6$] SHELL NANOCATALYST FOR EFFICIENT ELECTROOXIDATION AND SENSITIVE DETECTION OF TRYPTOPHAN

A. Jabbari, S. Majdi

Department of Chemistry, K. N. Toosi University of Technology,
P.O. Box: 16315-1618, Tehran (Iran)

Tryptophan is an important amino acid owing to its crucial roles in biological systems. It is a vital constituent of proteins and indispensable in human nutrition for establishing and maintaining a positive nitrogen balance. It is also an essential amino acid for brain functions and neuronal regulatory mechanisms [1,2].

Fe_2O_3 core-Co[Fe(CN)$_6$] shell nanocatalyst were synthesized and surface morphological studies were carried out using scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The electrocatalytical oxidation of tryptophan studied on a carbon paste electrode modified with nanoparticles of Fe_2O_3 core-Co[Fe(CN)$_6$]-shell using cyclic voltammetry and chronoamperometry. Voltammetric curves represent two quasi-reversible redox transitions. These redox transitions were attributed to Co(II)/Co(III) (lower potentials, transition I) and Fe(II)/Fe(III) (higher potentials, transition II). In the presence of tryptophan, the anodic peak current of transition II was increased following by a decrease in the corresponding cathodic peak current, while the peak currents related to transition II remained almost the same. This indicated that tryptophan were oxidized on the n-Fe_2O_3-Co[Fe(CN)$_6$] which immobilized mechanically on the carbon paste electrode via an electrocatalytic mechanism. In addition, values of k and α obtained for two peaks. A sensitive, simple, and time-saving amperometric was developed for the analysis of tryptophan, the determined parameters for calibration curves of tryptophan were reported.

[1] Ensafi, A.A., Hajian, R., Anal. Chim. Acta 580, 236-243 (2006)
[2] Liu, Y., X., Li, Sensors 7, 2446-2457 (2007)

P112- DETERMINATION OF MANGANESE AT DIFFERENT DEPTHS OF ROADSIDE SOIL

Y. Kalebaşi Aktaş* and A. Kocabaş

Trakya University, Department of Chemistry, 22030, Edirne (Turkey)
*yilaktas@yahoo.com

Concentration of manganese was determined at different depths of soil from roadside in Edirne (Turkey) using Flame Atomic Absorption Spectrometer (FAAS). In this study conducted between July 2006 and April 2007 roadside soil samples were collected from 8 sites (384 soil samples). Soil samples were collected at distances of 1, 5 and 10 meters from roadside and taken at depths of 0-10 and 10-30 cm from surfaces at every distance.

For the samples from the first 0-10 cm depth Mn concentration was found between 224.4-1019 mg/kg ; for the samples from 10-30 cm depth, this value was between 129.2-5.1389.2 mg/kg. The mean value for Mn in soil was found between 339.6-722.9 mg/kg. The concentration of manganese in the surface soil was generally higher than in subsoil.

P113- ANALYSIS OF FRAGRANCE ALLERGENS IN INDOOR AIR BY SPE-SPME GC-MS

J. P. Lamas[1], L. Sanchez-Prado[2], E. Becerril-Bravo[1,2], M. Lores[1],
C. Garcia-Jares[1], and M. Llompart[1]

[1]Departamento de Quimica Analitica, Nutricion y Bromatologia, Facultad de Quimica.
Campus Vida. Universidad de Santiago de Compostela, E-15782, Santiago de Compostela (Spain)
[2]Instituto de Ingeniería, Universidad Nacional Autónoma de México, Ciudad Universitaria,
04510 Mexico, D.F. (Mexico)

Indoor air quality is an increasingly important problem worldwide and allergens and pollutants home exposure represents one of the major public health issues of the moment.

A sensitive method based on solid-phase enrichment (SPE) and solid-phase microextraction (SPME) followed by gas chromatography-mass spectrometry (GC-MS) has been developed for the analysis of 24 volatile fragrance allergens in indoor air. Suspected allergens present in the air (0.2 m^3) were adsorbed onto a very small quantity of florisil (25 mg) and then transferred to a SPME fiber in the headspace mode (HS). The experimental parameters affecting the microextraction process have been optimized using a multifactor experimental design strategy. Accuracy, linearity, precision and detection limits (LODs) were evaluated to assess the performance of the proposed method. External calibration, not requiring the complete sampling process, demonstrated to be suitable for the quantification of all suspected allergens. Recovery studies were performed at various concentration levels, obtaining quantitative recoveries ($\geq$85%) in most cases. LOD values at the low ng m^{-3} were achieved for all the target compounds.

The application of the method to daily home air samples demonstrates the ubiquity of this kind of fragrance ingredients in quotidian indoor environments, which were found in all the samples, and frequently at quite high levels. Benzyl alcohol, linalool, citronellol, ionone and lilial were found in most analyzed samples.

P114- MULTI-RESIDUE ANALYSIS OF PAH, PCB AND OCP OPTIMIZED FOR ORGANIC MATTER OF FOREST SOIL

S. Hein, P.Lehnik-Habrink, I. Nehls, T. Win

Department I, "Analytical Chemistry, Reference Materials", BAM - Federal Institute for Materials Research and Testing, Richard-Willstaetter-Str. 11, D-12489 Berlin (Germany)

Analysing organic pollutants in forest soil is challenging because they are strongly physical and chemical bounded to soil organic matter (SOM). Within the framework of a forest soil inventory an analytical protocol for the determination of polycyclic aromatic hydrocarbons (PAH), polychlorinated biphenyls (PCB) and organochlorine pesticides (OCP) using one and the same extraction- and cleanup procedure was established and validated.

Different soil samples representative for the humic layer from typical mixed and coniferous soil had been used for the analysis. Three extraction solvents of different polarity and six standard extraction techniques like pressurized liquid extraction (PLE), soxhlet extraction, fluidized bed extraction (fexIKA), sonication, shaking and one-step extraction recommended for analyzing agricultural soil in Germany [1] were compared concerning their extraction efficiency. For additional matrix separation cleanup procedures such as gel permeation chromatography (GPC) and solid phase extraction (SPE) with different sorbents were tested. Quantification was carried out using gas chromatography combined with mass spectrometry (GC-MS). Labelled internal standards, added prior to extraction, were used for method evaluation.

For the simultaneous extraction of PAH, PCB and OCP from organic forest soil PLE with acetone/cyclohexane (2/1, v/v) provided the highest extraction efficiency. A two step cleanup procedure consisting of gel permeation chromatography (GPC) followed by solid phase extraction (SPE) with silica gel was entirely sufficient for the separation of humic substances without discrimination of analytes. For sample injection best results were achieved using an optimized programmable temperature vaporizer (PTV) injection system as it highly reduced the breakdown of thermolabile pesticides. Recovery rates for the different extraction- and cleanup steps were determined and ranged between 89% and 106%.

The described method allows the determination of PAH, PCB and OCP in the trace level range (1 – 2 $\mu g\ kg^{-1}$). The protocol is applicable for field laboratories with a high level of automation and for analyzing high sample amounts in line with monitoring programs.

[1] Handbuch der landwirtschaftlichen Versuchs- und Untersuchungsmethodik; Bd. VII, 3 rd Edition, VDLUFA Verlag (2008)

P115- USING UV SPECTRAL DECONVOLUTION TO FOLLOW SORPTION EXPERIMENT IN SOIL AND COMPARISON WITH MEKC

G. L. Erny, V. I. Esteves, D. L. D. Lima, C. P. Silva

CESAM - Department of Chemistry, University of Aveiro, Campus de Santiago,
3810-193 AVEIRO (Portugal)
Department of Complementary Sciences, Superior School of Health Technology of Coimbra,
Rua 5 de Outubro S. Martinho do Bispo Apartado 7006, 3040-854 Coimbra (Portugal)

In this study a simple and rapid procedure for monitoring sorption of atrazine onto soil samples was developed. This method is based on a multiwavelength UV spectral deconvolution (UVSD) where the UV spectrum of a sample is considered as a linear combination of absorption spectra, named reference spectra. The combination of the reference spectra allows the restitution of the shape of the UV Spectrum of any unknown sample [1-3]. In order to evaluate the accuracy of this method, a sorption study of atrazine to three different soil samples was monitored using both UVSD and micellar electrokinetic chromatography (MEKC) methods. The Freundlich parameters (KF and N) obtained for all soil samples tested were similar for both methods and UVSD has proven to be an accurate methodology, since the results did not present statistical significant differences at 95% confidence level. Moreover, the LOD obtained using UVSD presented lower values (0.066–0.12 mgL^{-1}) than the one obtained using MEKC (0.26 mgL^{-1}). The proposed UVSD method has been proven useful as a valid alternative, to the more common procedures to follow sorption experiment in soil matrix samples with no need of sample pre-treatment or column conditioning. This method is much faster and requires less sample manipulation than traditional analytical separation methods. Moreover, most modern spreadsheet-applications, such as Excel, now include statistical packages that allow performing multi-linear regression, which make this approach particularly inexpensive since the only requirement is a UV spectrometer. The regression output was made using the Microsoft Excel, a very easy and fast program, allowing anyone, with less knowledge about complex statistical programs, to perform the UV spectral.

[1] Nam, P.H., Alejandra, B., Frédéric, H. and Didier, B., Talanta 76, 936–940 (2008).

[2] Hassouna, M., Theraulaz, F. and Massiani, C., Talanta 71, 861–867 (2007).

[3] Coulomb, B., Richarson, Y., Brach-Papa, C., Boudenne, J.-L. and Theraulaz, F., Inter. J. Environ. Anal. Chem. 86, 1079–1093 (2006).

P116- IDENTIFICATION OF PLATINUM-HUMIC ACID COMPLEXES IN SOILS AND STREET DUST SAMPLES BY MALDI-TOF-MS

R. G. Djingova and V. V. Lyubomirova

Department of Analytical Chemistry, Faculty of Chemistry, University of Sofia,
J. Bouchier blvd., 1, 1164, Sofia (Bulgaria)

Increasing platinum concentrations have been detected in environmental samples since the introduction of catalytic converters in Europe. It may be presumed that metallic Pt is oxidised in the soil and that the majority of the Pt species formed in the oxidation are immobilised; these compounds could be humic acid complexes of Pt.

The aim of the present paper is the characterization of Pt-humic acid complexes in spiked soils and street dust samples using MLDI-TOF-MS.

Different ionization modes and MALDI matrices (e.g. CHCA, DHBA) have been tested.

DHBA yielded the best results, exhibiting superior ionization efficiency, low spectral background arising from the matrix and the matrix peaks were almost completely suppressed and caused no interferences with identified analyte peaks.

The application of MALDI-TOF-MS shows its suitability for humic acid characterization. The comparison of the MALDI-spectra of humic acids, extracted from spiked and no spiked soils proved that Pt undergoes transformation in the environment and is immobilized in the form of humic acid complexes.

