

DIVISION OF ENVIRONMENTAL CHEMISTRY

238th ACS National Meeting

Washington, D.C.

August 16-20, 2009

MONDAY MORNING

Advances in Analytical Chemistry for Environmental Applications

T. Jones-Lepp, *Organizer*

D. D. Dionysiou, *Presiding*

D. A. Alvarez, *Organizer, Presiding*

8:30 — Introductory Remarks.

8:40 —15. Characterization of nanoparticle size and concentration for ecotoxicological studies. **D. Griffiths**, P. Hole, R. Carr, J. Smith, A. Malloy

9:00 —16. Gold nanoparticle based colorimetric assay for the detection of TNT. **S. Dasary**, D. Senapati, A. Singh, P. C. Ray, H. Yu, Y. Anjaneyulu, R. Venkatraman

9:20 —17. Carbon nanotubes as sorbents for micro-concentration devices. C. M. Hussain, **C. Saridara**, S. Mitra

9:40 —18. Source characterization for emission inventories: HRTEM and XPS analyses. **R. Vander Wal**, V. M. Bryg, M. D. Hays

10:00 — Intermission.

10:20 —19. Molecular composition of dissolved pyrogenic carbon using ultra-high resolution Fourier-transform ion cyclotron resonance mass spectrometry and its relationship to bioavailability. **D. C. Podgorski**, A. Mukherjee, A. R. Zimmerman, W. T. Cooper

10:40 —20. Fast evaluation of arsenic sorption dynamics on iron-based sorbents by continuous flow hydride generation atomic fluorescence spectrometry (CFHG-AFS). **A. Hussam**, S. Ahamed

11:00 —21. Monitoring of arsenic and bacteriological contamination in drinking water of Mardan, Pakistan. **I. Ullah**, A. Khan, M. Ahmad, A. R. Khan, Q. Mahmood, I. Hussain Balouch, R. Farooq, J. Khan, M. Haseeb, M. Amjad Sabir, N. Ghani

11:20 —22. Analysis of iron(II) and iron(III) polyaminocarboxylate complex speciation using capillary electrophoresis. J. M. Wilson, **R. F. Carbonaro**

ABSTRACTS

ENVR 15

Characterization of nanoparticle size and concentration for ecotoxicological studies

Duncan Griffiths¹, *Duncan.griffiths@nanosight.com*, **Patrick Hole**², **Robert Carr**², **Jonathan Smith**², and **Andrew Malloy**². (1) NanoSight USA, 3027 Madeira Ave., Costa Mesa, CA 92626, (2) NanoSight, LTD, London Road, Amesbury, Wiltshire SP4 7RT, United Kingdom

Assessing the complete distribution of nanoparticle sizes within a suspension is notoriously difficult to carry out. This is especially the case for engineered nanoparticles in the environment which are frequently polydispersed. Accurate determination of the range of sizes is critical to properly understanding transport phenomena and fate of nanoparticles. Here we demonstrate the nanoparticle tracking analysis (NTA) technique that sizes nanoparticles in suspension, based on their Brownian motion. Unlike classical light scattering techniques, NTA allows nanoparticles to be sized on a particle-by-particle basis and also yielding a count/concentration measurement. Additionally, analysis of scattering intensity allows sub-populations of nanoparticles with varying characteristics to be resolved in a complex mixture. This technique has found significant use in the field of nano- and eco-toxicology, and results from several research groups will be shown that demonstrate the use of the technique to assess a range of engineered nanoparticles including gold, SiO₂, TiO₂ and polystyrene.

