3. Methods for Sampling/Analysis of Mercury in Water and Solids

QUANTITATIVE ANALYSIS OF THE DETECTION LIMITS FOR HEAVY METAL-CONTAMINATED SOILS BY LASER-INDUCED BREAKDOWN SPECTROSCOPY
Alexander, Dennis R.; Dana E. Poulain, Nebraska Univ., Lincoln
NTIS: ADA328435. 34 pp, Jun 1997

Laser-induced breakdown spectroscopy (LIBS) is a rapid remote measurement method for detection of metals in the environment. A major factor in the quantitative use of this technique involves the minimum detection limits under both laboratory and field operations. Research on limits of detection of heavy metals in different types of soils under various conditions using LIBS has been carried out. Pulses from a Nd:YAG laser operating at 125 mJ at lambda = 1.06 micrometers are focused on sample surfaces to produce laser sparks (plasmas). Atomic emissions from the plasmas are recorded using an optical multichannel analyzer after delays of a few microseconds when interference from broad-band emissions is reduced. Research has been performed on the detection limits of arsenic, cadmium, chromium, mercury, lead, and zinc in soil matrices. Results are reported on the lower detection limits of these six elements in sand, silt, clay, and kaolin matrices. Detection limits are significantly lower for heavy metals in sand matrices than silt and clay matrices due to differences between surface and volume contamination.

DETECTION OF MERCURY COMPOUNDS USING INVERTASE-GLUCOSE OXIDASE-BASED BIOSENSOR
Amine, A. (Faculte des Sciences et Techniques); C. Cremisini (ENEA); G. Palleschi (Univ. di Napoli Federico II)
Environmental Monitoring and Hazardous Waste Site Remediation
Proceedings of SPIE, Vol 2504, p 209-220, 1995

Mercury compounds have been determined with an electrochemical biosensor based on invertase inhibition. When invertase is in the presence of mercury its activity decreases; this causes a decrease of glucose production which is monitored by the glucose sensor and correlated to the concentration of mercury in solution. Parameters as pH, enzyme concentration, substrate concentration, and reaction and incubation time were optimized. Mercury compounds determination using soluble or immobilized invertase were reported. Results show that the inhibition was competitive and reversible. Mercury compounds can be detected directly in aqueous solution in the range 2 - 10 ppb.

SPECTRAL CHARACTERISTICS OF 254-NM MERCURY LINE WITH CONSIDERATION FOR HYPERFINE STRUCTURE AS APPLIED TO QUANTITATIVE MERCURY ANALYSIS
Antipov, A.B. (Institute of Optical Monitoring); E.Y. Genina; V.A. Sapozhnikova
13th Symposium and School on High-Resolution Molecular Spectroscopy
Proceedings of SPIE, Vol 4063, p 185-188, 2000

The differential atomic absorption spectroscopy method is widely used both in scientific investigationsand analytical applications. Absorption coefficient (absorption cross section) is an individual characteristics of every element therefore it provides for a high selectivity of an analysis. Differential absorption technique allows one to increase the selectivity by means of background absorption correction. In the cases where we should analyze gas mixtures at different pressures, we should take into account an influence of pressure on absorption line contour of the component to be analyzed. In the paper we present an estimation of such an influence. As an example, we consider an influence of pressure of analyzed gas mixture on sensitivity of RGA-11 differential atomic absorption analyzer with Zeeman background correction. This analyzer had been developed at Institute of Optical Monitoring SB RAS. The authors of the report are well experienced in its exploitation under different conditions.

MERCURY ENVIRONMENT MONITORING

Antipov, A.B. (Institute of Design and Technology OPTIKA); E.Y. Genina; N.G. Melnikov; G.V. Kashkan
Environmental Monitoring and Hazardous Waste Site Remediation
Proceedings of SPIE, Vol 2504, p 448-452, 1995

We report a development of analytical techniques and a portable high selective analyzer for measuring mercury content in the atmosphere, water, soil and biological objects to use them in ecological monitoring and to control technological processes with mercury and the compounds thereof. Provision of mercury monitoring is made from background to maximum permissible concentration (MPC).

THE EFFICACY OF ULTRAFILTRATION TECHNIQUES FOR FRESH WATER PARTITIONING STUDIES OF TOTAL AND METHYLMERCURY

Babiarz, C.L.; M.M. Shafer; S.R. Hoffmann; J.P. Hurley; D.E. Armstrong; A.W. Andren
ACS National Meeting, San Francisco, April 13-17, 1997. Division of Geochemistry. Abstract No 229

NEW ABSORPTION-BASED OPTODE FOR THE DETECTION OF HG(II) IN WATER

Baldini, F. (Istituto di Ricerca sulle Onde Elettromagnetiche Nello Carrara); A. Falai; A. Flamini (Istituto di Chimica dei Materiali); A.A. Mencaglia (Prodotec srl)
Chemical, Biochemical, and Environmental Fiber Sensors X
Proc. SPIE Vol. 3540, p. 191-195, 1999

The current paper describes a novel absorption-based optode for mercury (II) detection. The dye 2-(5-amino-3,4-dicyano- 2H-pyrrol-2-ylidene)-1,1,2-tricyanoethanide (L') is a specific ligand for Hg2+ in water, undergoing a color change from violet to blue on the formation of the corresponding monochelated complex HgL. The dye L' was fixed on different supports by means of anionic exchange. Controlled pore glasses, cross-linked styrene and cellulose paper were used as supports and two different optode configurations were developed in order to couple them to the optical fibers. Photodegradation and leakage of the dye were thoroughly investigated by means of an accurate spectrophotometric analysis in the presence of mercury acetate [Hg(AcO)2] solutions. In order to reduce the photodegradation of the dye, an optoelectronic unit was developed using light-emitting diodes as sources and a suitable electronic circuit as the detecting system.

