

DIVISION OF ENVIRONMENTAL CHEMISTRY

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MONDAY AFTERNOON

Advances in Analytical Chemistry for Environmental Applications

D. A. Alvarez, *Organizer*

B. G. Loganathan, *Presiding*

T. Jones-Lepp, *Organizer, Presiding*

1:30 — Introductory Remarks.

1:35 —29. Simple scheme for broad-spectrum molecular characterization of dissolved organic contaminants in wastewaters and ambient waters. **M. Ahel**, S. Terzic, I. Mikac, I. Senta

1:55 —30. Determination of polybrominated biphenyl in the environment by fluorescent quantitative immune-PCR. **H. Zhuang**, H. Chen

2:15 —31. Determination of cyanobacterial cyclic peptide hepatotoxins in drinking water using capillary electrophoresis. **S. F. Y. Li**

2:35 —32. Fabrication of novel Cu/TiO₂-based imprinted polymers for detection of phosphine. **S -M. Chang**, **Y -Y. Hsu**, S -I. Yen, S -N. Li

2:55 — Intermission.

3:15 —33. Nuclear magnetic resonance spectroscopy studies of the binding of Prussian blue to cesium in the presence of decontamination agent. **W. Kuang**, G. Facey, C. Detellier, K. Li, K. Volchek

3:35 —34. Effect of temperature on pressurized fluid extraction of PAHs in particulate matter. **E. A. McGaw**, M. M. Schantz

3:55 —35. Interlaboratory comparison study of the measurement of polychlorinated biphenyl (PCB) congeners from sediment samples with high resolution (HRMS) and low resolution mass spectrometry (LRMS). A. Wroble, J. Pietari, J. O'Keefe, P. P. Hamlett, G. Santacroce, T. Oliveira, S. Wilding, D. Revell, **W. Whipple**

4:15 — Concluding Remarks

ABSTRACTS

ENVR 29

Simple scheme for broad-spectrum molecular characterization of dissolved organic contaminants in wastewaters and ambient waters

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A scheme for a broad-spectrum molecular characterization of dissolved organic contaminants in wastewaters and ambient waters has been developed. The extracts were prepared by a large-volume extraction of filtered water samples using Oasis HLB cartridges, covering both hydrophobic and hydrophilic organic contaminants. Before the analysis using mass spectrometric techniques, including gas chromatography/mass spectrometry (GC/MS) and liquid chromatography/quadrupole time-of-flight mass spectrometry (LC-QToF), the extracts were fractionated into three distinct fractions on a partially deactivated silica gel column, involving sequential elution with hexane, dichloromethane and methanol as eluting solvents. The first two fractions, containing nonpolar and medium polar contaminants, respectively, were characterized by electron impact GC/MS, while LC-QToF was applied for the analysis of the polar contaminants, contained in dichloromethane and methanol fractions. The developed analytical scheme was applied for the molecular characterization of contaminants in wastewaters and river water collected in the area of the city of Zagreb, Croatia.

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Determination of polybrominated biphenyl in the environment by fluorescent quantitative immune-PCR

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A novel fluorescent quantitative-IPCR assay was developed to determine the polybrominated biphenyl (PBB) congener PBB15 in the environment. 4-(4,4-bibromine diphenyl) butanoic acid, 4-oxo-(PBBA), was synthesized using the F-C reaction as a hapten. The artificial antigen was synthesized using the active ester method (AEM) by coupling PBBA to bovine serum albumin (BSA), and the coating antigen was formed by coupling PBBA to ovalbumin (OVA) using the mixed anhydride reaction (MAR). Male New Zealand white rabbits were immunized with artificial antigen to obtain polyclonal

antibodies (pAbs), with which, the novel fluorescent quantitative-IPCR assay for the determination of PBB15 was established, and the linear range for the determination of PBB15 is 10.0 fg mL^{-1} to 1 ng/mL^{-1} with a correlation coefficient of 0.98 and a detection limit of 10.0 fg mL^{-1} . Analyses of various environmental soil samples gave satisfactory results, which predicated that the SYBR Green \pm fluorescent quantitative IPCR assay established in this study was accurate and suitable for analyzing PBBs in the environment. Keywords: Polybrominated biphenyls, hapten, polyclonal antibody, real-time immuno-PCR. We acknowledge the financial support by the National Natural Science Foundation of China (project no. 20 677 008), the Research Fund for the Doctoral Program of Higher Education (project no. 20 060 255 004) and Shanghai Leading Academic Discipline Project (project no. B604).

ENVR 31

Determination of cyanobacterial cyclic peptide hepatotoxins in drinking water using capillary electrophoresis

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Four cyanobacteria hepatotoxins: microcystin LR, microcystin RR, microcystin YR and nodularin were simultaneously determined in drinking water using capillary zone electrophoresis (CZE) and micellar electrokinetic capillary chromatography (MEKC) coupled with UV detection. The toxins separated clearly in the CZE and MEKC modes using formic acid as a background electrolyte (BGE). Detection limits were in the range of $0.77\text{-}4.77 \text{ }\mu\text{g/mL}$, with R^2 values of $0.995\text{-}0.999$ in the CZE and MEKC modes. The linearity range tested for the standards was $5\text{-}100 \text{ }\mu\text{g/mL}$ and RSD percentage were in the range of $0.4\text{-}1.5\%$ for retention time and $2.3\text{-}8.8\%$ for peak area. When a known amount of standard was spiked into a known volume of water and extracted, recoveries were 90.3% (RR), 101.5% (nodularin), 90.6% (YR) and 88.2% (LR). The use of solid phase extraction (SPE) enabled cleanup and pre-concentration of a real sample to achieve a 100 fold concentration factor. Detection limits after SPE of the real sample spiked with microcystins were $0.090 \text{ }\mu\text{g/L}$ (RR), $0.076 \text{ }\mu\text{g/L}$ (YR), $0.110 \text{ }\mu\text{g/L}$ (LR), with RSD percentage values of $9.9\text{-}11.7\%$ for area and $2.2\text{-}3.3\%$ for retention time.