P117- DETERMINATION AND ELECTROCATALYTIC OXIDATION OF METHIONINE BY NANOPARTICLES OF IRON(III) OXIDE CORE-COBALT HEXACYANOFERRATE SHELL-MODIFIED CARBON PASTE ELECTRODE

A. Jabbari, S. Majdi

Department of Chemistry, K. N. Toosi University of Technology, P.O. Box: 16315-1618, Tehran (Iran)

Methionine is an essential amino acid with an important role in biological methylation reactions. It constitutes the main supply of sulphur in the diet, preventing disorders in hair, skin or nails. Moreover, it helps to reduce cholesterol levels by increasing the lecitin production in liver, being also a natural chelating agent for heavy metals. Methionine can be present in real samples at different concentration level in blood plasma. [1-3]

In this work, the electrocatalytic oxidation of Methionine was studied on nanoparticles of iron(III) oxide core-cobalt hexacyanoferrate shell (Fe_2O_3@CoHCF)-modified carbon paste electrode (MCPE) using cyclic voltammetry and chronoamperometry. Voltammetric studies represented two quasi-reversible redox transitions for Fe_2O_3@CoHCF in a 100 mM phosphate buffer solution, pH 7.4 (PBS). These redox transitions were attributed to Co(II)/Co(III) (lower potentials, transition I) and Fe(II)/Fe(III) (higher potentials, transition II). In the presence of Tryptophan, the anodic peak current of transition II was increased following by a decrease in the corresponding cathodic peak current, while the peak currents related to transition I remained almost the same. The results indicate that Tryptophan was oxidized on Fe_2O_3@CoHCF which was immobilized in the carbon paste electrode via a surface mediation electrocatalytic mechanism. The catalytic rate constants, the electron coefficients and the diffusion coefficient involved in the electro oxidation process of Methionine on Fe_2O_3@CoHCF were reported. It was found that the nanostructured catalyst can efficiently oxidized Methionine with a high rate. Following by the study of the reaction mechanism and its kinetic, a sensitive and time-saving procedure was developed for the determination of Methionine.

[1] Sochasky, M. A., Jenkins, A. J., Lyons, T. J., Thorpe, S. R., Baynes, J. W., Anal. Chem. 73, 4662-4667 (2001).
[2] Wang, W., Kramer, P. M., Yang, S. M., Pereira, M. A., Tao, L. H., J., Chromatogr. B 762, 59-65 (2001)
[3] Agü´ı, L., Manso, J., Yáñez-Sedeño, p., Pingarrón, J. M., Talanta 64, 1041–1047 (2004).

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P118- DETECTION OF XANTHATES BY HPLC-MS/MS AND QUANTIFICATION BY CAPILLARY ELECTROPHORESIS IN MINE TAILINGS AND SOILS

J. Mendoza, T. Garrido, V. Briones and J. Parada

Facultad de Ciencias Químicas y Farmacéuticas, Universidad de Chile, Santiago (Chile)

Mining activities produce large amounts of wastes with variable contents of heavy metals and other compounds, among them the xanthates used in the ore flotation process. This activity implies a permanent transport of wastes between the production center and the storage place (tailings ponds or deposits). Several accidental release events of these wastes have been described, involving contamination of the surrounding soils [1]. One strategy to decrease the effect of these wastes is the application to the soil of biosolid from sewage treatment plants. The objective of this study was therefore to identify the presence of two compounds used extensively in mining, isobutyl xanthate (IBX) and isopropyl xanthate (IPX), by HPLC-MS/MS and optimizing the conditions for their quantification by zone capillary electrophoresis (ZCE) in matrices consisting of soil, tailings, biosolid, or mixtures of these substrates.

In the study a Clay Loam soil was collected near the city of Rancagua, from an area adjacent to a duct that transports tailings pulp (suspension) from copper mining activity in the high mountain range. The soil was treated with tailings and incubated for 30 days at 25 ºC with constant humidity. Mixtures containing 30% w/w of tailings and the equivalent of 200 Mg ha^{-1} of biosolid from sewage treatment plants were prepared. The solutions for analysis consisted of aqueous extracts of the treated and incubated soils and of the aqueous phase of the tailings pulp. The identification of analytes was carried out by HPLC-ESI-MS/MS by direct injection of solution, and the MS spectra were examined in the m/z 20-190 interval in positive and negative polarity. The determination of xanthates by ECZ was made on Quanta 4000 equipment and the optimum conditions were: positive polarity of the power supply, 40 cm long capillary, 25kV, 20 mM borate electrolyte at pH 9.0, wavelength of 254 nm, and a hydrostatic injection time of 30 s [2].

The analysis of the standard IBX and IPX spectra in positive mode indicated the absence of signals, but in the negative mode IBX had a signal at m/z 149, which would correspond to the M1-H species. This compound in turn generates MS^2 fragments at m/s 73, 71, 77 and 91. In the case of IPX there was a signal at m/z 135, which would correspond to the M2-H species, with its corresponding MS^2 fragments at m/z 59, 77, 57 and 43. This fragmentation scheme made it possible to identify the presence of IPX in the aqueous phase of the tailings and the absence of IBX. Optimization of the method by ECZ gave a good correlation, with a correlation coefficient better than 0.995 and a linear range until 150 µmol L^{-1} for both analytes. The limits of detection and migration times for IBX and IPX were 6.3 and 4.1 µmol L^{-1}, and 2.2 and 2.5 min, respectively. The repeatability of the measurements had a coefficient of variation of 5.1% (n=5). Application of the optimized method gave a concentration of 15.5 µmol L^{-1} of IPX in the aqueous phase of the tailings and trace amounts of the compound in the soil-tailings-biosolids mixture.

[1] Sastre, J., Hernandez, E., Rodriguez, R., et al. Sci. Total Environ., 329, 261-281, (2004)
[2] Kumar, A. and Faubel, W., Fresenius J. Anal. Chem. 367, 211-214 (2000).

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P119- APPLICATION OF SURFACTANT MODIFIED MAGNETIC NANOPARTICLES FOR REMOVAL OF METHYL VIOLET FROM AQUEOUS SOLUTIONS

M. Faraji[1], M. Hesabi[2], F. Keyhanian[2] and S. Shariati[2*]

[1] Faculty of Chemistry, Tarbiat Modares University, Tehran (Iran)

[2] Department of Chemistry, Faculty of Sciences, Islamic Azad University, Rasht Branch, Rasht (Iran)
*shahabshariaty@gmail.com

In this research, the potential of Fe_3O_4 magnetic nanoparticles for efficient removal of methyl violet as a cationic dye from aqueous solutions was investigated. For this purpose, Fe_3O_4 magnetic nanoparticles were synthesized via chemical precipitation method with addition of sodium hydroxide to solutions of Fe^{2+} and Fe^{3+}. The size and structure of synthesized nanoparticles were characterized by XRD and SEM techniques. To remove methyl violet properly, the surface of magnetic nanoparticles was modified with sodium dodecyl sulfate as an anionic surfactant. Also, the various parameters affecting dye removal such as pH of solution, surfactant concentration, ionic strength, adsorption time and stirring rate of dye solution, were investigated. The kinetic studies for methyl violet adsorption showed a rapid sorption dynamics by a second-order kinetic model, suggesting chemisorption mechanism. Dye adsorption equilibrium data were fitted well to the Longmuir isotherm rather than Freundlich isotherm. The maximum monolayer capacity q_{max} was calculated from the Langmuir as 414.7 mg g^{-1}. The results show that, surfactant modified magnetic nanoparticles, can be used as a cheap and efficient adsorbent for removal of cationic dyes form aqueous solutions. Also, these results can be used to design an appropriate adsorption treatment plant for removal and recovery of dyes from wastewater samples.

[1] S. Glassstone, D.Sc., PH.D. Text Book of Physical Chemistry, Second Edition, (1955) 1195.
[2] J.-F. Liu, Z.-S. Zhao, G.-B. Jiang, Environ. Sci. Technol. 42 (2008) 6949.

P120- SEMI-CONTINUOUS SYSTEM FOR ANALYSIS OF WATER-SOLUBLE FRACTION OF METALS IN ATMOSPHERIC AEROSOLS

P. Mikuška, M. Vojtěšek, Z. Večeřa and K. Křůmal

Institute of Analytical Chemistry, Academy of Sciences of the Czech Republic, v.v.i., Veveří 97,
602 00 Brno (Czech Republic)

Metals released into air from both natural and anthropogenic sources are associated with particulate matter. Recent studies indicate that particulate metals are correlated with the pulmonary toxicity and for a lot of metals, their carcinogenic effects and/or their potential to attack the nervous system, are now well established.

The routine method for the determination of metals in atmospheric aerosols involves aerosol sampling on filters with off-line analysis of filters in laboratory, which provides time averaged results. To obtain high time-resolved particle composition, the real-time methods have been developed such as mass spectrometry [1] or aerosol collectors operating mostly on the principle of steam condensation [2,3] or a Venturi-scrubber [4] that provide simple and cheap alternative way of real-time measurement of chemical composition of aerosols.

The new system for the semi-continuous determination of water-soluble metallic components of atmospheric aerosols is presented. Aerosol particles are continuously collected in an Aerosol Counterflow Two-Jets Unit (ACTJU) [5] from air (air flow rate of 5 L/min) into a stream of deionised water (water flow rate of 1 mL/min) and the ACTJU concentrate is subsequently on-line analysed for the content of at collected aerosols. Metal analysis includes preconcentration, HPLC separation and chemiluminescent detection by the reaction with luminol using a continuous flow system [6].

Fe^{3+}, Cu^{2+} and Co^{2+} were selected as model metals to show a potential of the method for the analysis of water-soluble fraction of metals in atmospheric aerosols with high sensitivity and high time resolution. The detection limit of particulate Co^{2+}, Cu^{2+} and Fe^{3+} (S/N=3) is 0.3 ng m^{-3}, 37 ng m^{-3} and 65 ng m^{-3}, respectively. The system allows the determination of concentration of water-soluble fraction of particulate metals in real time with time resolution of 30 min. The whole system is sufficiently robust for the field application. The method was applied to the measurement of metals in atmospheric aerosols in the Czech Republic.

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[1] Wood, S.H. and Prather, K.A., TRAC-Trends in analytical chemistry 17, 346-356 (1998).
[2] Khlystov, A., Wyers, G.P. and Slanina, J., Atmos. Environ. 29, 2229-2234 (1995).
[3] Poruthoor, K.S. and Dasgupta, K.P., Anal. Chim. Acta 361, 151-159 (1998).
[4] Belostotsky, I., Gridin, V.V., Schechter, I. and Yarnitzky, N.C., Anal. Chim. Acta 429, 215–226 (2001).
[5] Mikuška, P. and Večeřa, Z., Anal. Chem. 77, 5534-5541 (2005).
[6] Fletcher, P., Andrew, K.N., Calokerinos, A.C., Forbes, S. and Worsfold, P.J., Luminescence 16, 1-23 (2001).