AUTOMATIC MONITORING OF HEAVY METALS IN WATERS

Beinrohr, Ernest, Department of Analytical Chemistry, Slovak Technical University, Bratislava, Slovakia, (beinrohr@chelin.chtf.stuba.sk)
International Conference on Heavy Metals in the Environment, 6-10 August 2000, Ann Arbor, MI
Elsevier Science Publishers, Oxford, UK

An automatic system for continuous monitoring of trace concentrations of heavy metals in water is presented and characterized. The computer controlled analyzer consists of a simple flow system with a robust coulometric cell enabling the measurement of various trace elements such as Ag, As, Bi, Cd, Cr, Cu, Fe, Hg, Mn, Pb, Sb, Se, Zn, as well as chlorides, bromides, iodides, phosphates, acids, bases and ammonia. The device was tested with the monitoring of Hg in industrial waste waters and Fe and Mn in mineral water. Metal concentrations down to the mg/L (ppb) level can be measured at measurement frequencies up to 10-40 in an hour. Papers/abstracts available at http://www.sph.umich.edu/eih/heavymetals/TechnicalProgram.html

SAMPLING DESIGN FOR CONTAMINANT DISTRIBUTION IN LAKE SEDIMENTS

Ben-Jemaa, F. (Univ. of Calif., Davis, CA); M.A. Mariño; H.A. Loaiciga (Univ. of Calif., Santa Barbara, CA)

Journal of Water Resources Planning and Management, Vol 121 No 1, p 71-79, Jan/Feb 1995

A sampling design methodology for monitoring contaminant distribution in lake sediments is presented in this paper. Two optimization approaches are employed: a minimization of the variance of estimation approach and a sampling cost minimization approach, allowing an economically efficient sampling design and a decision-making tool given the multi-objective nature of the problem. The geostatistical method of cokriging is used as a tool on which the proposed sampling design is based. The adopted technique incorporates spatial as well as intervariable correlations, to improve the prediction and estimation of sampled quantities. The methodology is applied to Clear Lake, California, to design a network for sampling mercury concentrations in lake sediments. The network design takes advantage of the cross correlation between the mercury concentrations and sediment grain size index. A sensitivity analysis is carried out to assess the sensitivity of the solution to the optimization model inputs.

ESTIMATION OF MERCURY-SULFIDE SPECIATION AND BIOAVAILABILITY IN SEDIMENT PORE WATERS USING OCTANOL-WATER PARTITIONING

Benoit, J.M. (Univ. of Maryland, benoit@acnatsci.org); R.M. Mason; C.C. Gilmour (The Academy of Natural Sciences)

Limnology and Oceanography: Navigating into the Next Century. The 1999 Aquatic Sciences Meeting of the Society of Limnology and Oceanography, 1-5 Feb 1999, Santa Fe, NM

An inverse relationship between pore-water sulfide concentration and bulk sediments methylmercury concentration has been observed in aquatic ecosystems. Furthermore, sulfide has been shown to have an inhibitory effect on Hg methylation by sulfate reducing bacteria. We hypothesize that uptake of inorganic Hg prior to methylation occurs via passive diffusion across the cell membrane, so the observed inhibition can be explained by a decrease in neutral dissolved Hg species with increasing sulfide. This hypothesis was tested by measuring changes in the octanol-water partitioning of inorganic mercury across a sulfide concentration gradient from 1 uM to 10 mM. Thermodynamic modeling indicated that the neutral dissolved HgS complex dominated at low sulfide but was replaced by charged disulfide species as sulfide concentration increased. The overall partitioning coefficient for Hg decreased in a manner that could be predicted based on the concentration of this complex. These
results are consistent with decreased bioavailability of Hg to methylating bacteria in sediments with sulfidic pore waters.

DETERMINATION OF TOTAL MERCURY IN COAL

Blanchard, L.J; J.D. Robertson

Preprints of Papers, American Chemical Society, Division of Fuel Chemistry, Vol 41 No 3, p 811-814, 31 Jan 1996

The determination of mercury in coal is of interest due to its extreme volatility during coal combustion and its potential to be toxic if released into the environment. However, the low concentration of mercury in coal, frequently at the low μg/g level, makes analysis extremely difficult. In addition, mercury's volatility makes sample cross-contamination more likely. Despite the emphasis placed on mercury analysis, the analytical method of choice to give accurate, reproducible results for coal samples remains debatable. This report describes the radiochemical neutron activation analysis method based on pyrolysis followed by double gold amalgamation. During pyrolysis, volatile elements such as mercury and selenium are liberated, and the mercury is preferentially collected by amalgamation with the gold.

