LAWRENCE
LIVERMORE
NATIONAL
LABORATORY

UCRL-JRNL-211102

Trends in Environmental Analysis

C. J. Koester, A. Moulik

April 6, 2005

Analytical Chemistry

Trends in Environmental Analysis

UCRL-JRNL-211102

Carolyn J. Koester*
Forensic Science Center
Lawrence Livermore National Laboratory
Livermore, CA 94551-0808

Amal Moulik
Technical Information Department
Lawrence Livermore National Laboratory
Livermore, CA 94551-0808

Review Contents

This article discusses developments in environmental analytical chemistry that occurred in the years of 2003 and 2004. References were found by searching the *Science Citation Index* and *Current Contents*. As in our review of two years ago (A1), techniques are highlighted that represent current trends and state-of-the-art technologies in the sampling, extraction, separation, and detection of trace concentrations, *low-part-per-billion* and less, of organic, inorganic, and organometallic contaminants in environmental samples. New analytes of interest are also reviewed, the detections of which are made possible by recently developed analytical instruments and methods.

In our review of two years ago, we discussed developments in analytical techniques published in 2001-2002 in the context of analysis trends that have occurred over the past decade in the areas of sample collection and extraction, separation and detection, and analytes of emerging environmental interest. We highlighted techniques and methods that best demonstrated the evolution of environmental analysis. In this review, we explore a narrower historical perspective. Beginning with the focus areas that were identified in our last review, we re-examine these areas and emphasize recent contributions to their development. Although there is a trend towards making measurements of environmental contaminants in the field with portable instruments, we have restricted the scope of our review to cover only laboratory-based techniques.

Because all method development work starts with information learned from previous studies, we first discuss information collection strategies. In the area of sample collection and extraction, we highlight developments in semi-permeable membrane devices, solid-phase microextraction, hollow fiber, liquid-phase microextraction, and new materials for solid phase extraction. In our discussion of important separation and

detection techniques, we mention developments in novel chromatographic stationary phases, chiral separations, two-dimensional gas chromatography, time-of-flight mass spectrometry, and inductively coupled plasma mass spectrometry, including its use for isotope measurements, its coupling with chromatographic separations techniques, and its use with laser ablation, and nuclear magnetic resonance spectroscopy. As emerging detection techniques, we highlight accelerator mass spectrometry and high-field asymmetric waveform ion mobility spectrometry. As in our last review, we have also tabulated a list of contaminants of current concern and the analytical strategies that are used for their detection in environmental media.

Because the requirements of the editors necessitate that we be selective in our review, we acknowledge that we will not be able to mention all of the noteworthy developments in the analysis of trace pollutants present in environmental matrices that have occurred since 2003. For this reason, we encourage our readers to examine the other articles published in the *2005 Application Reviews* issue of *Analytical Chemistry* and the reviews cited in this article. Two reviews of particular relevance to anyone interested in the analysis of environmental contaminants are a recent review about the use of mass spectrometry in environmental analysis by Richardson (A2) and a review about atomic spectroscopy applied to environmental analysis by Butler *et* al. (A3).

INFORMATION COLLECTION

Since the "Environmental Analysis" review first appeared about fifteen years ago, there have been quantum changes in both the volume and the delivery of scientific and technical information. The numbers of mainstream scientific journals and the numbers of articles that they contain has continued to increase at a steady rate. For example, the

number of pages published in *Analytical Chemistry* in 2004 (7400) was almost three-fold higher than in 1990 and the number of pages contained in *Environmental Science and Technology* in 2004 (6906) was close to 4-fold higher than in 1990. Fortunately, the ability to easily search published information has accompanied this proliferation of information. The web-based versions of *Current Contents* and *Science Citation Index* are valuable tools that allow us to quickly find information that is relevant to our needs.

In addition to the plethora of information contained in mainstream journals, there is now a wealth of information on the World Wide Web. However, navigating this data and finding reliable information sources is not always easy. Because the first step in developing a new analysis method or exploring an environmental problem is information collection, we wish to devote some discussion to the evolution and use of the World Wide Web as an information source.

Before the advent of the Web, there were many commercial databases of scientific and technical information. Examples of these database services were Dialog, STN International, Questel-Orbit, and Lexis-Nexis. Each database had its own search engine (proprietary software), subscriber communities, and cost structures. While these services succeeded in providing fast access to large amounts of data, they did not serve the general public because access to them was restricted to subscribers.

The development of the World Wide Web in the early 1990s led to the linking of a vast diversity of sources, such as academic communities, corporate storefronts, and individual publications and resource lists, and opened access to these information sources to the general public, who were not always required to pay for the information obtained. Search engines that could easily be used by the general public were developed to navigate

the Web; these search engines indexed the information content of each website and provided the user with a set of results that matched the keyword combinations used in their information requests. The engines differed in the number of indexed sites, the complexity of the search language, and in the strictness of the algorithms used to define the relevancy of the search results. Not all search engines were born equal and not all answers were equally reliable. The Web also enabled a kind of browsing, through hyperlinks, which had not been available before.

When most people search the Web for information, they opt to use commercial search engines such as Yahoo or Google, which are well-known for producing directory structures for the Web. However, while these search engines provide large amounts of information, the data that they provide are not always relevant to technical questions and have not always been peer-reviewed. To obtain data that are useful to a technical audience, it is often desirable to return to the Web's original catalog. The Web's creator, Time Berners-Lee (CERN, Geneva), first published a Web catalog as the WWW Virtual Library at http://vlib.org . Unlike their commercial counterparts, the Virtual Library is maintained by a group of volunteers, who prepare pages of key links for specific content areas in which they are expert. This collection of topics is widely recognized as being amongst the highest-quality guides to particular sections of the Web. The Links for Chemists (the Chemistry section of the Virtual Library) at http://www.liv.ac.uk/Chemistry/Links/ includes the topics heading of "Analytical chemistry"; the subtopics include pages on analytical technologies, encyclopedias, subject guides, areas of applications, and professional associations.

Two pages of the Chemistry section of the Virtual Library that are particularly relevant to those who are interested in methods of analyzing pollutants in the environment are the National Environmental Methods Index (NEMI) at http://www.nemi.gov/ and the NIOSH Manual of Analytical Methods (NMAM) at http://www.cdc.gov/niosh/nmam/. NEMI was released in October 2002 by the U. S. Environmental Protection Agency and the U. S. Geological Survey to provide method summaries of laboratory and field methods for regulatory and non-regulatory related water quality analyses. Users can search analyte by name or CAS Registry Number, analyte subcategory, type of media, source of method, or instrumentation and use the results to compare analytical methods and to select those that best match their needs. NMAM is a collection of methods for sampling and analysis of contaminants in workplace air and in the blood and urine of workers who are occupationally exposed. NMAM can be searched by NIOSH method number or by chemical name. The page also contains Chapters A through R on areas such as quality assurance, method evaluation, biological monitoring and aerosols.

Publishers of scientific and technical information have leveraged Web technology not only as a delivery mechanism for online journals and reference works but also as developers of specialty search engines which give direct access to their primary literature holdings. The Elsevier online journal product ScienceDirect (price based on cost of printed journals to which an organization subscribes) has been an established presence in libraries and information centers, whereas their search engine Scirus is a relative newcomer. Scirus (http://www.scirus.com) combines the power, flexibility, and free access of much larger engines and a collection of Web sites selected for their rich

scientific content, and also access to the original articles available to subscribers of ScienceDirect. For example, searching "ed-xrf" (energy dispersive X-ray fluorescence) on Google produces 239,000 hits. The same search on Scirus produces 229 hits, of which 68 are from Elsevier-published journals and 161 hits are from its subset of the Web. Scirus also provides a short list of suggested search terms for the same topic. An advantage of the Scirus search engine is that it only references pages that are scientific in nature and excludes pages that are news- and sales-related.

Another specialty search engine focused on scientific and technical content is Science.gov (http://science.gov/), produced through a collaboration of U.S. government agencies. Its content can be browsed by exploring the topics in a directory or searched directly by using combinations of terms. The results are ranked by relevance within each source, which is a fairly effective way of presenting the context and therefore the overall relevance of the result. Science.gov represents another example of the open archive movement, in which sites are selected for their rich content in specific disciplinary areas and made available to the Web public.