P121- INDOOR MONITORING CAMPAIGN OF Rn-222 IN PUBLIC BUILDINGS OF THE CITIES OF VALPARAISO (CHILE) AND CACERES (SPAIN)

F. Cereceda-Balic[1], J. Christie[1], C. Miro[2], E. Pinilla[3] and M. Reis[4]

[1]Environmental Chemical Laboratory, Environmental Technology Centre (CETAM), Technical University Federico Santa María, Av. España 1680, Casilla 110-V, Valparaíso (Chile)
[2]Department of Applied Physics, University of Extremadura,
Av. de la Universidad sn, 10071-CÁCERES (Spain)
[3]Department of Analytical Chemistry, Faculty of Science, University of Extremadura,
Av. de Elvas sn, 06071- Badajoz (Spain)
[4]Unit of Protection and Radiological Safety Nuclear Technology Institute, Estrada Nacional 10,
2686-953 Sacavém (Portugal)

Radon is a naturally occurring radioactive noble gas, having variable distribution in the geological environment as a decay product of natural uranium found, in differing degrees, in a wide range of rocks and soils and in building materials incorporating or manufactured from these. There are three naturally occurring isotopes, Rn-222, a direct product of Ra-226 in the U-238 decay-series, Rn-220, a decay product of Th-232, and Rn-219, a decay product of U-235. Radon has high mobility, enabling it to move out of underlying rocks into caves, mines and the built environment. Of the three isotopes, Rn-222 is the most significant, its relatively long half-life enabling it to migrate quite significant distances within the geological environment before decaying.

Ionising radiation is well known to have adverse health effects, and inhalation of radon and its progeny Po-218 and Po-214 adsorbed onto atmospheric particulates is currently believed to provide the majority of dose to the respiratory system. This damages the sensitive inner lining of the lung, increasing the risk of cancer [1].

Indoor Rn-222 levels in air of two public buildings in the cities of Valparaíso (Chile) and Cáceres (Spain) have recently been measured using the continuous radon monitor RTM1688-2 of SARAD. This monitor measured values in the range of 0 -10 MBq/m^3 and has an internal sampling pump (0.30 L/min continuous). The detection limit is 5 Bq/m^3 for measurement cycles of 2 h. Chilean building was built in the 30s of the twentieth century and spanish building in the XIX century but restored the second half of the twentieth century. Currently they are used for administrative purposes.

The range of average concentration of atmospheric radon were from 63 to 594 Bq/m^3 in Valparaiso, and 14 to 327 Bq/m^3 in Cáceres, while the average concentrations were 278 Bq/m^3 and 72 Bq/m^3, respectively. Therefore, higher concentrations than those recommended by European Union, 400 Bq/m^3 (Old Building), were reached in some cases.

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[1] Darby, S., Hill, D., Doll, R., Annals of Oncology, 12, 1341-1351 (2001).

P122- APPLICATION OF A POLYMERIC COATING ON GOLD WIRE FOR HS-SPME OF PAHs

M. H. Banitaba[1], S. Seyedhosseinidavarani [1], A. Mehdinia[2], A. A. Mohammadi [2]

[1] Department of Chemistry, Faculty of Sciences, Shahid Beheshti Universit G. C.,
Tehran (Iran) (1983963113)
[2] Department of Marine living science, Iranian National Center for Oceanography (INCO),
Tehran (Iran) ( )

Among many kinds of fibers, including metal oxides [1] and carbon based fibers [2], conductive polymers have some advantages. They can be synthesized chemically or electrochemically under various conditions which can affect chemical, mechanical and morphological properties of the polymer.

In this work, we introduce a new fiber, based on electro-polymerization of 2- and 3-aminothiophenol monomers on gold wire for SPME application. SEM images shows that this coating has nano structure with good porosity (Fig. 1). This fiber also shows good mechanical and thermal stability up to 300°C which can be attributed to covalently attachment of polymeric layer through sulfur-gold bond to the substrate. The ability of fiber for extraction of various compounds with different polarity and functional groups has been examined using the extraction of 2- butanol, benzene, n-hexane, toluene, which shows that our fiber has the ability of extracting various classes of compounds. The extraction of five PAHs, including phenanthrene, anthracene, pyrene, 9, 10-dimethylanthracene and benzo[a]anthracene has been also accomplished. Dynamic ranges of 1-250ppb for phenanthrene and anthracene, and 1-100ppb for three others were obtained. Detection limits for all of these compounds was found to be in the range from 0.1 to 0.32ppb. The real sample (seawater, Oman) analysis using this method was also performed.

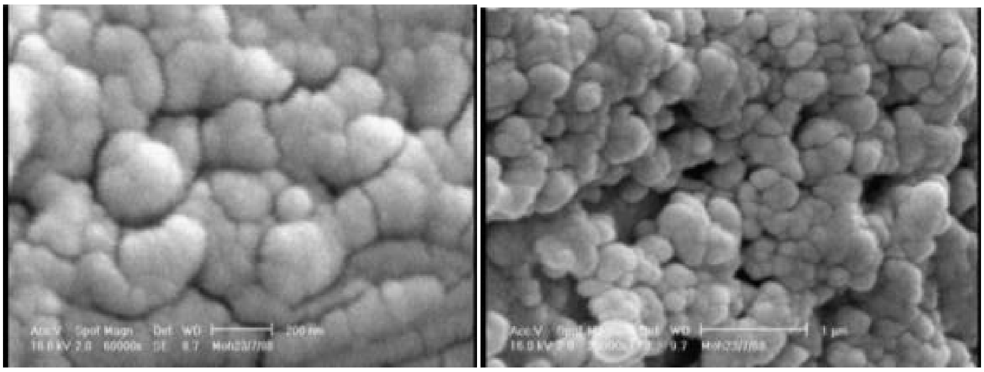

Fig. 1 SEM images of PATP with magnification of 60000(left) and 20000 (right)

References
[1] D. Budziak, E. Martendal, E. Carasek, Analytica Chimica Acta, 628 (2008) 92.
[2] A. Gierak, M. Seredych, A. Bartnicki, Talanta, 69 (2006) 1079.

P123- SOLID-PHASE MICROEXTRACTION FOLLOWED BY GAS CHROMATOGRAPHY MASS SPECTROMETRY FOR THE DETERMINATION OF INK PHOTO-INITIATORS IN PACKED MILK

R. Cela, N. Negreira. I. Rodriguez, E. Rubí

Departamento de Química Analítica, Nutrición y Bromatología; Instituto de Investigación y Análisis Alimentario; Universidad de Santiago de Compostela. 15782 Santiago de Compostela (Spain)

Photo-initiators are compounds added to some printing inks. Their use in the external face of multilayered packaging cartons can lead to their occurrence in food. In 2005, the European Food Safety Authority (EFSA) reported the presence of 2-isopropylthioxanthone (ITX) in several liquid foods, particularly packed milk, and solid infant formula [1]. Further studies confirmed the presence of ITX not only in milk [2-3], but also in fruit juices [4] and even wine [4], at concentrations up to several hundreds $\mu g\ L^{-1}$. In addition, other photo-initiators such as 2-ethylhexyl-4-dimethylaminobenzoate (EHPABA) [4] and benzophenone [4] have been also found in carton packed foods and beverages. Potential long-term effects of photo-initiators exposure on human health remain unknown; however, they are considered as undesirable compounds, whose presence in packed foodstuff has to be controlled. Milk is a particularly concerning matrix, since it is considered a basic food.

The aim of this study is to present a single step sample preparation method, based on the SPME technique, for the determination of a group of seven ink photo-initiators (benzophenone, BP; 1-hydroxycyclohexyl-phenylketone, CPK; ethyl-4-dimethylaminobenzoate, EDMAB; 4-methylbenzophenone, 4-MBP; 2,2-dimethoxy-2-phenylacetophenone, 2,2-DMPA; EHPABA and ITX) in packed milk samples. To the best of our knowledge, this is the first application of SPME to the determination of this family of compounds in milk. Parameters affecting the performance of the extraction were systematically evaluated using univariant and also experimental factorial designs studies. After extraction, fibres were thermally desorbed and compounds determined by GC-MS, in the selected ion monitoring (SIM) mode.

Acknowledgments

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[1] Anton, R., Barlow, S., Boskou, D., Castle, L., Crebelli, R., Dekant, W., Engel, K.H., Forsythe S., Grunow, W., Heinonen, M., Larsen, J.C., Leclercq, C., Mennes, W., Milana, M.R., Pratt, I., Rietjens, I., Svensson, K., Tobback, P., Toldrá, F, EFSA J 293, 1-15 (2005).

[2] Allegrone, G., Tamaro, I., Spinardi, S., Grosa, G., J. Chromatogr. A 1214, 128-133 (2008).

[3] Bagnati, R., Bianchi, G., Marangon, E., Zuccato, E., Fanelli, R., Davoli, E., Rapid Commun. Mass Spectrom. 21, 1998-2002 (2007).

[4] Sagratini, G., Caprioli, G., Cristialli, G., Giardiná, D., Ricciutelli, M., Volpini, R., Zuo, Y., Vittori, S., J. Chromatogr. A 1194, 213-220 (2008).

P124- METHOD FOR SCREENING EMERGING CONTAMINANTS WITH LIQUID CHROMATOGRAPHY TIME-OF-FLIGHT MASS SPECTROMETRY

J. Nurmi

Department of Environmental Sciences, University of Helsinki, Niemenkatu 73,
FIN-15140 Lahti (Finland)

The significant increase in economical welfare during last twenty years has enhanced the use of chemicals tremendously as a part of industrial production, agriculture and everyday life. Term chemicalisation indicates the increased use of chemicals and environmental pollution happening in consequence of that. Since 1960's, attention has been paid to the health effects of chemicals. In addition to impacts on human, chemicals may also harm environment. Hence, use of many toxic chemicals has been restricted by international conventions. However, although the number of restricted chemicals grows constantly, new chemicals are synthesized and introduced at the same time. Although a compound itself may not be harmful, it is possible that various chemical reactions in the environment change the physical properties and toxicity of the compound. Despite previous research, the knowledge of the concentrations of organic compounds in environment is still limited to few compounds and for even smaller fraction of compounds reliable results of ecotoxicological research are available.

When environmental samples are analysed, often only certain beforehand chosen regulated compounds are measured. This pre-targeted approach leads up to very biased information about the general view of sample and the other components of sample remain unknown. Thus, it is most probable that novel contaminants end up into the environment all the time. However, in recent years especially emerging contaminants have gained a lot of interest in the field of environmental research. [1-3] Identification of these emerging pollutants requires non-target screening of environmental samples. For quantitative analysis novel sensitive instrumental techniques of analytical chemistry are also needed.