RECENT ADVANCES IN METHODS FOR SAMPLING AND ANALYSIS FOR MERCURY

Bloom, Nicolas S., Frontier Geosciences, Inc., Seattle, WA (nicolasb@frontier.wa.com)
USGS Workshop on Mercury Cycling in the Environment, 7-9 July 1996, Golden, Colorado

The past year (1995-1996) has seen a slowing in the number of new developments in low level mercury speciation—an indication that the current technology is maturing. Several significant developments are discussed, however: Two methods for the determination of gaseous Hg(II) in air at ambient levels have been fully developed, and are currently being intercompared. These are the mist chamber scrubber and the ion exchange membrane techniques. Although these methods differ significantly in principle, integration time, and specific limitations, both have been showing similar results, indicating atmospheric Hg(II) levels of approximately 0.01 to 0.1 ng/m3. Another recent finding of importance is that the distillation procedure commonly used to extract MMHg from waters and sediments can create a positive MMHg artifact through the action of natural organic matter with inorganic Hg. The risk of error is greatest in samples with a very low natural MMHg/Total Hg fraction (< 0.1%>, such as Hg(II) contaminated waters and sediments. Another significant development is the availability of a growing choice in very sensitive automated mercury analyzers (both AFS and AAS based), which have estimated detection limits as low as 1-2 ng/L Hg. Although insufficient for low-level research, these instruments are proving popular for monitoring purposes, where the required MDL is typically 12 ng/L Hg. Finally, it is noted that with the partial support of the Florida DEP, a twice-yearly ambient level inter-laboratory intercomparison program for Hg and MMHg in water is now available through FGS.

EFFECTS OF COAL MINING ON MERCURY SPECIATION IN BLACK WARRIOR RIVER BASIN, ALABAMA

Buciak, M.A. (Univ. of Alabama); J.A. Bonzongo (Austin College); A.C. Green; W. Lyons (Univ. of Alabama)
Limnology and Oceanography: Navigating into the Next Century. The 1999 Aquatic Sciences Meeting of the Society of Limnology and Oceanography, 1-5 Feb 1999, Santa Fe, NM

The methylation of inorganic-Hg can be arbitrated to both abiotic and biotic processes, although sulfate-reducing bacteria (SRB) are shown to be the primary Hg-methylators in aquatic ecosystems. From previous investigations, it has been established that several physiochemical parameters affect Hg methylation in aquatic ecosystems. These include the influence of dissolved organic carbon (DOC), pH, and sulfate. To investigate the effects of varying sulfate concentrations on the production of methylmercury (MeHg), tributaries draining reclaimed coal mines in Tuscaloosa County, Alabama, were sampled. Water samples were analyzed for total Hg (THg) and MeHg, DOC, total suspended solids (TSS), and major ions. Particular emphasis was placed on determining the dissolved MeHg to dissolved THg ratio. Total Hg concentrations have been analyzed at near background levels ranging from 0.18 to 8.0 ng/L. It was hypothesized that the dissolved MeHg to dissolved THg ratios would be low at locations where sulfate concentrations were very low and Hg-methylation was limited. Conversely, dissolved MeHg to dissolved THg ratios were expected to be high at locations were sulfate concentrations were elevated. Preliminary results confirm our initial hypothesis in that while dissolved THg values are low, the dissolved MeHg concentrations are relatively high in tributaries with elevated sulfate levels.

MERCURY CONTAMINATED SITES: CHARACTERIZATION, RISK ASSESSMENT AND REMEDIATION

Ebinghaus, R.; W. Salomons; R.R Turner; L.D. de Lacerda; O. Vasiliev (eds.)
Springer, Berlin. 555 pp, 1998

This book presents an overview of the characterization, risk assessment and remediation of mercury-contaminated sites. Many industrial activities, including the mining of gold, silver, and mercury itself, have caused mercury contamination of terrestrial and aquatic systems. Unlike other metals, which are generally not very volatile, mercury from contaminated sites can have a significant impact on remote ecosystems via the atmospheric pathway. This book summarizes work from Europe, Russia, and the American continent. Review chapters are supplemented by detailed international case studies.

DETECTION OF TRACE LEVELS OF MERCURY IN AQUEOUS SYSTEMS VIA A FIBER OPTIC PROBE

Ewing, K.J. (Naval Research Lab.); G.M. Nau; J. Jaganathan; T.G. Bilodeau; I. Schneider; I.D. Aggarwal; G.E. Robitaille (U.S. Army Environmental Ctr.)
Chemical, Biochemical, and Environmental Fiber Sensors V
Proc. SPIE Vol. 2068, p. 286-295, 1994

Currently there is a great deal of interest in the development and use of fiber optic chemical sensors for characterization of contaminated waste sites. Development of remote, in-situ sensors for rapid determination of the presence, and concentration of hazardous materials will significantly reduce site remediation costs. The state-of-the-art technology for assessing site contamination is the cone penetrometer system. This system consists of a 2-1/2 ton truck, a hydraulic ram, and a steel tube. The steel tube, which is generally 1-3/4 inches OD and 1 inch ID, has a sharp tip on one end. To begin site characterization the penetrometer tube is placed into the hydraulic ram then the tube is pushed into the ground. Sensors are mounted in the penetrometer tube to measure contaminants in the surrounding soil and ground water. This system has several distinct advantages over conventional drilling techniques. Additionally, site characterization can be performed much quicker than standard drilling techniques. Fiber optic chemical sensors are readily applicable towards use in cone penetrometer systems since they are small in size and can report real time, in-situ results. Some fiber optic chemical sensors have been deployed and tested in the cone penetrometer system.