SAMPLE COLLECTION AND EXTRACTION METHODS

Methods that are used to collect and extract analytes from environmental media can be either passive (equilibrium-based) or exhaustive in nature. An excellent review discussing recent developments in extraction technologies and explaining the theoretical basis behind their operation has been published (B1). Although grab samples and exhaustive sample collection techniques, for example high volume air sampling, will continue to be used in the future, passive samplers, which originally emerged in the early 1990's, are becoming increasingly important in environmental sampling. Passive

sampling of a chemical is achieved as it moves, driven by differences in chemical potentials, from an environmental medium to a collection medium, which is an organic liquid or a polymer material. The amount of analyte collected by the sampler depends on the concentration of that analyte in the environment and sampler's exposure time. In most applications, it is important that equilibrium be achieved between the analyte in the sampling medium and in the environment; the time necessary to achieve equilibrium depends on a compound's partition coefficient ($K_{sampler,\ medium}$). The theory of operation of equilibrium sampling devices was recently reviewed (B2). Passive samplers are attractive because they require no electricity and are easily deployed. Passive samplers, which include semi-permeable membrane devices, solid phase microextraction fibers, and hollow-fiber, liquid-filled membranes, have been used in studies that seek to identify new contaminants in air and water, to determine time-integrated concentrations of pollutants in air and water, and to estimate bioaccumulation of toxic pollutants.

Semi-permeable Membrane Devices (SPMD). According to the *Science Citation Index*, the number of articles describing SPMD increased from 39 during the period of our last review (2001-2002) to 63 published in 2003-2004. Clearly, the use of SPMD is gaining popularity as the physical processes behind the operation of these samplers are being elucidated.

Air. SPMD provide an inexpensive method of collecting organic compounds from multiple locations simultaneously. Persistent organic pollutants, including PCB and HCB, were collected with triolein-filled, low-density polyethylene (LDPE) at various locations across Europe. When data collected during 1998-2000 were compared with data collected during an earlier study (1994-1996) using identical samplers, it was

established that concentrations of PCB and HCB were seen to have decreased. This trend was consistent with other observations in the Northern Hemisphere (B3).

SPMD made of polyurethane foam disks were used to demonstrate the feasibility of obtaining ambient air data on a continental scale in order to better understand large-scale pollutant sources, sinks, and transport issues. Air samples were collected at 22 sites across Europe (samplers were exposed for 6 weeks) and concentrations of PAH and PCN were measured; total PAH concentrations ranged from 60 to 10,000 pg/m^3 and total PCN concentrations ranged from 0.03 to 30 pg/m^3 and were influenced by local sources (B4). The same group that performed the previous study also examined concentrations of PCB, PBDE, and organochlorine pesticides collected by the polyurethane foam disks. Total PCB concentrations ranged from 20 to 1700 pg/m^3 and total PBDE concentrations ranged from 0.5 to 250 pg/m^3 and were influenced by local sources (B5).

Because analyte levels collected by passive samplers (based on equilibrium partitioning) cannot be interpreted as easily as the amounts of analytes collected by high-volume samplers (exhaustive extraction), investigations are underway to determine accurate methods of correlating analyte concentrations in air to the amount of analytes collected by passive samplers and to understand the factors that influence the uptake of these analytes by SPMD. Triolein-filled, LDPE tubing was used to collect PAH in air. SPMD sampling rates were measured for several PAH at one location and used to determine air concentrations of these PAH at another location. On average, SPMD-derived concentrations were within a factor of two of concentrations measured by co-located, high-volume air samplers. However, total PAH concentrations less than 50 pg/m^3 were not always detected with SPMD (B6). Another study also used triolein-filled

LDPE to collect PAH and PCB in air and documented that pollutant uptake increased with increasing wind speed, thus suggesting that analyte uptake was controlled by the boundary layer at the membrane-air interface. In this same study, performance reference compounds (deuterated PAH and ^{13}C-labeled PCB), which were spiked into the triolein prior to sample collection, were used to compensate for differences in sampling conditions (B7).

Ethylene vinyl acetate (EVA)-coated glass cylinders were used to sample PCB in indoor air with high concentrations of gas-phase PCB. The high surface-to-volume ratio of the EVA-coated sampler allowed rapid equilibrium (hours) with gas phase PCB; uptake of PCB was calculated based on relationships describing the air-side mass transfer coefficient and the EVA-air partition coefficient (B8).

XAD-2 resin was used in passive samplers designed to capture organochlorine pesticides. The behaviors of these samplers were characterized in field calibration studies (42 samplers were deployed), wind tunnel experiments, and flow field simulations. Data produced by the XAD-2 samplers were comparable with those obtained with high volume sampling (B9).

Permeation passive samplers are attractive because they are least affected by conditions such as ambient temperature changes and humidity. However, they require calibration with each analyte being determined. A method to estimate calibration constants for unidentified analytes has been proposed (B10).

Water. As with their application to air sampling, SPMD provide an inexpensive method of collecting organic compounds from multiple locations simultaneously. Triolein-filled LPDE devices were used to determine PAH at different locations across a

river. The amounts of PAH collected by identical SPMD placed at three distinct locations were statistically different, indicating either differences in SPMD uptake that were attributed to the samplers themselves or that resulted from differences in aqueous concentrations of PAH at the varying locations; these results indicated that it should not be assumed that analyte concentrations measured at a single location reflect conditions elsewhere in a water system (B11).

SPMD have been used to sample a broad range of organic compounds in water. A sampler constructed from a LDPE bag filled with trimethylpentane solvent (TRIMPS) was used to sample several pesticides in a river. Endosulfan and chlorpyrifos-ethyl concentrations collected with this sampler over 7- and 22-day periods were within a factor of two of the average daily concentrations of pesticides determined by standard extraction protocols (B12). A triolein-filled LDPE sampler was used to collect methyl triclosan from lake water, suggesting that this compound might be bioavailable; this was confirmed when methyl triclosan, at concentrations up to ~360 ng/g (lipid basis) was measured in fish (B13).

In an unusual application, triolein-filled, LDPE samplers were used to collect and concentrate PAH in river water prior to compound-specific carbon and hydrogen isotope analyses. SPMD sampling did not cause C or H isotopic fractionation and provided an easier sample collection/preconcentration strategy than the conventional collection, filtration, and extraction of 1000 L water—the amount of water necessary to collect a sufficient quantity of PAH to allow isotopic analyses (B14).

Several different types of SPMD for water sampling have been described. Unfilled polyethylene membranes were used to collect low concentrations of PAH (<17

μg/L) from water; these collectors were found to perform as well as triolein-filled samplers and losses of accumulated PAH were slow (B15). SPMD consisting of LDPE strips were used to sample PCB, PAH, and HCB in pore and surface waters; equilibrium times of 1-6 days were determined for compounds with K_{ow}<7 (B16). Samplers consisting of solid poly(dimethylsiloxane) rods enclosed in water-filled or air-filled LDPE membrane tubing were used to sample 20 persistent organic pollutants. The collected analytes were directly analyzed by thermal desorption GC/MS and pollutants in concentrations of pg/L to low ng/L could be measured (B17). Simple TLC plates (C_2- and C_{18}-modified) were evaluated for use as passive samplers for diazinon and chlorpyrifos in river waters; C_2-modified TLC plates were less affected by interferences from humic acids than were the C_{18}-modified TLC plates. The TLC plates successfully provided qualitative information about the presence of pesticides; however, they could not be used to provide quantitative data (B18). A ceramic dosimeter, made of Dowex Optipore L-493 was used to characterize BTEX and naphthalene contamination in groundwater. Analyte concentrations determined with the dosimeter compared well to average concentrations measured with conventional extraction techniques, indicating that ceramic dosimeters were suitable tools for the determination of contaminant concentrations in water (B19).

As was stated previously, it is necessary to understand the factors that influence the uptake of analytes by SPMD in order to interpret the data provided by these devices. Scientists studied the uptake of PAH and PCB in both triolein-filled LDPE and LDPE-only samplers. No differences in PAH or PCB uptake were reported between these two samplers; however, the LPDE samplers reached equilibrium more quickly than the

triolein-filled samplers. Sampling rates at 30°C were approximately a factor of three higher than at 2°C; this indicated that, unless large geographic areas and time-scales are factors, temperature has minimal effect on field studies of analyte concentrations (B20).

Estimation of bioavailability. Because SPMD are composed of lipophilic materials (as are living organisms), they might someday be used in a regulatory context to mimic the uptake of bioavailable compounds by living organisms. Biological uptake experiments with living organisms are difficult to implement because organisms require specific living conditions and are subject to variables such as mortality, metabolic shifts, growth, and reproductive development. Thus, bioavailablity estimation methods using passive samplers that require no care and feeding would represent a simple alternative to work with live organisms. A LPDE sampler was used to estimate bioavailabililty of PAH to worms in contaminated sediments. PAH in the SPMD reached 90% equilibrium with sediment PAH in 60 days or less and PAH concentrations measured in worms were correlated with PAH concentrations in SPMD (B21). Factors that determined accumulation of sediment-associated PCDD, PCDF, and PCDE into SPMD and into worms were also studied; it was concluded the lipophilicity alone was not a sufficient predictor of contaminant bioaccumulation—molecular size, conformation, and sediment characteristics were also important. While the uptake of contaminants by SPMD was determined by physical-chemical properties only, biological factors also influenced contaminant uptake by worms (B22). Another study also found differences between biological uptake of PAH and its uptake by SPMD. PAH concentrations in oyster tissues were not directly proportional to PAH exposure measured by SPMD; biological factors,

such as apparent toxicity-induced cessation of feeding, were speculated to be important to PAH uptake in organisms (B23).