Time-of-flight mass spectrometry (TOF-MS) online with chromatographic separation is a powerful tool in screening emerging contaminants. The purpose of this study was to develop a generic multiresidue method based on solid phase extraction (SPE) and liquid chromatography TOF-MS for screening emerging contaminants in water matrices. Factors related to method optimisation and compound identification will be discussed.

[1] Richardson S.D., Anal. Chem. 81, 4601-4622 (2009).
[2] Derek C.G., Environ. Sci. Technol. 40, 7157-7166 (2006).
[3] la Farré M., Trends in Analytical Chemistry 27, 991-1007 (2008).

P125- TOXIC METALS AND ORGANOCHLORINE PESTICIDES IN THE ENDEMIC WHITE FISH (*PETENIA SPLENDIDA*) AND CONTAMINATION OF THE LAKE PETÉN ITZÁ, GUATEMALA

O. Martínez[1], B. E. Oliva-Hernández[1], J. F. Pérez-Sabino[1],
C. E. SilvaTorres[2], J. P. Torres[2]

[1]Escuela de Química, Edificio T-12, Universidad de San Carlos de Guatemala zona 12,
01012 Guatemala city, (Guatemala)
[2]Instituto de Biofísica Carlos Chagas Filho, UFRJ, CCS, Bloco G, Ilha do Fundão,
Rio de Janeiro, RJ, 21949-900 (Brasil)

Physicochemical and bacteriological contamination was evaluated in water of Lake Petén Itzá during the period September 2005-February 2006. Samples of fish, water and superficial sediments were taken during four different months for analyzing nutrients, metals and physicochemical and bacteriological parameters. The main sources of water pollution in Lake Petén Itzá are the direct discharges of wastewater, and the agriculture and cattle in the basin. The levels of nutrients found in Lake Petén Itzá correspond to lakes in eutrophic state with nitrate-N between 0.0330-0.220 mg/L and orthophosphate-P between 0.003–1.174mg/L. The eutrophic state of the lake was confirmed by the presence of phytoplankton genus which considered as indicators of eutrophication. The water of Lake Petén Itzá does not meet the quality criteria for human consumption nor for recreation, representing a risk for human health.

Toxic metals and organochlorine pesticides were analyzed in specimens of White Fish (*Petenia splendida*) along the period of the study. Levels of heavy metals higher than international recommended levels in fish for human consumption were found in several individuals (mercury: 143-708 ug/g; lead: 0.70-2.07 ug/g; nickel: 0.9-1.3 ug/g; zinc: 5.90-68.43 ug/g; chromium: 0.65-4.5 ug/g). This could represent a toxicological risk only if fish were consumed frequently as indicated in other studies [1]. Levels of ΣDDT were found between 7.385-22.367 ng/g in *P. splendida* muscle. These levels are not considered risky for fish population nor for sporadic consumption by humans.

Low levels of heavy metals were found in sediments of Lake Petén Itzá. However, relatively high levels of lead and chromium were found in sediments collected in Sacpuy and River Ixlú sites. The available fraction of toxic metals in sediments was high regarding the total content of metals. Mean levels of metals were: mercury (19-68 mg/kg d.w.), lead (8-65 mg/kg d.w.), nickel (1.5-83 mg/kg d.w.), zinc (18-47 mg/kg d.w.) and chromium (4.2-166.7 mg/kg d.w.).

[1] Freitas Terra, B., Araújo, F.G., Ferreira Calza, C., Lopes, R.T., Pires Teixeira, T. Heavy metal in tissues of three fish species from different trophic levels in a tropical brazilian river. Water Air Soil Poll. 187, 275-284 (2008).

P126- PARTICLE-INTO-LIQUID SAMPLER ON-LINE COUPLED WITH LIQUID CHROMATOGRAPHY - MASS SPECTROMETRY FOR THE DETERMINATION OF ORGANIC ACIDS IN ATMOSPHERIC AEROSOLS

K. Hartonen, M. Kivilompolo, M. Kulmala, J. Parshintsev,
M. L. Riekkola, J. Ruiz-Jimenez

Laboratory of Analytical Chemistry, Department of Chemistry, P.O.Box 55, FI-00014,
University of Helsinki (Finland)
Division of Atmospheric Sciences, Department of Physics, P.O.Box 64, FI-00014,
University of Helsinki (Finland)

Atmospheric aerosol particles play an important role in the global radiation budget. Qualitative and quantitative information about the compounds in aerosol particles is essential if we are to comprehend their role and effects in the atmosphere. Oxidized compounds, such as organic acids, contribute significantly to aerosol mass and increase their hydrophilicity. In the present study, sample collection and preparation were directly integrated with a chromatographic system by coupling a particle-into-liquid sampler for the first time on-line with solid - phase extraction - liquid chromatography - mass spectrometry. For sample pretreatment and concentration, strong anion exchange material was used in the extraction. Sampling, extraction and analysis conditions were optimized to obtain reliable information about aerosol chemical composition. To evaluate the performance of the on-line coupled system, half of each sample was analysed on-line and the other half was derivatized and analysed off-line by gas chromatography - mass spectrometry. Comparison of the two techniques with use of t-test showed the results to be in an excellent agreement (P values were greater than 0.05, and the null hypothesis could not be rejected). Concentration of studied compounds were in range of few ng per m^3 and are in agreement with previous studies [1].The on-line coupled system is fast and reliable and a promising tool for the real time analysis of organic acids in atmospheric aerosols [2].

[1] Parshintsev, J., Hyötyläinen, T., Hartonen, K., Kulmala, M., Riekkola, M.-L., Talanta, 80, 1170-1176 (2010).
[2] Parshintsev, J., Kivilompolo, M., Ruiz-Jimenez, J., Hartonen, K., Kulmala, M., Riekkola, M.-L., submitted to J. Chrom. A.

P127- CHARACTERIZATION OF TRACE ELEMENT PARTICLES DEPOSITED ON PLANT AND HUMAN HAIR SAMPLES COLLECTED FROM AREAS POLLUTED BY VARIOUS SOURCES

J. Bojarska, E. Leśniewska, T. Paryjczak, A. Pawlaczyk,
S. Sypniewski, M. I. Szynkowska

Institute of General and Ecological Chemistry, Technical University of Łódź, Żeromskiego 116,
90-924 Łódź (Poland)

The main field of application for bioindicative plants species is connected with air pollution monitoring. Most typically applied lichens and mosses have developed nonspecific stress-coping accumulation mechanisms with regard to heavy metals [1]. Hair is one of the most common forms of criminal, occupational or environmental trace evidence, both in the case of individuals and population groups, which can deliver information about the abnormal presence of toxic substances. However, the element concentration in hair varies greatly and depends on the factors such as: sex, age, smoking habits, etc. The aim of the present work was to evaluate the differences in the state of pollution of two areas based on the examination of a particulate matter accumulated on biological (moss and lichen) and human hair samples. Analyzed material was collected from two locations: Łódź city and rural area of Wiślinka/near Gdańsk. All three indicators were applied potentially as a natural monitor to investigate the influence of local pollution sources on atmospheric conditions specific to the studied regions. Łódź is recognized as a city where the impact of three big coal-power plants, heavy traffic and households with their own heating systems are main sources of contamination. The pollution of rural area of Wiślinka is universally assigned to the presence of a huge phosphate waste disposal place (approx. over 16 mln tonnes of phosphogypsum are deposited there) and peculiar natural location (absence of terrain barriers facilitating the distribution of contaminants). All samples for the quantitative analysis were mineralized with nitric acid in the microwave system MILESTONE 1200 MEGA. The bulk elemental content was determined by inductively coupled plasma by inductively coupled plasma mass spectrometry with the time of flight analyzer, ICP-ToF-MS (GBC Scientific Equipment, Australia). Scanning electron microscopy with energy dispersive X-ray spectrometer, SEM-EDX (Thermo Noran, USA) was applied as a non-destructive solid analysis method used for particle distribution studies and identification of type and composition of airborne particulate deposited on samples. As a complementary method the semi-destructive and semi-quantitative laser ablation system CETAC LSX equipped with ND:YAG laser and combined with ICP-ToF-MS was successfully employed in order to evaluate the spatial and depth distribution of elements and distinguish metals which can be attributed to lithological origin form those incorporated and associated with anthropogenic emissions. Additionally, phase composition of chosen studied samples was examined using polycrystalline difractometer X`PERT PRO MPD equipped with copper tube. HighScore Plus software and PDF-2 database constantly actualized by International Centre of Diffractive Data in Pennsylvania (USA) were used for the phase identification.

[1] Markert, B.A.., Breure, A.M., Zechmeister, H.G., “Bioindicators and biomonitors. Principles, concepts and applications”, 1st Edition, Elsevier, Netherlands (2003).

P128- DETERMINATION OF CHLOROPROPANOLS IN FOOD SAMPLES BY PRESSURIZED LIQUID EXTRACTION (PLE) AND GAS CHROMATOGRAPHY MASS SPECTROSCOPY (GC/MS)

A. M. Carro, R. Cela, P. González, R. A. Lorenzo, I. Racamonde

Department of Analytical Chemistry, Institute of Research and Food Analysis University of Santiago de Compostela, Avda de las Ciencias s/n 15782 Santiago de Compostela (Spain)

The chloropropanols were discovered by Velisek and their group in 1978 in Prague. These compounds are formed during the acid hydrolysis process that takes place in developing products such soy sauce and derivatives, bread, biscuits and other foodstuffs [1]. Due to their carcinogenic and toxicity, the FAO/WHO has established ceilings on consumer products, [2] therefore it has been necessary to develop an analytical methodology that allows detection and quantification at levels required. This study proposes a sensitive and reliable method to determine chloropropanols especially 3chloro 1,2 propanediol(3-MCPD) and 1,3 dichloro2propanol (1,3DCP) in foods by pressurized fluid extraction(PLE) with a in-situ derivatization using bis-(trimethylsilyl)trifluoracetamide (BSTFA) and quantification by GCMS. The method optimization was carried out using screening and response surface experimental designs. Influence of extraction parameters as temperature, number of cycles, time or volume of flush, were evaluated. The best conditions were 70ºC during 3 minutes of static extraction and one cycle, the volume flush was 80%. Various adsorbents (Florisil®, activated carbon, silica, Extrelut®) and dispersants (Diatomaceous earth and Extrelut®) have been evaluated for a one gram of sample and the best results were obtained with: 2,5 g of diatomaceous earth and 0,1 g of sodium sulphate anhydrous as dispersants and1g Florisil® as adsorbent. The solvent used was ethyl acetate and the internal standards were the d5deuterated compounds. In order to reduce the analysis time and improve the sensibility, the derivatization of the compounds was performed in the cell extraction with 70 µL of derivatizing reagent. After extracting the samples, extracts were concentrated and subsequently inject into GCMS The proposed method provides LODs of 1.62 ng/g to 1,3 DCP and 1.69 ng/g to 3-MCPD. Recoveries are around and 80% and 83% to 1,3DCP and 3MCPD respectively, with a %RSD less than 2%. This method was applied successfully to real samples of bread, breakfast cereals and biscuits. There was no excess of the limits set by European Union.