MICROFABRICATED VOLTAMMETRIC SENSORS FOR TRACE METAL ANALYSIS

Fiaccabrino, G.C. (Univ. de Neuchatel); P.D. van der Wal; N.F. de Rooij; M. Koudelka-Hep; M. Tercier (Univ. de Geneve); C. Belmont-Hebert; J. Buffle; F. Confalonieri (Idronaut Srl); G. Riccardi; F. Graziotin
Chemical Microsensors and Applications
Proceedings of SPIE, Vol 3539, p 157-160, 1998

In order to meet the stringent demands of natural and waste waters monitoring for artifact-free data, an increasing effort is directed towards developing on-line and in-situ measuring schemes. In this context, the development of microfabricated electrochemical detectors for stripping analysis of trace metals has attracted particular attention. In this paper we report on the fabrication and analytical performance of a microfabricated electrode for direct Square Wave Anodic Stripping Voltammetry analyses of trace metals in natural waters. It is based on a mercury-plated thin-film Ir microdisk array covered by a layer of an antifouling gel. To facilitate the control of the gel deposition and to improve its mechanical stability, a polymeric containment ring has been formed around the array. The sensor is then integrated within a complete Voltammetric In situ Profiling analytical system.

HEAVY METAL DETECTION COMBINING STRIPPING ELECTROCHEMISTRY AND PIEZOELECTRIC SENSOR TECHNOLOGY

French, L.A. (BIODE, Inc.); M.G. Schweyer; J.B. Foley; J.C. Andle; C. Watson (Univ. of Maine); M.R. Bruce; A.E. Bruce; J.F. Vetelino
Chemical Microsensors and Applications
Proc. SPIE Vol. 3539, p. 161-169, 1998

Mercury and other toxic, heavy metals must be detected at part per billion levels in drinking water and environmental monitoring applications. No portable technology is presently capable of providing the required sensitivity, simplicity or reliability. Piezoelectric sensor technology and electrochemical technology have both offered sound approaches to the detection of these pollutants. Both exhibit limitations which prevent their widespread acceptance in water quality assurance and in environmental remediation.

DEVELOPMENT OF A MERCURY VAPOUR AIR ANALYSER FOR MEASUREMENT OF HG IN SOLUTION

Hall, G.E.M.; P. Pelchat (Geological Survey of Canada, Ottawa, Ontario)
Water, Air and Soil Pollution, Vol 111 No 1, p 287-295, Apr 1999

The authors provide a description of the modifications to the Tekran 2537A mercury vapor analyzer that allow it to determine Hg in solution for analysis of vapor from acidified waters or acid leachates. It was originally designed to measure Hg in air by cold vapor atomic fluorescence spectrometry. Using 1% NaBH//4 as reducing agent, a 12 mL water sample can be analyzed at a rate of one every six minutes for Hg to a detection limit of 0.8 ppt. Instrumental precision is typically 1% relative standard deviation (RSD) at levels of Hg from 10 to 200 ppt.

MEASUREMENT OF MERCURY IN ENVIRONMENTAL SOLIDS BY ICPMS WITH ON-LINE SAMPLE ASHING AND HG CONCENTRATION USING THE AUTOMATIC MERCURY ANALYZER®.

Hiethmar, E.M.; J.V. Cizdziel, U.S. EPA, National Exposure Research Laboratory, Las Vegas, NV
2000 Winter Conference on Plasma Spectrochemistry Fort Lauderdale, Florida, January 10 – 15, 2000

RAPID SCREENING OF METALS USING PORTABLE HIGH-RESOLUTION X-RAY FLUORESCENCE SPECTROMETERS

Hewitt, Alan D., Cold Regions Research and Engineering Lab., Hanover, NH
Report No: CRREL-SR-95-14. NTIS: ADA299293. 20 pp, Apr 1995

Analysis of copper, zinc, arsenic, lead, chromium, cobalt, nickel, mercury, thallium, selenium, silver, antimony, cadmium, tin, and barium was performed on soils and other particle matrices using two field-portable high- resolution X-ray fluorescence spectrometers (XRF). Quantitative determinations were based on fundamental parameter analysis and a second method that relies on analyte response factors and uses the Compton K(sub a) incoherent backscatter peak far matrix normalization. These two methods af instrumental analysis require only a few reference materials and are relatively insensitive to sample matrix composition. This study assessed the capability of these two rapid XRF analysis methods by determining metal concentrations in reference materials, field samples, and laboratory spiked soils. With the exception of nickel, cobalt, and chromium, concentrations within 50% of the expected values were consistently obtained at and below 1000 micro g/g.