Improvements to the use of SPMD include the development of a rapid dialysis protocol to extract chlorinated compounds from a triolein SPMD. A procedure using accelerated solvent extraction reduced dialysis time from 2 days to 40 minutes; analyte recoveries were comparable to those obtained by conventional dialysis methods (B24).

SPMD have found many interesting applications. Although passive samplers cannot provide direct measurements of organic pollutants over short time intervals, they can provide information about integrated average pollutant concentrations, which can be used to assess water quality. In order to understand how amounts of contaminants collected by SPMD are related to their environmental concentrations, it is important to understand the factors controlling their uptake and release from the SPMD and to refine calibration strategies (*eg.* the use of performance reference compounds).

Solid Phase Microextraction (SPME). We reported previously that SPME, in which a small, polymer-coated fiber is used to collect analytes of interest, was being applied to environmental measurements with increasing frequency. This trend continues. SPME is a universal sampling and extraction method – it can be used to sample air, water, and the headspace above solids. Once sampling is complete, the SPME fiber containing the analytes of interest can be directly introduced into either a GC or LC inlet. In addition, the commercial availability of several different polymer coatings has increased the range of compounds that can be sampled with SPME fibers. Work to develop new materials to increase the sensitivity and selectivity of SPME fibers is

ongoing. For example, a sol-gel-derived silicone DVB copolymer has been found useful for sampling organic phosphonates (B25).

Air. SPME continues to be used to characterize components of air samples. A DVB/Carboxen/PDMS fiber was used to sample air from landfill sites; coupled with GC/MS, about 100 volatile compounds were identified (B26).

There continues to be interest in using SPME samplers for environmental and occupational monitoring. A 100-μm PDMS fiber was exposed in a 250-mL sample flask, which was set-up for dynamic sampling in order to determine concentrations of pesticides in air. Coupled with a GC/MS, SPME sampling offered detection limits that were compound-dependent and ranged 0.03 to 2 $\mu g/m^3$. Using this technique, concentrations of 200-500 $\mu g/m^3$ procymidone (pesticide) were measured in a greenhouse (B27). When used with sensitive, specific detectors, excellent detection limits can be obtained by SPME sampling. For example, a 100-μm PDMS fiber was used to collect organophosphate triesters (flame retardants and plasticizers); when analyzed by GC/NPD, detection limits of 10 pg/m^3 were obtained (B28).

A 75-μm Carboxen/PDMS fiber was used as a passive sampler to determine time-weighted average concentrations for volatile organic compounds in air. An unusual aspect of this application was that the fiber was *retracted* into its sheath during sampling. It was determined that Fick's first law of diffusion could be used to describe the sampling process and that environmental conditions, such as temperature and humidity, had negligible effect on sampling. Toluene concentrations, at occupationally relevant levels (5-80 ng/L), measured by this SPME method compared well with those determined using conventional, charcoal tube sampling (B29). Another study examined the use of

Carboxen/PDMS fibers, retracted into their sheaths during sampling, for determining time-weighted average (TWA) concentrations of volatile organosulfur species. Although this technique was suitable for monitoring Me_2S_2, it was not useful for the determination of TWAs for several other organosulfur species because their uptake rates varied greatly with humidity, temperature, and time. The investigators concluded that SPME might eventually be useful for measuring organosulfur compounds if a coating with higher affinity for these low molecular weight compounds could be developed (B30). Another study concluded that the use of a highly efficient sorbent for SPME sampling was one of the most important factors that affected sample preservation when SPME was hardened for field use (B31).

When using SPME to determine concentrations of pollutants in air, it is critical to develop reliable calibration strategies. One approach used a process called "stepwise solid-phase microextraction" to facilitate calibration. Using this technique, a known concentration of tetrachloroethylene was sampled with a 75-μm Carboxen/PDMS fiber; this fiber was selected because of its strong affinity and large capacity for volatile organic compounds. The SPME fiber was then used to sample BTEX in the air of a gas station (B32). Using a 75-μm Carboxen/PDMS fiber, it was determined that SPME grab sampling could be described by Fick's law of diffusion; this simplified calibration because only one sampling rate (determined from a single calibration curve) was needed to calculate concentrations collected under different sample durations at comparable temperature and air velocity conditions (B33). Another calibration strategy reported used a gas standard generation system that was specifically designed for use with SPME (B34).

Water. The range of compounds collected by SPME continues to grow. Headspace SPME with a 100-µm PDMS fiber and GC/MS was used to determine trihalogenated anisoles in water; quantification was aided by the use of *p*-iodoanisole as an internal standard and detection limits ranged from 0.03 ng/L for 2,4,6-trichloroanisole to 0.25 ng/L for 2,3-dibromo-6-chloroanisole (B35). Other examples of analytes sampled by SPME include fungicides (B36) and PBDE (B37).

In addition to being used in laboratory analyses, there is a tread towards applying SPME samplers in the field. An 85-µm polyacrylate fiber, placed in a steel mesh envelope and buried in sediment, was used to sample 2,4,6-trinitrotoluene (TNT) and its degradation products from sediment waters; recommended sampling times required to reach equilibrium were 48 hours at room temperature and up to 7 days at temperatures <5°C. Detection limits for TNT and its degradation products were 10-30 ng on fiber (B38). A 100-µm PDMS fiber was placed inside of a protective metal tube and used to collect *p,p'*-DDE and *o,p'*-DDE in coastal waters. Exposure times of 12 days were sufficient to attain equilibrium and concentrations for *p,p'*-DDE and *o,p'*-DDE determined by SPME compared well with those determined using an Infiltrex 100 sample collection system. The advantages of SPME sample collection were its low cost ($100 per SPME sampler) as compared to the cost of the Infiltrex system ($20,000) and its negligible sample preparation. The disadvantages of the SPME samplers were their vulnerability to damage in the rough, coastal environment and that the detection limits that they afforded were not as good as those provided by the Infiltrex systems — only concentrations of ≥0.1 ng/L could be detected by SPME sampling (B39).

In order to continue the development of SPME as a tool for water analysis, it is necessary to understand the processes that affect SPME sampling. The advantages and limitations of a 75-μm Carboxen-PDMS fiber used for sampling BTEX compounds from water were investigated. When analytes were present at high concentrations, competitive displacement became a problem, suggesting that the Carboxen-PDMS fiber might best be used when low concentrations of analytes are to be measured in the absence of interfering compounds (B40).

Because a SPME fiber is typically introduced into a gas chromatograph, the majority of SPME applications involve the analysis of volatile or semi-volatile compounds that are thermally stable. However, GC analysis is also possible for less volatile, thermally-fragile compounds if derivatization reactions are performed prior to introduction into the GC. Headspace SPME was used to determine organotins in water. The organotins were derivatized, *in situ,* with sodium tetraethylborate, sorbed to a 100-μm PDMS fiber, and detected at low ng/L concentrations using GC/MS, operated in the electron ionization mode and using selected ion monitoring (B41). On-fiber derivatization of aldehydes was performed using *o*-2,3,4,5,6-(pentafluorobenzyl)hydroxylamine hydrochloride and a 65-μm PDMS/DVB SPME fiber. When coupled with GC/MS, 0.1 μg/L of various aldehydes could be determined in water (B42). Polar aromatic amines were derivatized directly in water by diazotation and subsequent iodination and sampled with a 65-μm PDMS/DVB fiber; when coupled with GC/MS, detection limits for aminodinitrotoluene isomers and aminonitrotoluene were approximately 30 ng/L (B43).

Soil. In an interesting experimental set-up, microwave-assisted extraction was coupled with headspace SPME. Using this system, chlorophenols were extracted from soil samples into water, the headspace of which was sampled with an 85-μm polyacyrlate SPME fiber. Low part-per-billion concentrations of chlorophenols in soils could be detected (B44).

Estimation of partition coefficients and bioavailability. The use of negligible-depletion SPME and its application to the measurement of free concentrations of analytes in solutions and bioavailability has been reviewed (B45). SPME has been used to measure the partition coefficients (K_d) of bifenthrin and permethrin isomers. K_d determined by SPME, using a 30-μm PDMS fiber, were 0.6 to 5-fold greater than those obtained by conventional liquid-liquid partition for creek sediments and 7 to 22-fold greater than those obtained by conventional liquid-liquid partition for nursery runoff sediments. Because chemicals are adsorbed to dissolved organic matter and measured in the aqueous phase by conventional liquid-liquid partition methods, this results in the underestimation of K_d values determined for many hydrophobic compounds using a liquid-partition method; thus, SPME might provide a more accurate method for measuring K_d (B46). SPME was used to measure dissolved (and, therefore, bioavailable) concentrations of PCB in soil using a 30-μm PDMS fiber. Equilibrium between PCB in the soil and in the SPME fiber was reached within 20 days; concentrations of PCB measured by SPME allowed accurate estimates of PCB concentrations in earthworms (B47).