References

[1]Hamlet, C.; Sadd, P.; Gray, D. J. Agric. Food Chem 52 20592066 (2004)
[2] Joint FAO/WHO Food Standards Programme, "Position Paper on Chloropropanols for the thirty third Sesion of the Codex Committe on Food Addittives and Contaminants" (2001)

P129- DEVELOPMENT OF AN ENVIRONMENTAL ANALYTICAL METHOD FOR THE DETERMINATION OF HORMONAL STEROIDS AND VETERINARY COMPOUNDS, AT TRACE LEVELS, IN SOIL

R. Baudot, C. Cren-Olive, M. V. Salvia, E. Vulliet, L.Wiest

Service Central d'Analyse du CNRS, USR 59, Echangeur de Solaize, Chemin du Canal,
69360 Solaize (France)

Chemical products are more and more used for agriculture and domestic activities and are responsible for the spread of several substances in the environment which are harmful for humans. Among these products, hormonal steroids and pharmaceutical compounds are of growing concern [1]. If several analytical methods are available to determine the content of hormonal steroids or veterinary substances in aquatic environment [2, 3], few methods were described to allow their analysis in solid matrices. Only few data concerning the content of hormonal steroids in soil are available and these ones reveal contaminations which can reach hundreds of ng/kg [4]. Consequently, the aim of this study was to develop an environmental analytical method for the analysis of traces of hormonal steroids or veterinary substances in soil. Thus, 47 products were selected including 25 veterinary products, 11 hormonal steroids and 11 other well-known compounds as human contaminants and used in this study as pollution tag. An analytical method both selective and sensible based on liquid chromatography – tandem mass spectrometry was developed. The optimization allowed the determination of the best conditions for the separation by chromatography (choice of the column, the gradient…) and for the detection by mass spectrometry (ionization mode, MRM transitions).

The analysis of complex matrices such as soil needed a rigorous sample preparation to obtain a repeatable and enough sensible analysis to achieve the detection limits required. For this purpose, an extraction step by PLE (Pressurized Liquid Extraction) was developed. As the 47 studied molecules have characteristics and physical/chemical properties totally different, this stage was really delicate to optimize. In order to obtain the best parameters for this extraction (pressure, temperature, static time, cycle number and the choice of the solvent) and to find the best compromise to extract well each compound, a chemiometric approach by an experimental design was done. The analytical procedure allows the determination of the target analytes in the lower ng/g range.

[1] Kuldip Kumar, Satish C. Gupta, Yogesh Chander, and Ashok K. Singh, Advances in Agronomy, 87, 1-54 (2005).

[2] Marıa J. Lopez de Aldaa, Silvia Dıaz-Cruzb, Mira Petrovica, Damia Barcelo, Journal of Chromatography A, 1000, 503-526 (2003).

[3] Emmanuelle Vulliet, Laure Wiest, Robert Baudot, Marie-Florence Grenier-Loustalot, Journal of Chromatography A, 1210, 84-91 (2008).

[4] O. Finlay-Moore, P. G. Hartel and M. L. Cabrera, Journal of Environmental Quality, 29, 1604-1611 (2000).

P130- FIRST APPROACH TO THE STABILITY STUDY OF THE PRESERVATIVE BRONIDOX

M. Fernandez-Alvarez, L. Sanchez-Prado, J. P. Lamas, M. Llompart,
C. Garcia-Jares, M. Lores

Departamento de Quimica Analitica, Nutricion y Bromatologia, Facultad de Quimica.
Campus Vida. Universidad de Santiago de Compostela, E-15782, Santiago de Compostela (Spain)

Preservatives ensure cosmetics safety and quality, playing an important role to protect the health of the consumer from undesired infection risks and to maintain the potency and stability in every personal care formulation, avoiding microbial growth that leads to product spoilage. Recently, preservatives have attracted attention as potential allergens. In addition, preservatives degradation, that reduces their antimicrobial potency and might lead to the occurrence of unexpected by-products, should be considered and avoided. Bronidox (5-bromo-5-nitro-1,3-dioxane) is used as a broad-spectrum antimicrobial preservative in cosmetics, mainly in aqueous products, but also in raw materials like detergents. In the European Community, the use of bronidox as a preservative is regulated by the European Cosmetic Products Regulation [1]: it is restricted to rinse-off cosmetics, with a maximum authorized concentration of 0.1 % and with the requirement of avoiding the formation of carcinogenic nitrosamines.

Information regarding degradation, bio accumulative potential and aquatic toxicity is not available for bronidox. In this work we examined the effects of light and temperature on the stability of bronidox. Our results showed that the bronidox stability in shampoos under regular conditions of temperature and light exposure, guarantee the safety of the ingredient to manufacturers and consumers. Nevertheless, bronidox degradation might take place (67-100%) when other experimental conditions are used, probably due to a combination of redox and photolytic processes, which are the starting point of current investigations.

[1] Regulation (EC) N° 1223/2009 of the European Parliament and of the Council of 30 November 2009 on cosmetic products (recast of the Council Directive 76/768/EEC and its successive amendments as one single text in the interests of clarity) Official Journal of the European Union (2009) L 342/59.

P131- INVESTIGATE OF ALUMINIUM CONCENTRATIONS IN SOIL AND SUNFLOWER (*HELIANTHUS ANNUUS L.*) BY ICP-OES IN ERGENE FIELD, TURKEY

G. Seren and O.Yoruk

Trakya University, Faculty of Science, Department of Chemistry, Edirne (Turkey)

Soil is both the principal source of trace elements entering the food chain and a major sink for pollutant elements. Trace elements accumulate in the soil and influence the ecosystem nearby. So, the investigation of trace elements in soil and plant samples is very important in the point of environmental pollution. The bioaccumulation of trace elements long time periods, which may result in the gradual damage of living organisms. Aluminium is the most abundant metal in the earth's crust and it is widely distributed and occurs naturally in soil, water, and air. Most aluminium-containing compounds do not dissolve to a large extent in water unless the water is acidic or very alkaline. Aluminium is primary among the factors that reduce plant growth on acid soils. Metal-accumulating plants, such as *Brassica* species and *Helianthus annuus L.*, can accumulate unusually high concentrations of trace elements in parts from polluted soil and waters [1]. Aluminium may accumulate in plants and cause health problems for animals that consume these plants. In this study, the Al concentrations in soil and sunflower (*Helianthus annuus L.*) parts have been investigated. Soil and plant samples collected from five different locations (in total, 72 samples from 24 sampling points) in Ergene field, Edirne were determined by Inductively Coupled Plasma Emission Spectroscopy (ICP-OES) after microwave-assisted digestions.

[1] Dushenkov, V., Kumar, P.B.A., Motto, H., Raskin, I., Environmental Science&Technology, 29, 1239-1245, (1995).

P132- A NEW SPME FIBER FOR EXTRACTION OF 1,4-DIOXANE FROM ALKYL ETHER SULFATES AND COSMETICS USING HS-SPME AND GC ANALYSIS

M. H. Banitaba, S. Seyedhosseinidavarani*, L. Masoomi, H. R. Lotfi- Zadeh- Zhad, O. Sadeghi

Department of Chemistry, Faculty of Sciences, Shahid Beheshti University G. C.,
Tehran 1983963113 (Islamic Republic of Iran)

1,4-Dioxane is a very concerned chemical in cosmetics and environment due to its potential carcinogen to human and animals [1,2]. This paper presents a simple and convenient analytical method using a novel SPME fiber within Gas chromatography method for determination of 1.4-dioxane in alkyl ether sulfates and cosmetics. 1,4-Dioxane is a polar molecule and has only two etheric oxygen as a functional groups. Hence as can be expected, commercially available SPME fibers haven't good performance for extraction of it. In contrast, our proposed fiber which provides Lewis acid-base and hydrogen bonding interaction between its surface and analyte functional groups is more suitable for extraction of 1,4-dioxane. For preparation of fiber, a sol gel process was used for modification of a fused silica surface using aluminum tri-tert-butoxide (Fig 1).

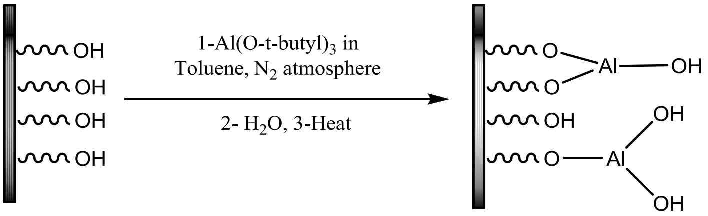

Fig. 1 Proposed possibilities of covalent attachment of aluminum to the substrate

The optimization of main factors affecting extraction using central composite design method leads to the following optimum conditions: temperature of 45°C, extraction time of 7min, salt content of 35% and stirring rate of 500rpm. The statistical analysis of results of the experimental design reveals that extraction time, extraction temperature and salt content are most important factors that affect the extraction process, respectively. The ratio of sample/headspace volume was not a main factor for this extraction method. The optimum conditions were used to obtain calibration curve and evaluation of LOD and LOQ of method. Experiments show two linear ranges from 5ppb to 1ppm (R^2=0.998) and 10ppm to 100ppm (R^2=0.996). LOD and LOQ were estimated to be 1.5 and 5 µg/l, respectively. This method was also applied for analysis of real samples including fatty alcohol ethoxylate, sodium lauryl ether sulfate, dishwashing liquid and shampoo using standard addition method.

References

[1] C. Bor Fuh, M. Lai, H. Y. Tsai, C. M. Chang, Journal of Chromatography A, 1071 (2005) 141.
[2] Y. M. Park, H. Pyo, S. J. Park, S. K. Park, Analytica Chimica Acta, 548 (2005) 1

P133- ANALYSIS OF AFLATOXIN B1 IN GRAINS BY HOMOGENEOUS LIQUID-LIQUID EXTRACTION METHOD

N. Sheijooni-Fumani*, R. Yousefi and S. Mirza

International Goods Inspection Company, P.O. Box: 15875-3619, Tehran (Iran)
*n.sheijooni@yahoo.com

A simple and rapid method based on homogeneous liquid-liquid extraction (HLLE) and utilizing high performance liquid chromatography (HPLC) with fluorescence detection combined with post-column derivatization was developed for determination of Aflatoxin B_1 in rice and grain samples. Since sample pre-treatment plays a key role in analysis, parameters affecting recovery and preconcentration such as type and volume of organic solvent for HLLE process, volume ratio of water-methanol, concentration of phase separator reagent and extraction time were optimized. Under the optimum conditions the calibration curve was linear in the range of 0.01 – 1.0 ng g^{-1}. Also the limit of detection (3σ) and the relative standard deviation (R.S.D) were 0.003 μgL^{-1} and 10%, respectively.

