

DIVISION OF ENVIRONMENTAL CHEMISTRY

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SUNDAY AFTERNOON

Advances in Analytical Chemistry for Environmental Applications

T. Jones-Lepp and D. A. Alvarez, *Organizers*

C. E. Rostad and M. M. Schultz, *Presiding*

1:30 — Introductory Remarks.

1:35 —8. Polar organic compounds in surface waters collected near lead-zinc mine and milling operations. **C. E. Rostad**, C. J. Schmitt, J. G. Schumacher

1:55 —9. Capillary liquid chromatography coupled to ESI-MS/MS for analysis of environmental estrogens in the environment. **J. Tso**, D. S. Aga

2:15 —10. Use of stir bar sorptive extraction-liquid desorption for determination of triclocarban and other PPCPs in wastewater. D. R. Klein, D. F. Flannelly, **M. M. Schultz**

2:35 — Intermission.

2:55 —11. Determination of bisphenol-A in water samples using enzyme-linked immunosorbent assay. S. Vemu, **B. G. Loganathan**

3:15 —12. Molecular imprinting xerogels for tetracyclines. **E. R. E. Mojica**, J. Autschbach, F. V. Bright, D. S. Aga

3:35 —13. Comparison of automated and manual methods for solid phase extraction of endocrine disrupting chemicals. **K. E. Studer**, D. A. Reckhow

3:55 —14. Advances in the analysis of halogenated flame retardants in environmental matrices. L. Shen, S. Zhou, N. Riddell, P. Crozier, F. Dorman, T. Kolic, K. MacPherson, I. Brindle, C. Marvin, **P. Helm**, E. Reiner

ABSTRACTS

ENVR 8

Polar organic compounds in surface waters collected near lead-zinc mine and milling operations

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Surface-water samples were collected in the vicinity of a lead-zinc mine and mill to determine if polar organic compounds could account for negative impacts to downstream biota. Polar organic compounds were isolated by three types of solid phase extraction followed by positive and negative electrospray ionization/mass spectrometry. Because large amounts of xanthates are used in the milling process, techniques were developed to extract and analyze for sodium isopropyl xanthate and sodium ethyl xanthate. Although these xanthates were not found, trace amounts of the degradates isopropyl xanthyl thiosulfonate and isopropyl xanthyl sulfonate were found in most locations sampled, including the tailings pond downstream. However, dioctyl sulfosuccinate, a process filtering aid, was found at concentrations estimated at 350 micrograms per liter; its degradation product, octyl sulfosuccinate, was also found. Release of these organic compounds downstream from lead-zinc milling areas has not previously been reported.

ENVR 9

Capillary liquid chromatography coupled to ESI-MS/MS for analysis of environmental estrogens in the environment

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Detection of endocrine disrupting compounds have been commonly reported in the environment. Estrogens have always been identified as one of the most serious endocrine disrupting compounds found. Many major hurdles still exist in the analysis of estrogens in the environment which include high detection limits and matrix effects. A capillary liquid chromatography analytical method was developed to separate free and conjugated estrogens simultaneously. At lower flow rates it has been observed that free estrogens improve their ability to be ionized into the gas phase by at least 10 fold. Soil

and aqueous sample preparation was performed prior to sample injections by accelerated solvent extractions and/or dual cartridge solid phase extractions. Initial results showed improved detection limits and a potential to reduce matrix effects when performed at lower flow rates. This method has been applied to water and soil agricultural samples.

ENVR 10

Use of stir bar sorptive extraction-liquid desorption for determination of triclocarban and other PPCPs in wastewater

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Triclocarban (TCC) is an antimicrobial and antibacterial agent found in personal care products and is a prevalent wastewater contaminant. A quantitative method was developed for the analysis of TCC in wastewater using stir bar sorptive extraction and liquid desorption (SBSE-LD) followed by liquid chromatography tandem mass spectrometry. SBSE-LD is a relatively new extraction technique in which analytes are extracted onto a coated magnetic stir bar and recovered by liquid desorption directly in the LC vial. The conditions and parameters for the SBSE-LD using the polydimethylsiloxane coated stir bar were optimized and included selecting the desorption solvent and extraction time. Recoveries were on the order of 80%. The validated method was applied to a set of municipal wastewater samples, and the TCC concentrations observed were in the high parts-per-trillion range. Work is underway to expand the SBSE-LD method to additional pharmaceuticals and personal care products such as antidepressant pharmaceuticals.