Hollow Fiber, Liquid-Phase Microextraction. Hollow fiber, liquid-phase microextraction is an interesting cousin of SPME. In this technique, a small,

polypropylene hollow fiber membrane is attached to the tip of a syringe that contains a receptor solvent. Before the membrane is used to sample an aqueous fluid, it is filled with the receptor solvent from the syringe; after sampling is complete, the solvent is drawn back into the injection syringe, the fiber membrane is discarded, and the solvent is injected directly into a GC or LC system. This sampling technique has been reviewed with a discussion of its operating principles, implementation, and application (B48). Hollow fiber membrane, liquid-phase microextraction, with toluene as a receptor fluid, was used to sample organochlorine pesticides and PAH in rainwater. Detection limits were compound dependent and ranged from 2 to 50 ng/L (B49). Another group filled a small hollow fiber membrane with 8μL octanol and sealed it at both ends. The sampler was then placed in water and agitated to sample penta- and hexa-chlorobenzenes. This method provided high enrichment of the chlorobenzenes (~100-fold with respect to water) in 10 minutes (B50).

Solid Phase Extraction (SPE). As we reported in our last review, SPE continues to be a leading technology for the extraction of both organic and inorganic species from aqueous samples. SPE is attractive because it affords easy concentration of the species of interest, requires minimal amounts of solvent, and can be tailored to extract either a broad range of compounds/metals or to provide specific extraction of a pollutant or compound class. Because the recent applications of SPE are too numerous to report, we will examine the trends in SPE of using new materials for analyte extractions and in developing automated sample processing methods.

Multiwalled carbon nanotubes (MWNTs) were applied to the extraction of phenols from water. MWNTs afforded comparable or better extraction efficiencies

(>90% recoveries), especially for the more polar phenols, than commonly used XAD-2 and C_{18} materials. Detection limits for bisphenol A, 4-*tert*-octylphenol, and 4-*n*-nonylphenol, were 0.8, 0.2, and 0.2 μg/L, respectively, when a 500-mL sample was extracted with MWNT and analyzed by LC-fluorescence detection (B51). For the analyses of organic compounds, molecularly imprinted polymers (MIPs) are of interest because they provide selective extraction of a single compound/compound class. MIPs offer the advantages of high adsorption capacity for analytes, easy synthesis, and, theoretically, low cost. The main disadvantage of MIPs is that it is difficult to remove all of the template molecules, which would cause contamination problems in trace-level analyses. A recent article in *Analytical Chemistry* discusses their preparation, application, and challenges (B52). Analyses are hindered by the fact that, although "the imprinting of small, organic molecules (*e.g.*, pharmaceuticals, pesticides…) is now almost routine" (B52), MIPs are not yet commercially available.

An ideal SPE method would extract all analytes of interest from a sample. A group at the Centers for Disease Control and Prevention developed an automated SPE method for the extraction of many different classes of persistent organic pollutants from human serum. Although several sorbents worked well for the extraction of the organic compounds and could be used without causing adversely high backpressure and leaking of the automated SPE system, Oasis HLB provided slightly better recoveries and was selected for use. After appropriate purification and analysis by GC/HRMS, instrumental detection limits, assuming a 1-g sample, were ~ 1 pg/g for many persistent organic pollutants (B53).

SPE has also been combined with derivatization chemistry. An on-line SPE, derivatization, and LC analysis procedure was used to determine biogenic amines. A C_{18} guard column was placed in the sample loop of an LC system. This column was eluted with benzoyl chloride (derivatizing agent) prior to sample introduction. Derivatization and extraction of the biogenic amines occurred as the sample was introduced into the guard column. After extraction, the contents of the guard column were transferred into the LC system and the biogenic amines were detected by UV absorption spectroscopy. Detection limits, with a 1-mL water sample, were ~100 ng/L (B54).

Although not emphasized in this article or our previous review, SPE strategies incorporating chelating ligands and ion exchange resins have long been used to collect inorganic compounds from water. Some SPE techniques currently used for the collection of inorganic compounds are included as part of a review on preconcentration of water contaminants (B55). The use of styrene-divinyl benzene copolymers in metal analysis has also been reviewed (B56). In an interesting innovation, colorimetric SPE was used to determine Ag(I), a biocide added to water, Ni(II), a metal leachate from a water system, and sample pH. Colorimetric reagents were impregnated on membranes and the analytes reacted with these reagents; the resulting complexes were then interrogated by diffuse reflectance spectroscopy. Using a 3-mL water sample, Ag(I) concentrations of 0.05 -5 mg/L, Ni(II) concentrations of 1.8-5 mg/L, and pH of 2.5-5 could be determined in 120 sec. This method is proposed for use aboard the International Space Station to monitor water quality (B57).

The use of materials for the SPE of metals by ion-imprinted polymers has been reviewed (B58). Analogous to molecularly imprinted polymers, ion-imprinted polymers

offer the promise of selectively extracting inorganic analytes. A hierarchical double-imprinting procedure was used to prepare a Cd(II)-selective, organic-inorganic hybrid, sol-gel sorbent. This sorbent's selectivity for Cd(II) was approximately 100-times better than for Zn(II) (B59).

IMPORTANT SEPARATION AND DETECTION TECHNIQUES

Novel Stationary Phases. Although GC is a mature technology, work towards developing novel stationary phases continues. 1-benzyl-3-methylimidazolium trifluoromethanesulfonate and 1-(4-methoxyphenyl)-3-methylimidazolium trifluoromethanesulfonate (two high-stability ionic liquids) were tested for use as GC stationary phases. These materials were stable to 260ºC, afforded different analyte retention mechanisms than those of commercially-available GC stationary phases, and were tested with several compound classes, including alkanes, aromatics, alcohols, amines, and carboxylic acids (C1). While their utility with regards to environmental analysis is unproven, these stationary phases are worthy of note as they potentially could be used to facilitate compound identification in GC x GC experiments, in which it is desirable to work with columns having different retention mechanisms. In another study, ionic liquids (based on N,N-dimethylephedrinium) were used, for the first time, as GC stationary phases to achieve chiral separations; the use of these liquids as stationary phases is advantageous because they can be synthetically produced (unlike the natural-product-based cyclodextrin stationary phases) and their stereochemistries can be controlled. These ionic liquids are useful for separations of alcohols, diols, sulfoxides, acetylate amines, and epoxides (C2).

As stationary phases for liquid chromatography, monolithic columns are recent developments. Simply stated, a monolithic column consists of a column that is filled with a single large particle. The monoliths are highly permeable and, for this reason, create less back-pressure than packed columns. Thus, monolithic columns can be operated at high flow rates, achieving fast separations with high chromatographic resolutions. Commercially-available, monolithic columns are currently marketed towards the analysis of biomolecules; however, they might eventually be applied to the field of environmental analysis (C3).

Chiral Separations. As we reported in our last review, the resolution and quantitation of different enantiomers of chiral compounds has become important in environmental science. Because enantiomers of a chiral compound have different properties (*eg*. toxicities, bioaccumulation rates, biodegradation pathways, *etc.*), it is important to distinctly observe their presence in the environment. ß-cyclodextrins remain the most commonly-used GC stationary phase. ß-cyclodextrin columns have been used to separate enantiomers of chlordane (C4), PCB (C5), PBB (C6), methylsulfonyl-PCB (C7), and cypermethrin and cyfluthrin (C8). A strategy of chiral GC separation and automated fraction collection was used to isolate enantiomers of chiral compounds, such as hexachlorocyclohexane, so that their individual estrogenic potentancies could be determined (C9).

In our last review, we speculated that chiral separations would become important in LC analyses. Indeed, chiral separations have been demonstrated using LC. Enantiomers and diastereomers of pesticides (phenthoate, uniconazole, diniconazole, propiconazole, fempropathrin, cypermethrin, cyfluthrin, and fenvalerate) were separated

using a cellulose *tris*-3,5-dimethylphenyl-carbamate stationary phase (C10). Allethrin enantiomers were separated by LC, using a monolithic silica column, and then transferred to a cellulose-based chiral column for further separation (C11). Chiral LC methods to separate compounds of pharmaceutical interest were adapted for use for LC/ESI-MS. It was discovered that polar organic mobile phases were easily adapted to LC/ESI-MS; normal-phase separations were possible if post-column dilutions of a large excess of ESI-MS-compatible solvent was possible without sacrificing sensitivity and peak shape. Using LC/ESI-MS, detection limits of ~0.1-1 µg/L could be obtained (C12).