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Fabrication of novel Cu/TiO₂-based imprinted polymers for detection of phosphine

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In this study, we successfully prepared a novel Cu/TiO₂-based molecular imprinted polymer (MIP) for detection of PH₃ through a sol-gel manner. TiO₂ and phosphate ions were used as the cross linker and templates for the MIP, respectively. The recognition of PH₃ by the MIP involves mainly with the transformation of the target compound to H₃PO₄ followed by capture of the derivative product in the preformed cavities in terms of hydrogen bonding and shape selectivity. Copper ions (Cu²⁺) act as the active sites for the transformation. Dissociative chemisorption of PH₃ on the Cu²⁺ centers accompanied with dehydration and dehydrogenation resulted in Cu-P=O species. Meanwhile, the dehydration turned the color of the Cu/TiO₂ from blue to black because of the conversion of Cu(OH)₂ to CuO. After stopping the adsorption of PH₃, rehydration then converted the Cu-P=O species to H₃PO₄. The XPS results show that the binding energy of the P 2p state was 131.98 eV in the as-adsorbed MIP, and it shifted to 133.1 eV after exposure of the MIP to ambient air. Moreover, the FTIR spectra display the intensive peak of PO₄³⁻ stretching at 1018 cm⁻¹ in the post-air-exposed sample. These results proved the chemisorption and transformation of PH₃ in the MIP. The capacity of the imprinted sample for PH₃ was 20.32 µg/g, which was 15-fold higher than that of non-imprinted materials (1.39 µg/g). The high capacity reveals that the Cu/TiO₂-based MIP is the promising material for adsorption and monitoring of trace PH₃.

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Nuclear magnetic resonance spectroscopy studies of the binding of Prussian blue to cesium in the presence of decontamination agent

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Prussian blue has been widely used for the decontamination of radioactive cesium. In this work, the binding of Prussian blue to cesium ion is studied by NMR spectroscopy. The ¹³³Cs NMR spectrum shows that one main cesium peak appears and shifts from high field region to low field region when the ratio of Prussian blue to cesium increases from 1:5 to 3:1. In contrast, the peak of Cs⁺ is almost identical in ion chromatography for cesium and cesium with Prussian blue samples. In the presence of both Prussian blue and decontamination agent, only one main cesium peak appears and still shifts to low field region, although decontamination agent contains high percentage of inorganic and organic chemicals. The effect of the concentration of cesium ion, the ratio of Prussian

blue to cesium ion, and the amount of decontamination agent on the binding of Prussian blue to cesium ion are investigated.

ENVR 34

Effect of temperature on pressurized fluid extraction of PAHs in particulate matter

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Polycyclic aromatic hydrocarbons (PAHs) are semivolatile organic pollutants. These contaminants are carcinogenic and are found in airborne particulate matter, particularly in urban or industrial areas. PAHs must be extracted from the particulates prior to analytical analysis. It is widely believed that pressurized fluid extraction (PFE) gives overall recoveries equal to or greater than the more traditional Soxhlet extraction technique. It has also been noted that using high temperatures (>100°C) in PFE can yield more extracted PAHs as compared to Soxhlet. The increase in efficiency of extraction varies with the chemical structure and molecular weight of the PAH. This study was intended to look at the effect of temperature on the extraction of a broad range of PAHs (MW 128-302) from particulate matter. Two types of Standard Reference Materials, urban dust and diesel particulates, were used and extracted at temperatures of 100, 150, and 200°C.

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Interlaboratory comparison study of the measurement of polychlorinated biphenyl (PCB) congeners from sediment samples with high resolution (HRMS) and low resolution mass spectrometry (LRMS)

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An interlaboratory study was performed to evaluate the comparability of multiple determinative methods on a set of extracts from sediment samples contaminated with polychlorinated biphenyls (PCBs). Three extracts containing varying PCB levels (± 10 , 1, and <0.02 $\mu\text{g/g}$) and quality control samples were distributed to several laboratories for clean-up and analysis of 28 PCB congeners by gas chromatography combined with high or low resolution mass spectrometric detection (HRMS or LRMS). Analysis of individual PCB congeners was chosen because of the extreme complexity of analyzing the possible 209 congeners and the necessity for a less expensive and comprehensive PCB determination. Overall, comparable performance was observed for HRMS and LRMS analyses of PCB congeners present above 0.5 $\mu\text{g/kg}$ in the quality control samples with most interlaboratory congener-specific relative standard deviations less than 25%. Relatively consistent reporting was also observed for congeners present above 2.5 $\mu\text{g/kg}$ in the PCB contaminated sediments with 58% interlaboratory precision. These results suggest the validity of a performance based measurement (PBM) approach for the determination of PCB congeners in medium to high level PCB contaminated samples. Below sample-specific thresholds, HRMS instrumentation may be necessary to detect lower concentrated congeners, although poor interlaboratory agreement was observed at this level.