P134- EVALUATION OF SEVERAL TECHNIQUES FOR DETERMINATION OF VOLATILE ORGANIC COMPOUNDS IN AIR SAMPLES

J. Auger[1,2] and V. Simon[1,2]

[1] Université de Toulouse, INPT, LCA - Laboratoire de Chimie Agro-Industrielle, ENSIACET,
4 Allée Emile Monso, F-31029 Toulouse (France)
[2] INRA; LCA - Laboratoire de Chimie Agro-Industrielle, F-31029 Toulouse (France)

During the recent decades, volatile organic compounds such as benzene, toluene, ethylbenzene and xylene isomers (BTEX) have gained interest in the field of indoor and outdoor air quality. They are ubiquitous contaminants widely distributed in the environment due to both, natural and anthropogenic sources. These compounds are often found in air due to their extensive use in industrial paints, adhesives, degreasing agents and aerosols but are also emitted as combustion products of wood, gasoline and fuels. Their atmospheric concentrations can be quantified by active or passive sampling.

Radiello® diffusive samplers filled with graphitised carbon Carbograph 4 have been evaluated by solvent extraction and thermodesorption. No significant differences between both techniques were observed. Passive samplings were then compared with Carbotrap 200 active samplings which were carried out on several Toulouse sites in 2008 and 2009. The mean values obtained from active samplings are most of the time higher than those obtained with Radiello® tubes. The differences are very strongly correlated with the temperature parameter and concentrations.

P135- SAMPLING AND ANALYSIS OF PAHs IN ZAGREB AIR

I. Jakovljević, G. Pehnec, M. Šilović Hujić, A. Šišović and V. Vađić

Institute for Medical Research and Occupational Health, Ksaverska c. 2, 10000 Zagreb (Croatia)

Polycyclic aromatic hydrocarbons (PAHs) are a product of incomplete combustion of fossil fuels and other organic materials. They consist of two or more fused aromatic rings. PAHs with fewer rings are gases, but PAHs with five and more rings are bound to particles which then move into the soil, water, sediment and vegetation, through dry or wet deposition. Benzo(a)pyrene is the most commonly measured PAH since it has always been present and used as an indicator of carcinogenic hazard in polluted environments.

Samples were collected at two measuring sites, located at different part of the city of Zagreb. Measuring site A was located in the northern low-rise residential part of Zagreb with small population density, individual heating, and modest traffic. Site B was located in the southern part of the city near a busy crossroads, parking, and a garage. At both sites twenty-four hour samples of PM_{10} particles were collected on quartz filters with a low volume PM_{10} Sven Leckel sampler from about 50 m^3 of air. The samplers were set at about 1.5-2 m above the ground, and about 10- 20 m away from the road. Samples were taken only on working days in the winter and summer. After collection, samples were wrapped in aluminium foil and kept in deep freeze at -18 ^oC until analysed.

The analysis was performed using a Varian Pro Star high performance liquid chromatograph (HPLC) with a fluorescence detector and programmed changes in excitation and emission wavelength to optimise selectivity and sensitivity. Samples were analysed for the following PAHs: fluoranthene (Flu), pyrene (Pyr), benzo(a)antracene (BaA), chrysene (Chr), benzo(b)fluoranthene (BbF), benzo(k)fluoranthene (BkF), benzo(a)pyrene (BaP), benzo(ghi)perylene (BghiP), and indeno (1,2,3-cd) pyrene (Ind).

Average mass concentrations of all PAHs over the summer were low at both sampling sites, but all PAHs at site B were about two times higher. Average BaP mass concentrations at site A was 0.041 ng/m^3 and at site B 0.073 ng/m^3. In the winter, all PAHs were 2-3 times higher at site B. Average BaP mass concentrations at site A was 1.147ng/m^3 and at site B 2.762 ng/m^3. This investigation has shown that concentrations of all PAHs correlated with traffic intensity.

P136- POTENTIAL OF NATURAL AND MODIFIED MEDITERRANEAN SOIL TO PROTECT WATER SUPPLIES FROM TRIAZINE HERBICIDE RESIDUES

V. Drevenkar[1], M. Rožić[2], L. Sekovanić[3], S. Stipičević[1]

[1]Institute for Medical Research and Occupational Health, Ksaverska cesta 2, HR-10000 Zagreb (Croatia)
[2]University of Zagreb, Faculty of Graphic Arts, Getaldićeva 2, HR-10000 Zagreb (Croatia)
[3]University of Zagreb, Geotechnical Faculty, Hallerova aleja 7, HR-42000 Varaždin (Croatia)

Sorption/desorption interactions of three structurally different triazine herbicides (atrazine, atratone, and ametryn) and three breakdown products of atrazine (deisopropylatrazine, deethylatrazine, and didealkylatrazine) were studied in native, acidified, and organically enriched forms of two representative Mediterranean soils (terra rossa): a surface soil collected in the area of Izmir in Turkey and a subsurface soil collected at a location on the Istrian peninsula in Croatia. The native soils were of clayey to silty-clayey type and differed significantly in mineral composition and cation exchange capacity. Triazine sorption/desorption experiments were performed using a batch equilibration method [1]. Sorbate equilibrium concentrations in the aqueous phase after sorption/desorption were determined by high performance liquid chromatography using an UV diode-array detector. The results of sorption experiments, evaluated in terms of Freundlich isotherm, were compared with respect to the physicochemical properties of sorbates and sorbents. Sorption intensity of all triazines in native soils was very low ($\Delta G° \leq -2$ kJ mol^{-1}) despite relatively high soil organic carbon content (15 %). Acidification of native soils to pH ≈ 4 with hydrochloric acid significantly enhanced sorption intensity of more basic herbicides (atratone and ametryn) and of two most polar atrazine degradation products. Enrichment efficiency of native soils with a cationic surfactant (hexadecyltrimethylammonium) was highly influenced by soil cation exchange capacity. Retention of triazines in organically enriched soils increased significantly with triazine hydrophobicity due to additional hydrophobic interactions. The most intensive sorption of triazines was observed in soils fortified with cationic surfactant in an amount corresponding to 65 % of the native soil cation exchange capacity. Sorption capacity of hydrophobically modified soils was for most triazines greater than the capacity of native and acidified soils. Desorption experiments for each pair of sorbate/sorbent were conducted in a single desorption step. The results indicated partially or almost completely irreversible sorption of most sorbates in soils richer in organic carbon, save for polar degradation products, whose sorption was irreversible to a greater extent in acidified soils. Native Mediterranean soil seems to make no use as a permeable and stabile native barrier for hydrophobic pollutants to reach groundwater. Its acidification and organic carbon enrichment however show a promising potential in preventing water supplies pollution with triazine herbicide residues.

[1] Stipičević, S., Fingler, S. and Drevenkar, V., Arh. Hig. Rada Toksikol. 60, 43-52 (2009).

P137- MICROWAVE ‘DRY’ DISTILLATION IN THE EXTRACTION OF *ROSMARINUS OFFICINALIS* L. ESSENTIAL OIL

N. Tigrine-Kordjani[1], F. Chemat[2], B. Y. Meklati[3]

[1]Laboratoire d’Analyse Organique Fonctionnelle, Université des Sciences et de la Technologie Houari Boumediene El Alia,BP 32, Bab Ezzouar, 16111 Alger (Algeria)
[2]Université d’Avignon, UMR A 408 INRA, Sécurité et Qualité des Produits d’Origine Végétale, 33, rue Louis Pasteur, 84029 Avignon Cedex 1 (France)
[3]Centre de Recherche Scientifique et Technique en Analyses Physico-Chimiques CRAPC, BP 248 Alger RP 16004, Alger (Algeria)

Microwave ‘‘Dry’’ Distillation or solvent free microwave extraction SFME is proposed as a method for ‘‘green’’ extraction of edible essential oils extensively used in the fragrance, flavour, and pharmaceutical industries and also in aromatherapy.

It is a combination of microwave heating and dry distillation, performed at atmospheric pressure without adding any solvent or water. Isolation and concentration of volatile compounds is performed by a single stage. Rosemary was extracted with SFME at atmospheric pressure and 100 °C for 30 min. The extracted compounds were removed from the aqueous extract by simple decantation, determined by gas chromatography-flame ionization (GC-FID) and identified by gas chromatography–mass spectrometry (GC/MS). Hydrodistillation of rosemary was performed with 2 L of water for 3 h for comparison of the results with those provided by SFME: extraction time, yields, chemical composition and quality of the essential oil, efficiency and costs of the process. Extraction of essential oils from rosemary with SFME was better in terms of energy saving, extraction time (30 min versus 3 h), oxygenated fraction (59% versus 46%), exact product yield (0.6% versus 0.6%) and product quality.

SFME is a green technology and appears as a good alternative for the extraction of edible essential oils from aromatic plants used in aromatherapy and the food industry.

P138- ARSENIC LEVELS IN FINE PARTICULATE MATTER IN ZAGREB AIR

V. Vadjić, S. Žužul

Institute for Medical Research and Occupational Health, Ksaverska c. 2, 10000 Zagreb (Croatia)

Exposure to arsenic may occur via ambient air, tobacco smoke, water, food or beverages. Adverse health effects of arsenic may involve the respiratory, gastrointestinal, cardiovascular, nervous and haematopoietic system. In the atmosphere, arsenic is in the form of particulate matter or is adsorbed on particulate matter.

This paper presents the first results of arsenic monitoring in fine particulate matter with aerodynamic diameter of less than 10 µm, 2.5 µm, or 1 µm (PM_{10}, $PM_{2.5}$, or PM_1) in the city of Zagreb. Samples of particulate matter were collected on quartz membrane filters, destructed by microwaves, and arsenic the arsenic extracted with nitric acid. For analysis we used atomic absorption spectrometry with electrothermal atomisation and Zeeman background correction. Arsenic in $PM_{2.5}$ and PM_1 particles was 55% and 48% of its PM_{10} content respectively. Correlations between arsenic were the highest with the PM_{10} particle fraction and the lowest with the PM_1 fraction, which points to a mineral origin of arsenic in the air.