ENVR 16

Gold nanoparticle based colorimetric assay for the detection of TNT

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Trinitrotoluene (TNT) is a highly explosive compound. Due to its common use by militaries and industries, TNT can be found in landmines, contaminated water, and waste sites. Ever-increasing needs for a green environment makes it necessary to have a simple and reliable TNT detection assay for both humanitarian and security reasons. Such a sensor needs to be inexpensive, portable and reliable, absent of false positives. Current analytical techniques such as gas and liquid chromatography are very sensitive and reliable, but cannot be carried out in the field. The benefits of nanotechnology make

it ideal for sensor development and environmental/biological monitoring. Finally, their large surface areas are platforms for engineering multifunctional systems. Driven by the need, we discuss the development of a sensitive gold-nanoparticle (GNP) based colorimetric assay for the detection of TNT from water samples. Our experiment shows that cystine modified gold nanoparticle can detect TNT selectively (over DNT, NT, etc.) with high sensitivity (ppt level).

ENVR 17

Carbon nanotubes as sorbents for micro-concentration devices

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The application of carbon nanotubes as unique sorbents for the fabrication of micro-concentration devices is presented. The microtrap application requires high adsorption capacity as well as easy desorbability; the latter being critical for injection module in an integrated device. The micro-sorbent characteristics of single and multiwalled carbon nanotubes for gas-phase adsorption/desorption of several organic compounds has been studied. The nonporous nature of carbon nanotubes (CNTs) eliminates the mass transfer resistance related to diffusion into pore structures, thus allowing easy desorbability. At the same time, their high aspects ratios lead to large breakthrough volumes. As compared to a commercial sorbent Carbopack™, the breakthrough volume was as an order of magnitude higher in the CNTs, while the rate of desorption measured as the peak width at half height of the desorption band was eight times lower. We also found that the presence of disordered carbon impurities, which could be removed by controlled oxidative annealing, could greatly degrade the performance of CNTs. The CNT-based sorbents clearly offer a better alternative to conventional sorbent in monitoring device. References: 1. Preconcentration of volatile organics on self-assembled, carbon nanotubes in a microtrap (C. Saridara, R. Brukh, Z. Iqbal, and S. Mitra *Anal. Chem.* 2005, **77(4)**, 1183-1187). 2. Microtrapping characteristics of single and multi-walled carbon nanotubes (C.M. Hussain, C. Saridara, and S. Mitra *J of Chromatography* 2008, **A1185**, 161-166). 3. Carbon nanotubes as sorbents for the gas-phase preconcentration of semivolatile organics in a microtrap. (C.M. Hussain, C. Saridara, and S. Mitra *Analyst*, 2008, **133**, 1076-1082).

ENVR 18

Source characterization for emission inventories: HRTEM and XPS analyses

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Combustion produced soot is a highly variable material. Physically the nanostructure can range from amorphous to graphitic to fullerenic. Chemically nearly any element could be included, though the surface functional groups are predominantly oxygen-based. Electron microscopic and spectroscopic methods have great potential for carbonaceous aerosol characterization. Results will be presented for analysis of HRTEM images of the physical nanostructure and XPS analysis of the chemical composition of soots collected from plant, institutional and residential scale oil-fired boilers, diesel engine, gas-turbine combustor (jet engines) and a wildfire. Physically soots from these emission source classes may be differentiated based on carbon lamella length, mean separation and tortuosity using HRTEM and image analyses algorithms. Chemically these soots may also be distinguished by elemental composition, surface (oxygen) functional groups and carbon bonding by XPS.

ENVR 19

Molecular composition of dissolved pyrogenic carbon using ultra-high resolution Fourier-transform ion cyclotron resonance mass spectrometry and its relationship to bioavailability

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Recent reports found black carbon (BC: products of incomplete combustion of organic matter) to make up a considerable fraction of organic carbon in soils and sediments. Although BC production is well-understood, little is known about its degradation in the environment. Leaching of organic compounds from BC is a degradation mechanism and dissolved compounds produced may fuel microbial metabolism in soils or sediments. The current study examines effects of combustion temperature, atmospheric conditions (oxic versus anoxic), and biomass type on the amount and chemical properties of

compounds leached from biochars determined by FT-ICR MS. Additionally, biotic and abiotic oxidation of these materials were monitored by CO₂ emission from sterilized and microbial inoculated incubations. Initial results show that biochar derived from grass and softwood versus hardwood biomass and low versus high temperature combustion produce leachates that are more aromatic in nature and, counterintuitively, less susceptible to oxidation.