DETERMINATION OF MERCURY SPECIES USING ICP/MS TECHNIQUES

Hintelmann, Holger, Trent Univ., Dept. of Chemistry, Peterborough, ON (hhintelmann@trentu.ca)
International Conference on Heavy Metals in the Environment, 6-10 August 2000, Ann Arbor, MI
Elsevier Science Publishers, Oxford, UK

This paper presents an overview of different analytical methods using ICP/MS as a detector to determine mercury species in environmental samples. Total mercury is measured using either cold vapor flow injection analysis or cold vapor gold amalgamation preconcentration. Both techniques have absolute detection limits of approximately 1 pg of Mercury per isotope. Methylmercury is determined after GC separation on-line by ICP/MS. These techniques are used to carry out isotope dilution analyses and stable isotope tracing experiments. For such measurements, the achievable isotope ratio precision is of critical importance. The RSD for isotope ratio measurements was in the range of 0.5- 2 %, depending on the individual method used. For papers/abstracts from the conference: http://www.sph.umich.edu/eih/heavymetals/TechnicalProgram.html

DETERMINATION OF ARTIFACTUAL FORMATION OF MONOMETHYLMERCURY (CH3HG+) IN ENVIRONMENTAL SAMPLES USING STABLE HG2+ ISOTOPES WITH ICP-MS DETECTION: CALCULATION OF CONTENTS APPLYING SPECIES SPECIFIC ISOTOPE ADDITIONS

Hintelmann, H.; R. Falter; G. Iigen; R.D. Evans
Fresenius Journal of Analytical Chemistry, p 358, 363-370, 1997

EARTHWORMS AS BIOINDICATORS OF MERCURY POLLUTION

Hinton, Jennifer (hinton@interchange.ubc.ca); Marcello M. Veiga (veiga@mining.ubc.ca)
Dept. of Mining and Mineral Process Engineering, Univ. of British Columbia,
International Conference on Heavy Metals in the Environment, 6-10 August 2000, Ann Arbor, MI
Elsevier Science Publishers, Oxford, UK

Mercury (Hg) pollution can be evidenced by high levels in soils, water and biota. As the toxicological impacts of mercury are largely dependent upon speciation, understanding its transformations and impacts of the various chemical forms are vital to preventing harmful human and environmental health effects. Bioindicators play an important role in identifying the factors controlling Hg toxicity and bioavailability and can ultimately be used to evaluate hazardous situations. A simple, cost-effective methodology would be particularly beneficial in regions of the world such as developing countries, where mercury pollution can be extensive, yet resources limited. Earthworms are simple, well-studied creatures that can quickly provide indications of bioavailability at relatively low costs. A methodology using the earthworm Eisenia foetida has been developed to evaluate the bioavailability of Hg in mining tailings and

aqueous solutions. Results indicate that E. foetida do accumulate Hg and a positive correlation exists between Hg concentrations in worm tissues, the substrate they consume and the length of exposure. To investigate the effect of natural organic acids as mediators of Hg bioavailability, metallic Hg was dissolved in tannic acid and “fed” to the worms in a substrate of paper and silica sand. Total Hg and MeHg were analyzed to determine whether methylation of Hg was occurring in the substrate, directly within the worms (e.g. in the intestines), or in the tannic acid-Hg solution. The MeHg:Total Hg ratio was up to 160 times higher in worm tissues than both the tannic acid-Hg solution and the substrate. This result is particularly significant in darkwater systems,
where naturally occurring organic acids may be facilitating methylation internally within organisms. The reaction of metallic mercury with organic acids from sediments and darkwater systems is definitely an important pathway for mercury bioavailability. Papers/abstracts available at
http://www.sph.umich.edu/eih/heavymetals/TechnicalProgram.html

INVESTIGATION OF NATURAL FRACTIONATION OF STABLE MERCURY ISOTOPES BY MULTI-COLLECTOR INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY

Klaue, Bjoern; Stephen E. Kesler; Joel D. Blum
Univ. of Michigan, Geological Sciences, Ann Arbor
International Conference on Heavy Metals in the Environment, 6-10 August 2000, Ann Arbor, MI
Elsevier Science Publishers, Oxford, UK

Mercury is an intriguing element to study because it is highly volatile, has seven stable isotopes with a relatively large mass range (196 204 amu), forms bonds that have a high degree of covalent character, and exists in more than one oxidation state. These factors suggest that it may undergo kinetic isotopic fractionation in natural systems. The analysis of the Hg isotopic pattern in environmental samples may offer news ways of source and pathway identification for Hg species. However, neither the true isotopic composition nor the fractionation of Hg isotopes has been studied in detail with modern instrumentation. Multi-Collector Inductively Coupled Plasma Mass Spectrometry (MC-ICPMS) allows us for the first time to analyze the isotopic composition of Hg with a precision of better than 0.01%. We will present the methodology as well as preliminary data of Hg isotopic patterns in ore, coal, and environmental samples. For papers/abstracts from the conference:
http://www.sph.umich.edu/eih/heavymetals/TechnicalProgram.html

FIELD ANALYSIS OF MERCURY IN WATER, SEDIMENT AND SOIL USING STATIC HEADSPACE ANALYSIS

Kriger, A.A. (Lockwood Greene Technologies, Oak Ridge, TN); R.R. Turner (Oak Ridge National Lab., TN)
NTIS Order No: DE96009631. 10 pp, 1994