Chiral separations are also being performed by capillary electrophoresis. Mixed-mode electrokinetic capillary chromatography, using surfactants, and neutral and charged cyclodextrins has been used to perform separations of enantiomers of malathion, cruformate, and fensulfothion (C13). Cyclam-capped ß-cyclodextrin-bonded silica particles were also introduced as a chiral stationary phase in capillary electrophoresis and might find application to environmental analysis in the future (C14).

Two-dimensional Gas Chromatography (GC x GC). In GC x GC, components of a mixture are separated on two different GC columns. Typically, the two GC columns provide independent separation mechanisms. In contrast to conventional GC in a single dimension, GC x GC provides a greater peak capacity and a greater number of compound peaks can be resolved. However, the vast amounts of GC x GC data must be displayed in two-dimensional plots of retention time in dimension 2 *versus* retention time in dimension 1, making data interpretation more complex than it is for a traditional, one-dimensional chromatogram.

GC x GC, introduced in the 1990's, has become increasingly important in the field of environmental analysis. Evidence to support this claim is found in the fact that *the First International Symposium on Comprehensive Multidimensional Gas Chromatography* was held in March of 2003 in Volendam, the Netherlands, and the reported research was presented in a special issue of the *Journal of Chromatography A* (Volume 1019, Issues 1-2). GC x GC instruments are now commercially available. This separation technique has been reviewed in articles discussing its implementation and applications (C15) and information processing technologies (C16).

In the field of environmental analysis, GC x GC has been used to characterize components of a sample and also to identify and quantify selected analytes. GC x GC (BPX-5 x BPX-50) coupled with TOF/MS detection was used to characterize semi-volatile organic compounds in particulate matter; more than15,000 chromatographic peaks could be detected in a $PM_{2.5}$ sample. One novel aspect of this analysis was that thermal desorption, instead of liquid injection, was used to introduce the sample into the GC x GC (C17). Thermal desorption followed by GC x GC coupled with FID and TOF/MS was used to investigate volatile organic compounds in air; ~650 distinct peaks were detected (C18). GC x GC (HP-1 x HT-8) coupled with micro-ECD and TOF/MS was used to study technical toxaphene; more than 1000 different compounds were present (C19). The composition of an unresolved complex mixture of hydrocarbons in petroleum-contaminated sediment was studied by GC x GC coupled with FID; both Quadrex 007-1 x Quadrex 007-1701 and Quadrex 007-1 x Rt-γDEXsa column combinations were used to resolve thousands of individual components and provide

information that will eventually help to understand sources, weathering, and toxicity of sediment-bound hydrocarbons (C20).

Many environmental analysts would benefit from techniques that allow the separation and quantification of a great number of compounds in a short amount of time, with minimal sample preparation. For this reason, there has been interest in the use of GC x GC for separation of organohalogen compounds. GC x GC (DB-1 x HT-8), coupled with TOF/MS was used to measure 59 selected PCB, PBDE, and organochlorine pesticides in human serum and milk. In contrast to conventional GC/MS methods, the entire suite of analytes could be analyzed, with a single injection, in 50 minutes and most of the compounds of interest could be chromatographically resolved from one another (TOF/MS data could be used to deconvolute signals from those compounds that did coelute). Method detection limits were compound dependent and ranged from 1-15 pg/μL in sample extracts; analyte concentrations measured with GC x GC coupled with TOF/MS were comparable to those measured with conventional GC/HRMS (C21). GC x GC (Rtx-Dioxin2 x Rtx-500) coupled with TOF/MS was used to measure PCDD, PCDF, and coplaner PCB in ash, sediment, fish, and vegetation; the instrumental limit of detection was 0.5 pg for 2,3,7,8-TCDD and concentrations measured with GC x GC coupled with TOF/MS were comparable to those measured with conventional GC/HRMS (C22). In another study, 2,3,7,8-substituted PCDD, PCDF, and coplanar PCB from milk extracts were separated using GC x GC (DB-XLB x LC-50) coupled with electron-capture detection. Twenty nine congeners could be separated in 120 min and limits of detection ranged from 30-150 fg injected (C23).

GC x GC (HP5-MS x BGB-1701) coupled with FID or quadrupole MS was used to detect PAH present in urban aerosols at concentrations of 0.5-5 ng/m^3 (C24).

Although TOF/MS is a detector of choice for GC x GC because of the mass spectral data that it provides and its fast acquisition speed (*ie*. TOF/MS can easily detect peaks eluting over 100-300 msec), some work has been done to interface GC x GC (DB-1 x BPX-50) with the slower atomic emission detection (AED). AED can be set to respond to specific elements, for example S and N, in compounds and, thus, aid analyte identification. AED was found to be a useful tool for detecting pesticides and specific compound classes present in petroleum hydrocarbons when minor modifications, such as increasing the diameter of the transfer line to the AED and increasing gas flows to decrease the apparent dead volume of the AED, were made (C25).

GC x GC is well on its way to becoming a standard analytical technique. A comparative study involving four laboratories showed that a longitudinally modulated cryogenic system provided reliable GC x GC data when comparable columns (BPX5 x BP20), separation conditions, and FID were used (C26). However, there are still technical challenges in the application of GC x GC to real samples that need to be addressed. For example, methods of correlating retention times produced by GC x GC coupled with FID with those produced by GC x GC coupled with TOF/MS need to be developed; this would allow the use of a simpler, less expensive FID for routine detection and quantitation, once analytes' identities had been established by mass spectrometry (C27).

There are other issues in GC x GC that need to be understood before GC x GC can be considered to be a mature technique. Factors affecting the trapping and release of

compounds in the GC x GC modulator, for example the temperature in a cryogenic gas loop-type modulator, need to be optimized and are under study (C28). Software to aid quantitative analysis is being developed (C29). New modes of GC x GC operation are being considered. Operation of the GC x GC in stop-flow mode, in which gas flow is stopped in the primary column so that the modulation period for the primary column and the amount of time available for separation in the second dimension become independent variables, has been proposed as a means of improving the already impressive separation capabilities of GC x GC (C30).

Organic Mass Spectrometry (MS). Mass spectrometry continues to be one of the most important techniques applied to environmental analysis. The most frequently used types of mass spectrometers for analyses of organic compounds are single quadrupoles, triple quadrupoles, ion traps, and magnetic sector instruments. Gas chromatographic and liquid chromatographic separations are routinely coupled with mass spectrometric detection and GC/MS and LC/MS can achieve part-per-billion detection limits. In our *Environmental Analysis* review of 2003 (A1), we devoted significant space to the discussion of LC/MS for the determination of compounds that are polar, thermally labile, and not amenable to analysis by GC/MS; the role of LC/MS in the field of environmental analysis is routine and continues to expand. In this year's review, we have chosen to highlight the newer techniques of time-of-flight mass spectrometry and compound-specific isotopic analyses because these techniques are beginning to provide unique means of studying the environment. For an overview of organic mass spectrometry applied to the study of environmental contaminants, we encourage the reader to review an excellent article titled "*Environmental Mass Spectrometry: Emerging*

Contaminants and Current Issues" by Richardson (A2) and to peruse another review by Zwiener and Frimmel discussing mass spectrometry instrumentation, chromatographic separations, and sample preparation techniques used to analyze water samples (D1).

Time-of-flight mass spectrometry (TOF/MS). It is essential to correctly determine the identities of newly discovered contaminants. Within the past several years, TOF/MS systems (with both GC and LC sample introduction) have become commercially available and have proven to be useful in compound characterization. Like quadrupole mass spectrometers, TOF/MS are capable of collecting full scan mass spectral data. Although their resolving powers (~5000 resolution for a typical organic compound) are not as good as those produced by a high resolution, magnetic sector mass spectrometer (>10,000 resolution), TOF/MS affords better mass resolutions than can be obtained with quadrupole mass spectrometers. The characteristic of *simultaneously* providing both accurate mass measurements and full scan data on a short time-scale makes TOF/MS ideally suited to the characterization of environmental contaminants. TOF/MS can also be used to provide quantitative data. Recently, TOF/MS has been interfaced with a quadrupole mass filter and collision cell (QTOF/MS) – this combination offers the capability of performing MS/MS experiments with accurate mass measurement of the detected ions. The unique features of TOF/MS instruments and examples of their applications to environmental problems have been reviewed (D2). In this section, we will emphasize the use of TOF/MS as an LC detector. The utility of the TOF/MS as a detector for GC x GC has been demonstrated in a previous section of this review.

Several studies emphasized the utility of TOF/MS for the identification of new contaminants. LC/TOF/MS and LC/MS/MS were used to identify the presence of new

second amide degradation products of acetochlor, alachlor, and metolachlor in groundwater. Discovery of these compounds followed a well-implemented strategy which included hypothesizing the presence of these species, using LC/MS/MS to search for the suspected molecular ions and characteristic fragments of these compounds in samples, synthesizing and analyzing authentic standards to verify compound identities, and confirming the presence of the degradates in groundwater samples collected in the Midwestern United States (D3).