ENVR 20

Fast evaluation of arsenic sorption dynamics on iron-based sorbents by continuous flow hydride generation atomic fluorescence spectrometry (CFHG-AFS)

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Recently, we have developed a continuous flow hydride generation atomic fluorescence spectrometry (CF-HGAFS) for rapid evaluation of sorption and flow dynamics of trace arsenic in iron-based sorbents. The apparatus and the flow manifold consist of a column (length 9.0 cm, dia 1.5 cm) packed with 1.0 g of the desired active material between two sand layers connected to a sampling valve and a flow system using a two-channel peristaltic pump. The column outlet is mixed with acid through one channel and fed into the HGAFS for trace analysis. While a conventional batch experiment can take days to complete the isotherm, the system developed in our lab can be used to generate a complete isotherm in less than 100 minutes using only 1.0 g of the active material. The estimated contact time with the active bed was 100 ms. It also takes much less reagent, and the entire experiment is done under computer control. The isotherm generated was then used to obtain solid/solution distribution coefficient, capacity of the sorbent, intra-particle diffusion coefficient and other parameters based on theoretical models. The instrumental setup could be used to study the sorption of species containing As, Sb, Hg, and Bi at sub µg/L with detection limit of ng/L on materials such as soil, concrete and any porous and semi-porous materials.

ENVR 21

Monitoring of arsenic and bacteriological contamination in drinking water of Mardan, Pakistan

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A total number of 276 potable water samples along the Kalpani tributary have been collected and analyzed for arsenic using Quick Arsenic Testing Field Kit and bacterial contamination using UNICEF Wegtech Kit. The data has revealed that the concentration of arsenic is lying in the range of 0-10 ppb. The data indicates that there is no serious threat posed to the population of Mardan as the arsenic concentration in all the water samples has not exceeded from the WHO standard of 10 ppb. Bacteriological study has shown very disappointing results. It was observed that 59% water sources were contaminated with *E. Coli* form bacteria. The presence of fecal coliforms serves as an indication of contamination by sewage. The information presented in this study is based on a large number of water samples which definitely provide a base-line data for future investigations.

Table. 1. Arsenic Contamination in drinking water of Study Area

S.No.	Union council	As<10ppb		As=10ppb		Total
		Ho. of Sample	%age	Ho. of Sample	%age	
1	Turo	28	84	6	16	35
2	Sikandary	12	60	8	40	20
3	Shamat pur	8	80	2	20	10
4	Hoti	20	77	6	23	26
5	Parhoti	19	95	1	5	20
6	Mayar	20	100	-	-	20
7	Mardan khas	28	96.5	2	3.5	30
8	Dagai	7	70	3	30	10
9	Gujar Garhi	30	100	-	-	30
10	Baghdada	35	100	-	-	35
11	Kas Kurona	20	100	-	-	20
12	Ghaladir	20	100	-	-	20
Sub Total		247	89.63	29	10.4	276

Graph. 1. Arsenic Contamination in drinking water of Tehsil Mardan

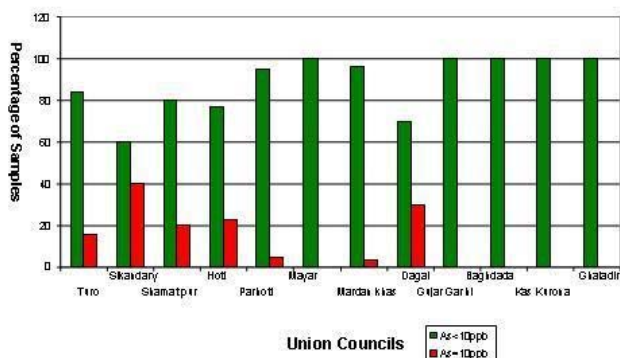
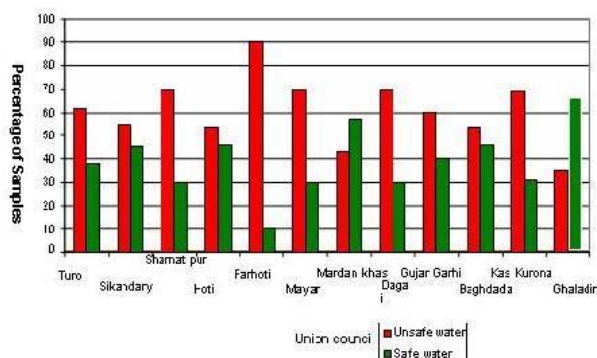