This paper describes a field screening method for rapid analysis of Hg in water, soil, and sediment that can be applied cost-effectively at Hg-contaminated sites. Samples are chemically pretreated in ordinary containers, followed by analysis of the sample headspace Hg vapor using a portable commercial analyzer. Hg in water samples is reduced directly by the addition of stannous chloride, while solids are first digested with aqua regia or piranha solution to liberate the Hg from the solids. Aided by vigorous agitation after adding the reductant, the elemental Hg partitions between solution and headspace according to Henry's Law. The method requires about 2 and 15 minutes to complete for water and solids, respectively. The method provides very useful detection limits for water (0.1 μg/L) and solids (2-3 μg/g). Intercomparisons with laboratory-analyzed environmental samples show good agreement

CAPILLARY OPTODE: DETERMINATION OF MERCURY(II) IN AQUEOUS SOLUTION

Kuswandi, B.; R. Narayanaswamy
UMIST, Manchester, UK. Dept. of Instrumentation and Analytical Science
Analytical Letters, Vol 32 No 4, p 649-664, Feb 1999

A capillary optode for determination of mercury(II) in aqueous solution has been developed whose sensors are composed of the capillary glass tubes with a chemically sensitive coating on the inner surface, which consists of a 4-(2-thiazolylazo) resorcinol (TAR) and Nafion composite thin film. The mercury(II) ions forms complexes with the immobilized TAR that result in a color change of the inner surface of the capillary when a sample solution is passed through a capillary tube. The color change can be monitored spectrophotometrically. This paper discusses sensitivity, reproducibility, linear range, life time, selectivity, the effect of flow-rate and pH, and other characteristics of these sensors.

A NEW SOLID STATE INSTRUMENT FOR OPTICAL TOXIC METAL IONS SENSING

Kuswandi, B. (Univ. Manchester, Inst. Sci. & Technol. (UMIST), Dept. Instr. & Anal. Sci., Manchester, England); M.N. Taib (ITM, Sch. Elect. Eng., Selangor, Malaysia); R. Narayanaswamy (UMIST)
Sensors and Actuators A-Physical, Vol 76 No 1-3, p 183-190, 30 Aug 1999

Multi-LEDs and double-photodiodes have been used to develop a new measurement system for chemical optrodes. Blue, yellow, red, and IR LEDs of high intensities illuminate a sensing area through one branch of a bifurcated fiber optics, and the second arm of the fiber optics guides reflected light from the sensing area to the detector. The sensing system is simple: no optical filters or monochromators are employed, and, as the LED is amenable to electronic modulation, there is no need for separate optical modulation. The light source and detector contain solid-state electronic components. The sensor system is also inexpensive, compact, and highly suitable for field applications. The optrode was tested for Hg(II) ions using 4-(2-thiazolylazo) resorcinol (TAR) immobilised onto XAD-4 with yellow LED (590 nm) as light source. The sensor showed good sensitivity in the range 0.1-20 ppm of Hg(II) ion and gave similar responses to other toxic metal ions. The sensor can be regenerated rapidly using 0.1 M Hcl.

CHARACTERISATION OF A HG(II) ION OPTRODE BASED ON NAFION(R)-1-(2-THIAZOLYLAZO)-2-NAPHTHOL COMPOSITE THIN FILMS

Kuswandi, B.; R. Narayanaswamy
Univ. Manchester, Inst. Sci. & Technol. (UMIST), Dept. Instr. & Anal. Sci., Manchester, England
Journal of Environmental Monitoring, Vol 1 No 1, p 109-114, Feb 1999

This paper discusses the development of an optrode for Hg2+ ions based on a Nafion-1-(2-thiazolylazo)-2-naphtol (TAN) composite thin film. The reflectance signal response shows a close correlation with the theoretical model derived. Depending on the concentration of Hg2+ ions, the response time of the optrode thin film was within 5-7 min to reach 95% of the final signal. The selectivity of optrode to Hg2+ ions in a phosphate buffer is good, with Co2+ and Ni2+ ions as the main interferences. This optrode has a wide linear response range of 1-75 mu M (pH 6) of Hg2+ ions with a limit of detection of 0.05 mu M (10 mu g l(-1)), which is sufficient for many environmental monitoring applications.

MICROWAVE-ASSISTED DIGESTION OF MERCURY POLLUTED SOILS

Lifvergren, T. (Man–Technology–Environment Research Centre, Örebro University, Örebro, Sweden. thomas.lifvergren@nat.oru.se); P. Suèr1; U. Wievegg (SAKAB, Kumla, Sweden)
International Conference on Heavy Metals in the Environment, 6-10 August 2000, Ann Arbor, MI
Elsevier Science Publishers, Oxford, UK

Two microwave assisted digestion procedures for determination of aqua regia soluble mercury in solid soil samples have been tested: Closed vessel and open focused microwave assisted digestion. The two methods were compared with a standardized conventional (DIN) heating method. The microwave digestion procedures were as efficient as the standardized method. The lowest deviation from the mean was observed for the open focused microwave system. Significant time was gained by using microwave digestions. The standardized method took over 14 hours, while the closed vessel procedure and the open focused procedure only took 1 hour and 10 minutes, respectively. No losses of volatile mercury species were observed during aqua regia digestion in the open focused microwave system. Papers/abstracts available at http://www.sph.umich.edu/eih/heavymetals/TechnicalProgram.html