P139- MEASUREMENTS OF *n*-ALKANES AND PAHs IN PM_{10} AND TOTAL SUSPENDED PARTICLES (TSP) IN URBAN AND INDUSTRIAL AREAS OF ALGIERS CITY

S. Khedidji[1], R. Ladji[2], N. Yassaa[1]

[1]Laboratoire d'Analyse Organique Fonctionnelle, Faculté de Chimie, Université des Sciences et de la Technologie Houari Boumediene, BP 32 El-Alia Bab-Ezzouar, 16111 Algiers (Algeria)
[2]Centre de Recherche Scientifique et Technique en Analyses Physico-Chimiques (C.R.A.P.C.), BP 248, Alger RP, 16004, Algiers (Algeria)

The distribution of *n*-alkanes and polycyclic aromatic hydrocarbons (PAHs) in particulate matter with aerodynamic diameter smaller than 10 µm (PM_{10}) and total suspended particles (TSP) is reported. It has been determined during period December 2009 to April 2010 in parallel in a big industrial district and a busy urban area located in Algiers. The airborne particulate matter was enriched onto glass fibre filters by using a medium-volume sampler with or without a size-selective inlet for PM10 and TSP, respectively. Extractable organics were recovered by refluxing the aerosol-enriched filters in soxhlet using a dichloromethane–acetone (4:1) mixture for 16h. The extract was fractionated through alumina column chromatography for separating non-polar compounds (e.g., *n*-alkanes) which were first eluted with pure *iso-octane*, from the bulk of medium-polar organics including PAHs which were recovered with dichloromethane-iso-octane. Finally, highly-polar species were eluted with acetone. Both n-alkanes and PAHs were analyzed by using a gas chromatograph coupled to a mass spectrometer (GC/MS). The potential emission sources of airborne contaminants were reconciled by combining the values of *n*-alkane carbon preference index (CPI) and selected diagnostic ratios of PAHs, calculated in both PM_{10} and TSP. Carcinogenic and mutagenic potencies associated to PAHs were evaluated by multiplying the concentrations of “active” compounds times the corresponding potency factors normalized vs. benzo(a)pyrene (BaP), and were found both acceptable. The total PAH concentrations ranged from 33 to 387 ng m^{-3} in PM_{10} particles suspended in the atmosphere of Algiers urban area.

P140- OCCURRENCE OF PHARMACEUTICALLY ACTIVE COMPOUNDS IN GUADIAMAR RIVER BASIN (SOUTH OF SPAIN)

D. Camacho-Muñoz, J. Martín, J. L. Santos, I. Aparicio and E. Alonso*

Department of Analytical Chemistry, University of Seville, C/ Virgen de África 7,
E-41011 Seville (Spain)
*ealonso@us.es

Guadiamar River basin (South of Spain) is one of the main water sources to Doñana National Park. Traditionally, Guadiamar River pollution has been caused by urban wastewater and wastes from olive oil mills. After the tailing-dam spill off from a pyrite mine to Guadiamar River occurred in 1998, scientific efforts have been focused to evaluate the contamination by heavy metals while other pollutants, such as pharmaceutically active compounds, have been scarcely studied [1].

Pharmaceutical compounds represent an overgrowing portion of trace organic contaminants in urban aquatic environment. Pharmaceuticals, after human consumption, reach wastewater treatment plants, where are not efficiently removed, ending up in surface water and ground water through wastewater effluent discharges [2].

In this work, the occurrence of five anti-inflammatory drugs (diclofenac, ibuprofen, ketoprofen, naproxen and salicylic acid), a nervous stimulant (caffeine), two antibiotics (sulfamethoxazole and trimethoprim), two lipid regulators (clofibric acid and gemfibrozil), an antiepileptic drug (carbamazepine), a β-blocker (propranolol) and four estrogens (17α-ethinylestradiol, 17β-estradiol, estriol and estrone) in Guadiamar River basin is reported.

The analytical procedure was based on a previously reported method [3]. Method involves sample treatment by solid phase extraction and determination by high-performance liquid chromatography with diode array and fluorescence detectors. Pharmaceuticals were separated by gradient elution with acetonitrile and a 25 mM potassium dihydrogen phosphate solution at a flow-rate of 1.2 mL/min.

Eleven of the sixteen studied pharmaceuticals were detected in Guadiamar River. Caffeine, gemfibrozil, ibuprofen, naproxen, propranolol and salicylic acid were the most frequently detected while clofibric acid, estriol, estrone, ketoprofen and sulfamethoxazole, were not detected in any of the analyzed surface water samples. The pharmaceuticals at the highest concentration levels in river water were ibuprofen and salicylic acid (mean concentration levels 0.56 and 0.45 $\mu g\ L^{-1}$, respectively) followed by gemfibrozil and caffeine.

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[1] Camacho-Muñoz D., Santos J.L., Aparicio I. and Alonso E., J. Hazard. Mat. 177, 1159-1162 (2010).
[2] Grujić S., Vasiljević T. and Laušević M., J. Chromatogr. A, 1216, 4989-5000 (2009).
[3] Camacho-Muñoz D., Martín J., Santos J.L., Aparicio I. and Alonso E., J. Sep. Sci. 32, 3064-3073 (2009).

P141- DETERMINATION OF INTERSTING TOXICOLOGICALLY ELEMENTS IN PM2.5 BY NEUTRON AND PHOTON ACTIVATION ANALYSIS

P. Avino[1], G. Capannesi[2], M. Manigrasso[1] and A. Rosada[1]

[1]Chemical Laboratory, DIPIA, ISPESL, via Urbana 167, 00184 Rome (Italy)
[2]UTFISS CATNUC, ENEA, via Anguillarese 301, 00123 Rome (Italy)

The element distribution in air is determined fundamentally by the resuspenction from soil and water of various substances of natural and/or artificial origin, by their circulation due to the meteorological events and by the chemical element behaviour. Furthermore, human activities introduce into the environment materials that give rise to increasing levels of many species which can endanger the environmental quality and represent an hazard for the population. In this way, among atmospheric pollutants trace elements in airborne particulate have a preminent position because the presence of the most toxic elements (e.g. Cd, Hg and Pb) and because their levels may affect the biological systems. The main problem of this task resides in the analytical determination of such species: in fact, their levels in atmosphere are at ultra-trace levels and a very specific methodology is necessary with regard to the accuracy and precision and contamination problems. The nuclear techniques such as Instrumental Neutron Activation Analysis (INAA) and Instrumental Photon Activation Analysis (IPAA) assure these requirements.

In this communication a retrospective analysis of elements in air particulate collected in the last 4 decades has been carried out in order to study the trend of their environmental levels; INAA and IPAA have been used to determine elements of primary concern.

The sample have been collected in rural and urban locations in order to determine only effects due to global circulation of the aerosols; semi-annual samples have been used to characterize the summer/winter behavior of natural and artificial origin.

The levels found for element of natural origin are higher than those in other countries owing to geological and meteorological factors peculiar to Central Italy. The levels found for artificial elements are sometimes less than those in other countries, suggesting a less polluted general situation for Central Italy. However, for a few elements (e.g., Pb) the levels measured are only slight lower than those proposed as air ambient standard.

P142- OPTIMIZATION OF PRESSURIZED LIQUID EXTRACTION (PLE) OF POLYCYCLIC AROMATIC HYDROCARBONS FROM MOSSES ASSOCIATED WITH SOLID PHASE EXTRACTION (SPE) CLEAN-UP

L. Foan[1,2], C. Sablayrolles[1,2] and V. Simon[1,2]

[1]Université de Toulouse, INPT, LCA - Laboratoire de Chimie Agro-Industrielle, ENSIACET,
4 Allée Emile Monso, F-31029 Toulouse (France)
[2]INRA, LCA - Laboratoire de Chimie Agro-Industrielle, ENSIACET, F-31029 Toulouse (France)

Polycyclic aromatic hydrocarbons (PAHs) are persistent organic pollutants emitted through incomplete combustion of organic material by industries, waste incineration, domestic heating and traffic. Due to their slow rates of degradation, their toxicity and potential for both long-range transport and bioaccumulation in living organisms, PAHs are monitored in the entire environment.

Bryophytes have been employed over the past decades as biomonitors for the assessment of airborne pollutant deposition. PAH determination in mosses is currently carried out by solvent extraction followed by solid phase extraction (SPE) clean-up, associated with analysis by high pressure liquid chromatography coupled with fluorescence detection (HPLC-FLD) [1].

For optimization of the analytical procedure, large quantities of mosses *Hypnum cupressiforme* Hedw. and *Isothecium myosuroides* Brid. were collected respectively in October 2008 and Febuary 2010 at Bertiz Nature Reserve (Navarra, Spain), then dried and grounded to form homogenous samples. Soxtec extraction with *n*-hexane combined with Florisil normal phase SPE clean-up (Supelco) showed average PAH recoveries of 60%. To reduce extraction time and solvent consumption, Pressurized Liquid Extraction (PLE) with *n*-hexane combined with Florisil SPE was investigated. After optimization of extraction temperature, time and number of cycles, PLE showed higher recoveries than Soxtec extraction, in average of 75%.

Several SPE phases generally used for organic matrix clean-up were also tested: Florisil, NH_2, Silica and Alumina (cartridges from Supelco and Phenomenex). The SPE choice barely influenced PAH recoveries. However, some adsorbents clearly eliminated more interferences, facilitating PAH analysis.

[1] Foan L., Sablayrolles C., Simon V., Elustondo D., Lasheras E., González L., Ederra A., Santamaría J.M., 2010. Reconstructing historical trends of Polycyclic Aromatic Hydrocarbons deposition in a remote area of Spain using moss material from a herbarium, *Atmospheric Environment*, *In Press, Accepted Manuscript, Available online 20 May 2010.*

P143- THE APPLICATION OF THE VOLTAMMETRIC METHOD TO DETERMINE THE DEGREE OF CHOSEN NUTRIENTS COMPLEXATION BY HUMIC SUBSTANCES

M. Huculak-Mączka, K. Hoffmann and J. Hoffmann

Institute of Inorganic Technology and Mineral Fertilizers, Chemical Faculty
Wroclaw University of Technology, ul. Smoluchowskiego 25, 50-372 Wrocław (Poland)

Organic matter performs many useful functions in soil and it constitutes one of fundamental factors determining practically all properties and transformations profile of the soil. Direct interaction of organic substance with the soil environment is related to the amount and the structure of humus substances contained in its composition. The chemical structure of these compounds and contents of reactive functional groups enable to obtain mineral-organic linkages of different kind. Cation-humic interactions exert control on the reactivity of the cation, including its bioavailability. The character of these linkages has influence on mobility of metal ions in the soil and possibility of their penetration into the soil profile. It is particularly essential from a fertilizing point of view. Mineral-organic complexes, called chelates prevent fertilizer elements leaching, facilitate and in consequence increase the efficiency of mineral fertilizers effects. Organic ligands, which humus acids are, constitutes particularly valuable elements, on account of the environmental protection, due to their abilities to bind to the pesticides contained in the soil, causing their fast degradation. They can also immobilize and neutralize heavy metals contributing to the process of soil detoxification [1-3].

Humus compounds constitute very important link in the natural environment by creating different mineral-organic linkages in the soil. Studying on the degree of metal ions complexation by humus substances can be helpful in predicting behaviours of fertilizer components in the environment, and influence the method for inventing fertilizer prescriptions taking the Principles of Sustainable Development into consideration.

The degree of humus compounds ability to form linkages with zinc; as well factors that can influence the stability of these linkages were determined in order to evaluate the behaviour of complexes in the natural environment. The degree of metal complexation was analyzed using method of Differential Pulse Voltammetry applying the mercury drop electrode operating in the SMDE mode (Static Mercury Drop Electrode). Measurements were carried out by the usage of electrochemical measuring computer-operated system - AUTOLAB PGSTAT 12 [4].