Table. 2. Village Wise Bacteriological Contamination in Tehsil Mardan

.No.	Union council	Villages	Unsafe		Safe		Total
			Ho. of samples	% age	Ho. of samples	%age	
Turo	Dafary		5	100	0	0	5
Turo	Gayum Abad		3	60	2	40	5
Turo	Rashid Abad		3	60	2	40	5
Turo	Banr baba		4	80	1	20	5
Turo	Sadiq Kheil		3	60	2	40	5
Turo	Nawan Kally		2	40	3	60	5
Turo	Zaid Kheil		2	40	3	60	5
Sub Total			21	61.8	13	38.2	34
Sikandary	Purdil/Abad		2	40	3	60	5
Sikandary	Noor Hassan Kheil		3	60	2	40	5
Sikandary	Sikandary Kurona		2	40	3	60	5
Sikandary	Bagh Kurona		4	80	1	20	5
Sub Total			11	55	9	45	20
Shamatpur	Savadyan		4	80	1	20	5
Shamatpur	Faqir Abad		3	60	2	40	5
Sub Total			7	70	3	30	10
Hoti	Jalawnd		2	40	3	60	5
Hoti	Khan Khoty		2	40	3	60	5
Hoti	Sher Abad		3	60	2	40	5
Hoti	Mohammad Kheil		3	60	2	40	5
Hoti	Mandomy		4	80	2	40	6
Sub Total			14	53.8	12	46.2	26
Par Hoti	Shago Daga		3	60	2	40	5
Par Hoti	Gadir Khan Kurona		5	100	0	0	5
Par Hoti	Khan Kchi		5	100	0	0	5
Par Hoti	Faram		5	100	0	0	5
Sub Total			18	90	2	10	20

Graph. 2. Bacterial Contamination in all the union councils



ENVR 22

Analysis of iron(II) and iron(III) polyaminocarboxylate complex speciation using capillary electrophoresis

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Capillary electrophoresis can be used to effectively speciate ferrous and ferric iron complexes with polyaminocarboxylate chelating agents. A 25 mM phosphate BGE and a 50 mM MOPS BGE, both buffered at pH 7.1, were each tested with Fe(II) and Fe(III) complexes with EDTA, HEDTA, EGTA, TMDTA, DTPA and CDTA. Adequate separation of all Fe(III)-chelating agent complexes was observed with the MOPS BGE. With the phosphate BGE, sharp peaks were observed for most of the Fe(III) complexes, however Fe(III)-EGTA showed excessive peak broadening, and Fe(III)-TMDTA showed no discernible peak. The effective electrophoretic mobilities of the complexes measured in the different BGEs were the same for Fe(III) complexes with DTPA and CDTA. However, mobilities of Fe(III)-EGTA, Fe(III)-EDTA, and Fe(III)-HEDTA were much larger when the phosphate BGE was employed, providing evidence for ternary complex formation with phosphate during electromigration. For Fe(II), complexes with TMDTA and EGTA were adequately separated with either BGE, but separations involving the other chelating agents resulted in their corresponding Fe(III) complexes due to rapid oxidation by molecular oxygen. Since the MOPS method is suitable for separating both Fe(II) and Fe(III) complexes with TMDTA and EGTA, reaction progress of this redox process can be easily monitored.