In addition to aiding in compound identification, LC/TOF/MS can also be used for quantitative analyses. The combination of LC/TOF/MS and LC/MS/MS has been used to unambiguously identify diphenhydramine (the antihistamine Benadryl) in aquatic sediments; concentrations of diphenhydramine ranged from non-detectable to 50 μg/kg (D4). In laboratory studies, LC/TOF/MS was used to tentatively identify a previously unknown nitrated derivative of benzo[*a*]pyrene; this suggested that PAH-nitroquinones can be formed by reaction of PAH with photooxidants (D5). LC/TOF/MS was used to determine cyanobacteria toxins in water. When collecting and processing a 100-mL water sample, method detection limits of ~1 μg/L for several cyanobacteria toxins were obtained (D6).

Data provided by LC/TOF/MS (with electrospray ionization) along with data produced by LC/MS^3, were used to identify a photoproduct of the antibiotic chlortetracycline; the concentration of this photoproduct in samples collected from a hog lagoon ranged from 50 to 300 μg/L, as estimated from LC-UV data (D7). In another study, LC/QTOF/MS was used to identify degradation products of triazine herbicides (D8).

QTOF/MS was interfaced with online-SPE preconcentation of a 2-mL water sample, LC separation, and electrospray ionization. This arrangement, along with some well-implemented data analysis strategies, allowed the identification of several water contaminants, including the veterinary fungicide enilconazole and the herbicides terbutryn and diuron (D9). The ability of QTOF/MS to screen for and confirm the identities of pharmaceutical compounds, including the analgesics acetylsalicylic acid, diclofenac, ibuprofen, and paracetamol, the antibiotics sulfamethoxazole, erythromycin, and chloramphenicol, blood-lipid regulators and beta-blockers fenofibrate, bezafibrate, clofibric acid, bisoprolol, and metoprolol, and the anti-epileptic drug carbamazepine was demonstrated. Limits of quantification for these compounds ranged from 5 to 25 ng/L (D10).

The capabilities of three MS techniques, triple quadrupole mass spectrometry, TOF/MS, and QTOF/MS, for the identification and confirmation of pesticide residues in water were discussed in the context of a new European Commission (EC) guideline for the identification and quantification of organic compounds. One of the goals of this guideline, which was proposed to guarantee effective control of contaminant residues in animals and meats, is to eliminate false positive detections by specifying the number of "identification points" that are necessary to confirm the presence of an analyte. TOF/MS was useful for analyte identification because it afforded accurate mass data that could not be obtained from MS/MS experiments and also provided full mass spectral data to aid in the characterization of unknown compounds. QTOF/MS was found to be a powerful technique in compound identification as it combined the desirable features of providing both MS/MS fragmentation information and exact mass measurement. However, the

detection limits achievable with TOF/MS (~0.05 μg/L) and QTOF/MS (~0.1μg/L) were not as good as those achievable with triple quadrupole mass spectrometry (~0.01 μg/L). (D11).

Compound-specific isotope measurements. According to a recent review, compound-specific stable isotope analysis using gas chromatographic isotope ratio mass spectrometry (GC/IRMS) is now a mature analytical technique (D12). It has found applications in environmental analyses in the areas of contaminant source attribution and in assessing the biodegradation of contaminants. Compound-specific isotope measurements for H and C are most commonly performed. Further development in GC/IRMS will seek to improve analyte detection limits. Recently, it was demonstrated that, using purge and trap concentration and GC/IRMS, $^{13}C/^{12}C$ could be determined for volatile organic compounds that were present at concentrations of 0.2-5 μg/L in water. Some isotopic fractionation as a part of the extraction process was observed, but was reproducible, and, for this reason, could be corrected (D13). Other studies have also observed isotopic fractionation. Systematic errors in $^{13}C/^{12}C$ measurement were observed as a function of analyte concentrations (and determined to be caused by conditions in the split/splitless injector) and a correction strategy of co-analyzing standards of varying analyte concentrations and known *delta*-^{13}C values was proposed (D14).

A recent study suggested that stable isotope-labeled semivolatile organic compounds might be used as tracers to provide a means of studying the atmospheric transport and air-earth exchange rates of persistent organic pollutants (D15).

The origin of perchlorate as a contaminant has been a topic of recent interest. $^{18}O/^{16}O$ and $^{17}O/^{16}O$ were measured in man-made perchlorate and natural perchlorate

extracted from Atacama Desert salts. The $\delta^{18}O$ value of man-made perchlorate was -18±1 ‰ and the $\delta^{18}O$ values of natural perchlorate ranged from -4 to -25 ‰; thus, it should be possible to use oxygen isotope ratios to identify the source of perchlorate contamination in the environment (D16).

Inductively Coupled Mass Spectrometry (ICPMS). ICPMS is, perhaps, the most important inorganic mass spectrometric technique. ICPMS boasts the ability to provide low detection limits (low part-per-billion, or less) for multiple elements (attributed, in part, to its efficient ionization of many species), good sensitivity, a wide linear range, good precision, and sufficient accuracy to provide isotope ratio measurements. The progress of and state-of-the-art in this technique has been summarized in recent reviews (D17, D18). Many elements of interest have been measured by ICPMS, although recent work has added the analysis of heavy metals such as Pu and U. An interesting article suggested that ICPMS can also be thought of as a simultaneous, element-specific detector and used to screen for P-, S-, Cl-, Br-, and I-containing pesticides at sub-part-per-billion concentration in fruit extracts (D19).

Isotope measurements. One of the most recent applications of ICPMS has been the determination of low concentrations of isotopes and isotopic ratios that have been afforded by ICPMS with multiple collectors (MC-ICPMS) and sector field instruments (SF-ICPMS). For example, low levels of elements relevant to nuclear contamination have been measured with SF-ICPMS. SF-ICPMS coupled with an automated sequential injection separation system, which used TEVA resin to capture the isotopes of interest, was able to detect 2.5, 2.1, and 0.42 pg/L of ^{237}Np, ^{239}Pu, and ^{240}Pu, respectively. Using this system, total separation and analysis time was 1 hour (D20). Another method using

SF-ICPMS, preceded by resin extraction, was able to detect 3 pg ^{90}Sr per liter urine (D21). A method was developed to determine low concentrations of Pu isotopes in seawater using TEVA resin concentration and both SF-ICPMS and MC-ICPMS detection. Using a 100-L water sample, detection limits were 0.1 fg/L using SF-ICPMS and 0.03 fg/L by MC-ICPMS. Pu concentrations in the Sea of Galilee were determined to be 0.4 fg/L with $^{240}Pu/^{239}Pu$ of 0.17, which was indicative of fall-out from nuclear testing (D22).

MC-ICPMS was used to study $^{206}Pb/^{207}Pb$ in peat bogs. Peat deposited in 1880 had $^{206}Pb/^{207}Pb$ of 1.168-1.178, which showed the influence of anthropogenic pollution; a higher $^{206}Pb/^{207}Pb$ value of 1.193 was obtained for samples that were 11,000 years old and not impacted by human activity (D23). Lead isotopes were also measured, using MC-ICPMS, in lichen around a copper smelter and could be used to resolve different lead sources (D24); one important observation in this study was that, while errors associated with isotope ratio measurements were on the order of 250 ppm, variabilities in the isotope ratios determined for samples collected from the same site were significantly higher at 400-5000 ppm. Thus, within-site variability of isotopic ratios must be considered in data interpretation. SF-ICPMS, equipped with a minicyclonic spray chamber and Peltier-cooled condenser, was used to detect lead isotopes (^{206}Pb, ^{207}Pb, and ^{208}Pb) in Arctic ice. Detection limits were 0.06 pg/g and precision of isotope ratio measurement was ~0.2%. Using this method it was observed that, although the concentrations of Pb measured in ice samples from 1974 (9 pg/g, with $^{206}Pb/^{207}Pb$ 1.169±0.002) and 1852 (6 pg/g with $^{206}Pb/^{207}Pb$ 1.147±0.003) were similar, the $^{206}Pb/^{207}Pb$ values were different, indicating contributions from different lead sources (D25). This study also demonstrated that the

precision with which isotope ratios can be measured by ICPMS is now comparable to that attainable by thermal ionization mss spectrometry. In contrast to thermal ionization mass spectrometry, ICPMS requires small samples (only 2 mL water were needed for the ice study), requires little sample pretreatment, and quickly and inexpensively provides quantitative isotopic data.