MERCURY IN WATER, GEOLOGIC, AND PLANT MATERIALS BY CONTINUOUS FLOW-COLD VAPOR-ATOMIC ABSORPTION SPECTROMETRY

O'Leary, R.M.; P.L. Hageman; J.G. Crock
Analytical Methods Manual for the Mineral Resource Surveys Program, U.S. Geological Survey
U.S. Geological Survey Open-File Report 96-525, p 42-50, 1996

TECHNIQUES FOR THE COLLECTION AND SPECIES-SPECIFIC ANALYSIS OF LOW LEVELS OF MERCURY IN WATER, SEDIMENT, AND BIOTA

Olson M.L.; J.F. DeWild, U.S. Geological Survey, Middleton, WI
U.S. Geological Survey Toxic Substances Hydrology Program: Proceedings of the Technical Meeting, 8-12 March 1999, Charleston, South Carolina. Volume 2: Contamination of Hydrologic Systems and Related Ecosystems
U.S. Geological Survey Water-Resources Investigation Report 99-4018B, p 191-198, 1999

The U.S. Geological Survey has established a laboratory to develop and implement methods for the analysis of low levels of specific species of mercury. This paper outlines sample collection and analysis techniques used to determine species specific mercury concentrations in environmental samples. The laboratory has the capability of determining the concentration of total, methyl, reactive, and dissolved gaseous mercury in surface water, and total and methylmercury in ground water, porewater, sediment, and biota. Until the analytical methods used by the Wisconsin District Mercury Laboratory are approved by the USGS Office of Water Quality, the data produced are classified as provisional. The analytical method for total mercury is scheduled for approval by the U.S. EPA in the spring of 1999. The Wisconsin District Mercury Laboratory will seek approval of the analytical method for methylmercury through the USGS Office of Water Quality. Currently, results are validated using matrix spikes, blanks, laboratory duplicates, quality-control check samples, and certified reference materials.

DIRECT QUANTIFICATION OF METAL-ORGANIC INTERACTIONS BY SIZE-EXCLUSION CHROMATOGRAPHY AND INDUCTIVELY COUPLED PLASMA MASS-SPECTROMETRY

Piatina, T.; J. Hering, California Institute of Technology
Limnology and Oceanography: Navigating into the Next Century. The 1999 Aquatic Sciences Meeting

of the Society of Limnology and Oceanography, 1-5 Feb 1999, Santa Fe, NM

Metal-organic interactions significantly influence the geochemical cycling of trace metals and can control metal bioavailability and toxicity. Advanced analytical techniques have been applied to address some difficulties encountered in identifying and quantifying metal-organic species. In this method, size-exclusion chromatography is used for fractionation of dissolved organic compounds. Molecular size calibration of the column was performed with polystyrene-sulphonate standards and the effects of hydrophobic interactions on the column were determined. Model studies using copper and well-defined organic ligands demonstrated that the technique is subject to kinetic limitations, since labile metal-organic complexes can dissociate during fractionation on the column. Studies with strong organic ligands that form 1:1 complexes with metals have shown that such ligands are inert on the time scale of the column fractionation and that the distribution of Cu-ligand species determined analytically corresponds to the calculated equilibrium speciation. Metal concentrations in the column eluent (i.e., corresponding to each organic fraction) were determined by inductively coupled plasma mass-spectrometry without any further preparation. Application to dissolved organic matter (DOM) will include direct metal analysis of size-fractionated organics as well as metal-titration and ligand competition studies.

SPECIATION AND FRACTIONATION MODELING STUDIES-DISSOLVED ORGANIC CARBON (DOC)-MERCURY INTERACTION

Reddy, M.M.; G.R. Aiken, U.S. Geological Survey

Limnology and Oceanography: Navigating into the Next Century. The 1999 Aquatic Sciences Meeting of the Society of Limnology and Oceanography, 1-5 Feb, Santa Fe, NM

The chemical form in which mercury exists in water is its speciation. Mercury species are distinguishable from one another, stoichiometrically, and with respect to their bioavailability. In addition, mercury can exist in different phases, for example, as gaseous species, as solid phases, or in adsorbed states. The concept of chemical speciation is central to the equilibrium, kinetic and biogeochemical aspects of mercury in the Everglades ecosystem. We have used the computer ionic speciation model WHAM (Windermere Humic Aqueous Model) to characterize the mercury-organic species present in Everglades surface water. WHAM focuses on humic and fulvic acid-metal interactions. These calculations indicate that the major mercury species in solution changes from uncharged chloro-and hydroxy-complexes to DOC-bound complexes in the presence of high DOC concentrations (that is, greater than about 10 milligrams per liter). Inorganic speciation calculated using WHAM has been compared with speciation determined with PHREEQC (pH-redox-equilibrium-equations) with good agreement. WHAM has also been satisfactorily tested using laboratory measurements of calcium ion binding to a soil fulvic acid. The presence of sulfide and sulfur-containing ligands shifts mercury speciation to mercury-sulfur and mercury-organosulfur complexes. Mercury sulfide solid phases appear to be supersaturated in some Everglades' surface and pore waters. Analysis of DOC and sulfide competition for mercury binding is in progress as well as measurement of Everglades fulvic acid mercury interaction, in cooperation with the Department of Civil Engineering, University of Colorado at Boulder.