ENVR 11

Determination of bisphenol-A in water samples using enzyme-linked immunosorbent assay

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Bisphenol A (2,2-bis(hydroxyphenyl)propane (BPA) in wastewater, river and lake water samples were analyzed using enzyme-linked immunosorbent assay (ELISA) method. Using this analytical procedure, BPA is detectable at low parts per billion levels in water samples. Among the samples analyzed, wastewater treatment plant (WWTP) influent had highest concentration of BPA (Range: 134-153 ng/L; Mean: 140 ng/L), followed by effluent (Range: 105-142 ng/L; Mean: 126 ng/L). Upstream Bee Creek contained lower

concentration than downstream, indicating input of BPA from WWTP to the Bee Creek. Clark River (Mean: 116 ng/L) and Kentucky Lake (Mean: 133 ng/L) had comparable concentrations to that of Bee Creek or WWTP samples. ELISA screening method allows rapid quantitation of BPA in a large number of samples in relatively short period of time.

ENVR 12

Molecular imprinting xerogels for tetracyclines

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Tetracycline (TC) antibiotics are intensively used in therapy and prophylactic control of bacterial infections in human and veterinary medicine and as food additives for growth promotion in the farming industry. The prevalent use and the inability of animals to metabolize these antibiotics result in TC and its degradation products arising in the environment. For the trace analysis of TC in complex matrices, sample preparation plays an important role and the protocol typically involves analyte extraction, clean-up, and enrichment to match the sensitivity of the analytical instrument. Silica-based molecular imprinted xerogels represent promising materials for developing TC-selective sorbents. This presentation will focus on the preparation of TC-imprinted xerogels and their performance as sorbents for selective binding with TC and TC-analogs. This presentation will also evaluate computational methods to provide theoretical underpinnings for the performance of the xerogel-based materials.

ENVR 13

Comparison of automated and manual methods for solid phase extraction of endocrine disrupting chemicals

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Endocrine disrupting chemicals (EDCs) are part of an emerging group of contaminants. This research focuses on a selected group of EDCs due to their endocrine-disrupting potential and their presence in natural water supplies. The set of compounds includes diethylstilbestrol, estriol, estradiol, 17 β -ethynylestradiol, and estrone. The purpose of this research is to compare one of the accepted manual solid phase extraction (SPE) methods with an innovative approach using an automated SPE/LC/MS (Waters

AquaAnalysis System) for trace analysis of EDCs. Since the EPA Method 1694 is the most widely used procedure, the EPA manual method was compared to the automated method for the AquaAnalysis. Results show a decrease in error when using the automated version because of the elimination of sample transfers and possible contaminants entering throughout the extraction steps. A significant decrease in cost was noted due to the decrease in labor hours and in the cost of consumables.

ENVR 14

Advances in the analysis of halogenated flame retardants in environmental matrices

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Brominated and chlorinated flame retardants remain the focus of environmental research and monitoring. Results of ongoing method development studies and environmental screening of sediment, biota, and biosolids are reported for a suite of brominated and chlorinated flame retardants which remain in use and/or are alternatives to the polybrominated diphenylethers (PBDEs). These include hexabromocyclododecane (HBCD), allyl 2,4,6-tribromophenyl ether (ATE), 2-bromoallyl 2,4,6-tribromophenyl ether (BATE), 2,3-dibromopropyl 2,4,6-tribromophenyl ether (DPTE), octabromotrimethylphenylindane (OBIND), pentabromoethylbenzene (PBEB), hexabromobenzene (HBB), 1,2-bis (2,4,6-tribromophenoxy) ethane (BTBPE), decabromodiphenylethane (DBDPE), Dechlorane Plus (DP), hexachlorocyclopentadienyl-dibromocyclooctane (HCDBCO), tetrabromocyclohexane (TBECH), 1,2,5,6-tetrabromocyclooctane (TBCO), 2-ethylhexyl-2,3,4,5-tetrabromobenzoate (EHTeBB), and bis(2-ethyl-1-hexyl)tetrabromophthalate (BEHTBP). Approaches include both gas chromatography coupled with high resolution mass spectrometric (GC-HRMS) detection and liquid chromatography-tandem mass spectrometry (LC-MS/MS). Optimized instrument conditions, limits of detection, and results of screenings of environmental matrices are included.