A single detector SF-ICPMS was used to measure $^{235}U/^{238}U$ in human urine to determine if a population had been exposed to depleted uranium as a result of this material being used in military munitions. Using a 10-mL sample, detection limits of 0.14 pg/g were obtained, the overall method was validated by comparison with a known reference material, and the major sources of measurement uncertainty were identified (D26). MC-ICPMS was used to measure $^{236}U/^{238}U$, $^{234}U/^{238}U$, and $^{238}U/^{235}U$ in groundwater samples to determine the source of contamination at the Hanford Site. Typical precisions (2σ) for the ratios of $^{236}U/^{238}U$, $^{234}U/^{238}U$, and $^{238}U/^{235}U$ were ±0.15%, ±0.15%, and ±0.05%, respectively (D27).

$^{240}Pu/^{239}Pu$ was measured in Arctic Ocean sediments with MC-ICPMS. Data suggested that Pu from sources in the Kara Sea and Novaya Zemlya was transported towards the North Atlantic Ocean (D28).

Hyphenated techniques for speciation analysis. ICPMS has also been essential to speciation analysis. It is important to understand metal speciation in the environment in order to understand the fate, uptake, and beneficial or toxic effects of metals and organometallic compounds. The use of SF-ICPMS and MC-ICPMS in speciation analyses has been reviewed (D29). Another recent review highlighted the use of plasma-source mass spectrometry, including ICPMS, for speciation analysis (D30). This

excellent review includes technical discussions of each technique presented and information about how a given technique might bias speciation measurements (*eg*. the electrospray source can affect speciation because redox chemistry can occur at electrospray needle).

GC-ICPMS has been used to determine speciation for volatile, organometallic compounds. The advantages of coupling GC and ICPMS include good resolution of analytes provided by GC and the multi-element detection capability, good sensitivity, and low detection limits afforded by ICPMS (D31). However, ICPMS does not always provide as good detection limits as those offered by microwave-induced plasma techniques (which can provide detection limits two orders of magnitude better than those offered by inductively coupled plasmas) or other detectors, for example cold vapor atomic fluorescence spectrometers. GC-SF-ICPMS was used to determine dibutyltin and tributyl tin in marine sediment. Detection limits for dibutyltin and tributyl were 0.3 and 0.4 ng/g, respectively, when a sample size of 0.5 g was used with an extraction procedure consisting of microwave digestion and derivatization with sodium tetraethylborate (D32). Dibutyl tin and tributyl tin can also be determined by LC-ICPMS. GC- and LC-ICPMS measured comparable concentrations of dibutyl tin and tributyl tin in sediment. However, because the GC peaks had larger signal-to-noise ratios than did the LC peaks, detection limits for these compounds by GC-ICPMS, ~0.03 pg, were a factor of ten better than those obtained by LC-ICPMS (D33).

GC-ICPMS was used to determine methyl mercury in water samples that were previously derivatized with tetraethyl borate, trapped on Tenax, and thermally desorbed into the GC. No artifact formation of methyl mercury (which is a problem in some other

sample preparation methods) was observed and detection limits of 4 pg/L (measured as Hg) were obtained when derivatizing a 100-mL water sample (D34). Methyl mercury was determined in tissues using microwave extraction with acetic acid, SPME, and GC-ICPMS. A detection limit of 4 pg/g was obtained and the method was validated using known reference materials (D35). SPME was also used in concert with sodium tetraethyl borate derivatization to determine 10 organometallic species composed of Pb, Hg, and Sn. Detection limits were <1 pg/g for the organo-Pb and organo–Sn compounds; detection limits for organo-Hg compounds were somewhat higher at ~ 1 pg/g (D36).

A method for the simultaneous extraction and analysis of methyl mercury and tributyl tin in biological samples was developed. Microwave assisted extraction and derviatization with tetramethyl ammonium hydroxide preceded GC-ICPMS analysis. Detection limit for methyl mercury and tributyl tin was ~0.1 μg/kg when a 0.25 g sample was used (D37)

The use of LC-ICPMS for determination of inorganic and organic arsenic speciation was reviewed (D38). This review lists 11 different arsenic compounds of environmental relevance, which are typically detected (as As) in amounts of 50-300 pg. A problem to overcome when coupling LC and ICPMS for the analysis of As include a potential interference of $^{40}Ar^{35}Cl$ that shares the same nominal mass as As; with proper correction, this interference can be subtracted from the analyte signal. In addition, when coupling LC and ICPMS, only volatile buffers can be used in the LC mobile phase. LC-SF-ICPMS was used to determine arsenic species in freshwater fish. Using a MicroMist nebulizer preceded by a high-pressure splitter, As detection limits in sample extracts were 1-2 ng/L (D39). Ion chromatography (IC) has also been coupled with ICPMS to provide

As speciation. IC-ICPMS was used to resolve and detect eight As species in waters at concentrations of 0.03-2 μg/L (D40).

LC-ICPMS can also be used for Se speciation measurements. Detection limits for selenate, selenite, and trimethylselenonium ion, selenomethionine, and selenoethionine ranged from 0.2-0.4 pg/L. Detection limits using LC-microwave-induced plasma mass spectrometry were slightly better at ~0.1 pg/L for all analytes (D41).

LC-ICPMS was used to determine Pt (contaminant from catalytic exhaust converters in automobiles) in extracts of road dust samples; calculated method detection limit was 0.6 μg Pt per liter sample extract (corresponding to ~2 ng/g in dusts). Measured concentration of Pt in dust was ~1 ng/g; this number is below the calculated detection limit which suggested that the extraction procedure requires optimization (D42).

Coupled with laser ablation. There has been interest in coupling laser ablation with ICPMS (LA-ICPMS). LA-ICPMS allows the determination of many trace elements with high spatial resolution, provides low detection limits (ng/g), consumes a minimal amount of sample, requires almost no sample preparation, and affords the opportunity for determining the depth-profiles of analytes in a sample. A new instrument for LA-ICPMS provided detection of tens to hundreds of femtograms of material and offered isotope-ratio measurements with precisions greater than 0.02% RSD (D43). LA-ICPMS was used to measure Pb isotope ratios in minerals; the precision for isotope measurements was affected by the focus of the laser and the conditions of the plasma (*eg*. a mixed Ar/N_2 plasma significantly increased sensitivity and reduced mass bias, D44). LA-ICPMS, with minimal sample preparation, was used to determine $^{235}U/^{238}U$, an indicator of depleted

uranium contamination, in soils with total U concentrations of ~ 1mg/kg (D45). LA-SF-ICPMS was used to determine 0.3 pg/g Pu in contaminated soils; isotope dilution successfully compensated for matrix effects (D46).

Nuclear Magnetic Resonance (NMR). Although the use of NMR in the study of environmental humic acids was first reported in 1989 (E1), it has only been within the past 5-7 years that NMR has been routinely used to investigate the structure of humic acids and to elucidate the interactions between environmental contaminants and soils. Improvements in NMR instrumentation (*eg*. the introduction of ultrahigh field NMR instruments and the development of cryogenic probe technology) with lower detection limits and the development of 2-D analysis techniques have allowed NMR to become an important tool in environmental analysis. In our *Environmental Analysis* review of 2003, NMR was discussed in the "Emerging Detection Techniques" section. Because the number of examples of the application of NMR to environmental problems has increased, its discussion with other commonly-used analytical techniques is now justified. A comprehensive review of NMR applied to environmental science (202 references cited) has been published which discusses the use of the technique to characterize humic substances, to study the sorption of compounds to humic materials and soils, and to analyze environmental contaminants and their degradation products (E2). Selected applications of the use of NMR to study the environment are cited below.

As reported in the previous review, NMR continues to be used to study dissolved organic matter (DOM) and biosolids. NMR was used to study the differences between DOM that was collected using SPE and DOM that was collected using ultrafiltration. 2-D NMR experiments showed that, while sugars were present in DOM isolated by both

techniques, DOM collected by SPE was composed of aliphatic esters, ethers, and hydroxyl groups and that DOM collected by ultrafiltration consisted of peptides/protein and aliphatic/fatty acid material (E3). Solid-state CPMAS ^{13}C NMR was used to study humic acid that had been fractionated by molecular size using ultrafiltration. The fractions larger than 100,000 Daltons were primarily aliphatic in character and the fractions smaller than 30,000 Daltons were dominated by aromatic compounds (E4). ^{1}H-NMR, along with GC/MS and LC/MS, was used to determine that 2,4-dichlorobenzoic acid was a component of chromophoric DOM. Data also suggested that polychlorinated biphenyl carboxylic acids, which had not previously been reported as components of chromophoric DOM, were present; however, the identity of these compounds must be verified when authentic standards become available (E5). A long-studied Laurentian fulvic acid was examined by 1-D and 2-D NMR techniques; the NMR data supported the mesostructural model of the fulvic acid and the presence of a carbohydrate base with strong metal binding moieties (E6). ^{13}C-NMR and several 2-D NMR experiments were used to determine that N-acetylated polysaccharides were present in the hydrophilic, high molecular weight fraction of biosolids and that the hydrophobic, high molecular weight fraction contained N-acetylated polysaccharides and aromatic compounds; DRIFT spectroscopy also confirmed these findings (E7). LC-NMR and LC-SPE NMR was used to study natural organic mater from oceans; SPE was advantageous because it afforded concentration, and, therefore, easier detection of components being studied (E8).