[1] Ashok, K., Pandey, S.D. and Misra, V., Ecotoxicol Environ Saf. 47, 195-200 (2000).
[2] Pandey, S.D., Misra, V. and Viswanathan, P.N., Sci. Total Environ. 231, 125–133 (1999).
[3] Tipping, E., "Cation binding by humic substances", 1st Edition, Cambridge environmental chemistry series 12, Cambridge University Press, Cambridge (2002).
[4] Zajt, T., "Metody woltamperometryczne i elektrochemiczna spektroskopia impedancyjna", Wydawnictwo Gdańskie, Gdańsk (2001).

P144- POSSIBILITIES OF MINI-SPECTROPHOTOMETER EYE-ONE PRO AS AN ALTERNATIVE OF THE DIFFUSE REFLECTANCE SPECTROMETER FOR DETERMINATION OF ORGANIC SUBSTANCES USING DIAZOTIZED POLYURETHANE FOAM

V. V. Apyari, S. G. Dmitrienko

Division of Analytical Chemistry, Chemical Department, Lomonosov Moscow State University,
Leninskie gory, 1/3, 119991 Moscow (Russia)

Determination of aromatic amino- and hydroxycompounds is an actual task of the environmental analytical chemistry. Often such a determination is performed using different colored derivatives. Thus, a search of new cheap and available approaches to a registration of the analytical response of colored samples is important for a development of simple and rapid analytical methods based on the signal measurement directly in the matrix of a sorbent or solid-phase reagent. A prospective way to solve this problem is using mini devices accumulating the new achievements of the optoelectronics and semiconductor industry. One of such devices is mini-spectrophotometer-monitor calibrator Eye-One Pro which is industrially manufactured by Swiss firm GretagMacbeth and serves as device for color control in printing industry as well as for automatic calibration of monitors, scanners and printers. From the view point of analytical chemistry it is important that this device can measure diffuse reflection coefficients in a range from 380 to 730 nm with a step of 10 nm as well as some colorimetric characteristics such as color coordinates in RGB, CMYK and Lab colorimetric systems. However, in spite of all the advantages of this device, the data on analytical applications of it are limited.

In this work, the estimation of possibility of Eye-One Pro application for determination of organic compounds using diazotized polyurethane foam is given. The way of synthesis of such a polymeric chromogenic reagent was developed by us previously.

1-Naphthylamine, estrone and 4-aminophenol were chosen as analytes. They react with diazotized polyurethane foam with formation of intensely colored polymeric azo-dyes (460, 440 and 640 nm respectively). These substances were chosen because, on the one hand, development of approaches to their determination is essential, on the other hand, maxima of their analytical responses appear in different parts of spectrum and absorbance bands overlap almost the whole visible range. A comparison of the diffuse reflectance spectra recorded with Eye-One Pro and colorimeter "Spectroton" as well as Lab colorimetric coordinates has been made, and the dependence of shape and height of the absorbance band on the substance concentration in water solution has been investigated. It has been shown that using mini-spectrophotometer Eye-One Pro one can measure the signals of small (a few millimeters) samples that allow reaching an essential decrease in detection limit. The estimation of reproducibility for Eye-One Pro has been made. In the most cases relative standard deviations were less then 0.01. The approach used was shown to be prospective for the determination of aromatic amino- and hydroxycompounds in waters.

P145- APPLICATION OF DIFFUSIVE GRADIENT IN THIN FILMS TECHNIQUE WITH DIFFERENT SPECIFIC RESINS IN CONTAMINATED AND UNCONTAMINATED RIVER SEDIMENTS AND ITS COMPARATION WITH OTHER COMMON TECHNIQUES

P. Diviš[1], H. Dočekalová[2], M. Kadlecová[1,3], B. Ouddane[3] , R. Szkandera[1] and J. Trávníčková[1]

[1] Brno University of Technology, Faculty of Chemistry, Purkyňova 118, Brno, 612 00 (Czech Republic)
[2] Mendel University in Brno, Zemědělská 1/1665, 613 00 Brno (Czech Republic)
[3] Laboratoire Géosystèmes, FRE 3298 CNRS, Université Lille 1 – Sciences et Technologies,
59655 Villeneuve d´Ascq (France)

The aim of this work was application of diffusive gradient in thin film (DGT) technique with selective resin gels for measurements of bioavailable mercury rate in river sediments taken from contaminated and uncontaminated area. In previous work [1] two resin gels containing thiol groups – SpheronThiol and Duolite, incorporated in the polyacrylamide resin gel were studied and compared in our laboratory. Now we present the results from field study in river ecosystems.
Concentrations of mercury measured by DGT in sediment cores taken from aquatic systems in France were compared with results obtained by other common techniques. Mercury species have been quantified for each sliced and dried part of sediment sample. For the total mercury analysis an advanced mercury analyser instrument (AMA 254) was used. Subsequent analysis of pore water and surface water was carried out. All results obtained by DGT and by common techniques from analysis of sediments, pore water and surface water are discussed.

[1] Diviš P., Szkandera R., Brulík L., Dočekalová H., Matúš P., Bujdoš M..: Application of new resin gels for determination of mercury by diffusive gradients in thin films technique, ANAL SCI 25, 575-578 (2009).

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P146- POLYCHLORINATED BIPHENYLES UPTAKE BY CARROTS AFTER SLUDGE COMPOSTS APPLICATION: WASTE-CASE AND OPERATIONAL PRACTICE IN GREENHOUSE CONDITIONS

C. Sablayrolles[1,2], C. Vialle[1,2], J. Silvestre[3], M. Treilhou[4], C. Lhoutellier[5],
V. Brochier[5], M. Montréjaud-Vignoles[1,2]

[1]Université de Toulouse; INP; LCA- Laboratoire de Chimie Agro-Industrielle; ENSIACET,
4 Allées Emile Monso, F-31029 Toulouse (France)
[2]INRA; LCA - Laboratoire de Chimie Agro-Industrielle; F-31029 Toulouse
[3]Laboratoire d'Ecologie Fonctionnelle, ENSAT, Avenue de l'Agrobiopole - BP 32607 Auzeville tolosane -
31326 Castanet-Tolosan (France)
[4]Centre Universitaire Jean-François Champollion, Laboratoire de Chimie et Biochimie des Interactions,
Place de Verdun, 81012 Albi cedex 9 (France)
[5]Veolia Environnement R&I, 291 av Dreyfous Ducas, F-78520 Limay (France)

Polychlorinated biphenyls (PCBs) are classified as priority pollutants by American and European environmental agencies [1]. The major problem with PCBs is their potential for transmission within the food chain [2]. In France, sewage sludge composts which answer to the norm NFU 44-095 are applied on arable crops and can be applied on market gardening. Accordingly, the objective of this study is to investigate potential PCBs transfer from sand/soil amended with sewage sludge composts into edible crop under real operational practice.

The experiment was conducted on carrot (*Daucus carota*) Amsterdam *A.B.K.* Bejo variety. The culture was carried out in a temperature and humidity regulated greenhouse. First, carrot plants were grown on sand + PCBs pure substances in order to study transfer pathways. Secondly, carrot plants were grown on sand and sandy soil amended with sewage sludge compost under operational practice.

Seven PCB isomers (IUPAC codes: 28, 52, 101, 118, 138, 153 and 180) were determined in soil, compost and carrots samples. 2g freeze-dried sample were taken for a solid-liquid extraction with 100 mL of *n*-hexane for 3 hours. All extracts are concentrated to a volume of 1 mL under nitrogen steam. Clean up is done by 1g Florisil Solid Phase Extraction cartridges and rinsed with 10 mL of *n*-hexane. PCBs were analyzed by high resolution gas chromatography coupled with low resolution mass spectrometry (HRGC-LRMS) on electron impact mode. Quantification with an internal standard is performed in Multiple Ion Monitoring mode.

PCBs uptake was followed into carrots core, peel and leaves. Two pathways by which PCBs can enter the carrot plants were identified: (1) uptake and transport in oil channels (2) foliar uptake of vapor from surrounding air. No PCBs uptake was observed from the real operational practice experiment. Indeed, PCBs levels in carrots were lower than the limit of quantification in all cases.

[1] United Nations Environment Program, Stockholm Convention on Persistent Organic Pollutants, 2001.
[2] Borja, J.; Taleon, D.M.; Auresenia, J.; Gallardo, S. Review on polychlorinated biphenyls and their biodegradation. Process Biochemistry. 2005, 40, 1999-2013.

P147- MEASUREMENTS OF GLOBAL UV IRRADIANCE, BY A VERY STABLE HOME MADE NARROW BAND FILTER RADIOMETER

S. Scaglione, I. Di Sarcina, D. Flori, F. Menchini

ENEA, Optical Coating Group,
CR Casaccia, Via Anguillarese 301, 00123 Rome (Italy)

The amount of the UV radiation reaches the heart surface is strictly correlated to the atmosphere conditions as the presence of clouds, aerosol and the ozone columnar content. The measurement of the spectral UV irradiance is very useful to monitor its effect on the human health and the environment. It's well known that the high dose UV radiation is responsible for the skin erythematic disease, melanoma and eye damage. Long period monitoring is necessary to monitor the effective dose of UV radiation as well as the daily variation of the UV irradiance. The high frequency measurements (about 1 min), the long time stability and the wavelength resolution are the main requirements for the UV radiometer devoted to UV measurements. Two different classes of UV radiometer are generally employed for UV measurements: spectroradiometer and filter radiometers.

The spectroradiometers have a spectral resolution of 0.5 nm but frequent calibration are necessary and a spectrum each 20 min is acquired. The filter radiometers in the market, measure the solar radiation in several channels (typically 4 to 7) with a bandwith from 2 to 10 nm. They require less maintenance than the spectroradiometer and they are able to work in hostile environment as for instance in the polar regions. Other than the robustness of this instrument, the main advantage of the filter radiometers is the high frequency with which all wavelengths can be measured, making this class of instrument well suited for investigating short term irradiance variation.

In this work is presented the UV irradiance measurements performed by a very narrow band filter (FWHM less than 1 nm) radiometer at the Antarctica Italia Base, Mario Zucchelli Station (MZS), Terranova Bay, lat. 74° 41.6084' south and lon. 164° 05.9224' est. All-dielectric Fabry-Perot filters were manufactured in the laboratories of the Optical Coating Group, ENEA, by the ion beam assistance physical vapor deposition technique. Nine filters select nine different wavelengths in the UV spectral range from 296.5 nm to 377 nm with $\approx$ 1 minute of measurement period, i.e. each wavelength is measured about 1250 times per day.

At the moment the radiometer are permanently located near MZS and the data are daily downloaded in ENEA, Rome, by a dedicated satellite channel.

NOTES

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