INVESTIGATIONS ON DIFFERENT HG-PHASES IN SOILS OF A HG-MINING AREA BY A PYROLYSIS TECHNIQUE

Reuther, Rudolf (ed.)

Geochemical Approaches to Environmental Engineering of Metals

Springer, New York. ISBN: 0387588485. Chapter 4, c1996

INVESTIGATION OF SEQUENTIAL EXTRACTIONS METHODS FOR DETERMINATION OF MERCURY SPECIES IN SEDIMENTS

Sladek, Chris (Dept. of Geological Sciences, Univ. of Nevada, Reno. csladek@scs.unr.edu); Mae Sexauer Gustin (Dept. of Environmental and Resource Sciences, University of Nevada, Reno, NV)
International Conference on Heavy Metals in the Environment, 6-10 August 2000, Ann Arbor, MI
Elsevier Science Publishers, Oxford, UK

This project evaluated the efficiency of some procedures commonly used in sequential extraction methods for determining mercury speciation in sediments. Pyrolitic methods were applied for the determination of volatile phases; leaching with chloride solutions was utilized for determination of soluble or mobile species; and acid digestions were used to extract strongly bound or relatively immobile species, and for total mercury analyses. It was determined that pyrolitic extraction can greatly over estimate elemental mercury. Ammonium chloride was found to be more efficient than $MgCl_2$ in removing soluble species. The organic content of a sediment was found to have a significant influence on sequential extraction results. Inorganic amendments also influenced extraction results but not as strongly as organic matter. For papers/abstracts from the conference: http://www.sph.umich.edu/eih/heavymetals/TechnicalProgram.html

REAL-TIME TRACE DETECTION OF VAPOR-PHASE ELEMENTAL MERCURY AND ITS COMPOUNDS

Tong, Xiaomei (New Jersey Inst. of Technology); R.B. Barat; A.T. Poulos (Optomechanical Enterprises, Inc.)
Environmental Monitoring and Remediation Technologies II
Proceedings of SPIE, Vol 3853, p 162-171, 1999

The high toxicity of mercury species (elemental and compound) has prompted a demand for accurate, real-time inventory and control of their emissions. Our method of choice for mercury compound vapor is Photofragment Fluorescence spectroscopy. Target compound concentrations can be related to the fluorescence intensity from an excited fragment. Fragment identities and distributions, as revealed in the fluorescence spectrum provide information on the composition of the parent species. In the first experimental phase, a static cell (no flow) containing mercury compound (e.g. $HgCl_2$ vapor was probed with a deep ultraviolet (UV) laser to generate characteristic spectra. An atmospheric pressure flow cell was used in the second stage. Limits-of-detection have been estimated. Detection schemes have included both photomultiplier tube (with interference filter) and charge- coupled-device camera (with monochromator). To reduce fluorescence quenching, we have expanded an argon gas stream containing Hg vapor through a micro-jet into a vacuum. The jet is crossed with a laser beam at 253.7 nm to excite atomic fluorescence, which is distinguished from the background by time gating.

ENVIRONMENTAL MERCURY SPECIATION ANALYSIS BY FLOW-HYPHENATION TECHNIQUES

Tseng, C.M. (Dept. of Marine Sciences, Univ. of Connecticut, Avery Point, Groton, ctseng@uconnvm.uconn.edu);D. Amouroux (Laboratoire de Chimie Bio-Inorganique et Environnement, Université de Pau et de l'Adour, Pau, France); O.F.X. Donard; W.F. Fitzgerald
International Conference on Heavy Metals in the Environment, 6-10 August 2000, Ann Arbor, MI

Elsevier Science Publishers, Oxford, UK

The behavior and fate of mercury in the environment are closely related to its ambient speciation. In order to follow the pathways of mercury in the environment, several analytical approaches were developed to determine mercury species in different ecosystem compartments. For gas-phase samples, mercury species are concentrated on chromatographic phases and desorbed in a cryotrapping/separating (CT-GC) unit coupled to a detector. For water samples, the mercury species are determined with a field cryofocusing device using flow injection and hydride generation. For environmental solid samples, mercury species are detected by an on-line D-CT-GC-QFAAS system after sample preparation by a microwave-assisted technique. The proposed approaches based on the hyphenation technique by means of flow analysis meet the need of environmental investigation in terms of rapid and accurate analysis and field operation. They were successfully applied to the estuarine environmental matrices for investigating the occurrences and fates of Hg. To view papers/abstracts from the conference:
http://www.sph.umich.edu/eih/heavymetals/TechnicalProgram.html

CONCENTRATION OF MERCURY SPECIES IN RELATIONSHIP TO OTHER SITE-SPECIFIC FACTORS IN THE SURFACE WATERS OF NORTHERN WISCONSIN LAKES
Watras, C.J.; K.A. Morrison; J.S. Host; N.S. Bloom
Limnology And Oceanography, Vol 40 No 3, 556-565, May 1995