NMR is useful for the identification of environmental contaminants. ^{1}H-^{31}P HSQMBC, HSQC, and ^{31}P decoupled HSQC NMR experiments were used to screen solutions for the presence of ppm concentrations of organophosphorus compounds

relevant to the Chemical Weapons Convention (E9). Solution ^{31}P-NMR, along with a two-step extraction procedure, was used to identify phosphorus compounds in manure. Water and $NaHCO_3$ extracted soluble DNA, phospholipids, and simple phosphate monoesters; these compounds were weakly sorbed to soil and mobile. NaOH and HCl extracted poorly soluble phosphorus compounds that were immobile in soil; the composition of this fraction was almost all phytic acid (E10). In another study, MAS and CP-MAS ^{31}P-NMR and ^{31}P{^{27}Al}-TRAPDOR were used to investigate phosphorus speciation in alum-amended and non-amended poultry litter. A complex mix of organic and inorganic orthophosphate phases was present and, in the alum-amended poultry litter, phosphate associated with Al comprised ~40% of the total phosphorous. This finding explained why amending poultry litter with alum reduced water-soluble phosphorus (E11).

^{99}Tc-NMR data suggested that Tc(I)-carbonyl species, in particular *fac*-$Tc(CO)_3(gluconate)^{2-}$, were the previously unknown Tc species present in Hanford waste tanks that were not removed during pertechnetate ion exchange (E12). Having identified these species, strategies for their removal from the waste stream can be developed.

NMR has also been used to study the binding of analytes to soils. ^{19}F NMR was used to study binding of trifluralin to soil; data suggested that the 2,6-diamino product of trifluralin reduction with iron and a 1,2-diaminotrifluralin derivative formed covalent bonds with fulvic acid (E13). ^{19}F NMR was used to study the sorption of hexafluorobenzene to humic acid and to suggest that several different binding sites were present. Hexafluorobenzene was less mobile in the large, aliphatic fractions of humic acid (E4). ^{1}H NMR and CPMAS ^{13}C NMR was used, along with various chemical

treatment protocols, to study the sorption of phenanthrene to humic acids from different sources; aromatic and carbohydrate compounds were found to be important to analyte sorption (E14).

In the future, NMR-based metabolomics might be used to provide rapid, multibiomarker analyses to assess the chronic effects of chemical, physical, and biological stressors on environmental organisms. NMR-based metabolomics (using 1-D ^{1}H-NMR and 2-D NMR techniques), along with pattern recognition, was used to study withering syndrome in red abalone and could successfully distinguish healthy, stunted, and diseased organisms (E15). ^{1}H NMR, along with principal component analysis, was used to detect potential biomarkers in earthworms that indicated exposure to toxic metals (E16). The continued use of NMR to study environmental samples suggests that NMR has become a standard tool applied to environmental problems; NMR will provide data that will aid our understanding of the complex nature of natural materials and the way in which they interact with environmental contaminants.

EMERGING DETECTION TECHNIQUES

Accelerator Mass Spectrometry (AMS). AMS is a technique in which a high-energy accelerator (with terminal voltages of 0.2-5 MeV) is used to selectively detect ions. Typically, negative ions are generated in a cesium sputter source, pre-accelerated to 30-200 keV, and mass analyzed by a magnet. The mass-analyzed negative ions are again accelerated to the positive, high voltage terminal of the accelerator and detected by a particle detector. Radiocarbon (^{14}C) dating is the most common application of AMS. However, other nuclides, such as ^{10}Be, ^{36}Cl, ^{26}Al, ^{99}Tc, ^{129}I, ^{236}U, ^{237}Np, ^{239}Pu, and ^{240} Pu, can also be detected by AMS (F1). Advantages of AMS include low detection limits (1

x 10^6 ions can be detected) and excellent selectivity; disadvantages of AMS include its high equipment costs and the fact that only specialized facilities perform AMS experiments.

^{239}Pu and ^{240}Pu have been measured, using AMS, in environmental and bioassay samples (F2); the ability to perform these measurements is important because the ratio of the plutonium isotopes provides information about releases from nuclear weapons production and from the nuclear industry. Relatively low ^{240}Pu/^{239}Pu ratios were found in Asanov Swamp samples (water, vegetation, and biota), indicating contamination from early discharges of weapons-grade plutonium; ^{236}U/^{235}U ratios were found to be different between weapons and civil sources (F3). ^{129}I concentrations measured by AMS were 20-times higher in Norwegian coastal waters impacted by nuclear reprocessing facilities, ~3 x 10^{10} atoms/L, than were measured in the Arctic Ocean, ~1.5 x 10^7 atoms/L (F4).

^{14}C measurements by AMS are important to the environmental community. Compound-specific, ^{14}C measurements were made on PAH from sediments from an urban reservoir and used to determine that, because the PAH in these sediments were ^{14}C-free, most of the PAH in these sediments were derived from fossil fuel combustion, rather than biomass burning (F5). Another study used compound-specific, ^{14}C measurements to investigate whether a bipyrrolic halogenated organic compound had an anthropogenic or biogenic source; the presence of detectable ^{14}C in the sample suggested a biogenic source (F6).

High-field asymmetric waveform ion mobility spectrometry (FAIMS). FAIMS is a technology that provides separation of ions at atmospheric pressure. When combined with chromatographic separation and mass spectrometry, it affords a great

degree of analytical specificity. The history, principles of operation, and application of FAIMS to the analysis of inorganic ions, organometalic ions, and organic ions has been described in a recent review (F7). FAIMS has been used in studies that require both the characterization and quantification of environmental contaminants. FAIMS combined with different mass spectrometric techniques was used in the characterization of naphthenic acids from commercial and naturally occurring sources; FAIMS coupled with MS/MS provided more structural information about naphthenic acids than could be obtained by other techniques (F8).

ESI-FAIMS-MS and ESI-FAIMS-MS/MS were used to characterize arsenic species in tissues from marine fauna. While sample preparation protocols helped eliminate matrix interferences so that many arsenic species could be determined by ESI-MS, FAIMS coupled with MS provided a greater degree of matrix removal, improving the signal-to-noise ratios of minor arsenic species and, thus, allowing the identification of arsenocholine and tetramethylarsonium ion in the samples (F9).

ESI-FAIMS-MS was used to directly determine haloacetic acids in drinking water; sub-µg/L detection limits could be obtained without any sample preparation or chromatographic separation (F10).

As FAIMS has been called a "new technology that offers significant promise for extending the capability of mass spectrometry to solve problems in chemical analysis" (F7), we expect that this technology will find increasing use in the field of environmental analysis. Currently, the major limitation of FAIMS coupled with mass spectrometry is that the user must have some knowledge of the analytes of interest in order to select appropriate ions to be monitored.

Miscellaneous Techniques. In this section, we include several techniques that appear to be of interest but that do not neatly fall into the previously discussed categories. Earlier, we mentioned that MIPs had been used as SPE materials. MIPs also offer the promise of functioning as selective substrates for sensors. An atrazine-selective MIP was used as a coating on an electrochemical sensor and used to demonstrate response to atrazine concentrations in solution of ~100 μg/L (F11). Parathion sensors based on a molecularly imprinted sol-gel film deposited on electrodes (liquid detection) and a quartz resonator (gas detection) were developed and tested. While non-specific binding of gas-phase analytes to the surface was a problem, this problem was not as severe when liquid samples were tested (F12).

A new, aromatic-compound-selective detector for GC was described. Multiphoton ionization at atmospheric pressure was achieved by the use of a diode-pumped, passively Q-switched, microchip laser. When interfaced with fast GC, detection limits for toluene, ethyl benzene, and xylene were < 1 pg; negligible signals were observed for non-aromatic compounds at injected amounts of ~ 100 ng. Because of its excellent detection limits and selectivity, this detector might prove to be a replacement to the traditional photoionization detector (F13).

Two-step laser mass spectrometry (L2MS) was used to measure PAH in water. A 30-mL sample was extracted from water into a solid PVC membrane, which was examined direcly with L2MS. Detection limits of 2-125 ng/L were obtained (F14). This technique was also used to determine PAH in Swiss Alpine aerosols collected on filters (F15). Advantages of this technique are that is a "soft ionization process" (*ie*. molecular

ions are produced), it is a sensitive technique, and that it requires little sample preparation.

Another two-step laser desorption/ionization experiment was performed with an aerosol time-of-flight mass spectrometer (ATOFMS) to determine pesticide residues on individual particles. Detection limits for pesticides adsorbed to soil particles ranged from 1 ppm for malathion to 1 part-per-thousand for atrazine and permethrin (F16).

ANALYTES OF EMERGING INTEREST

Monitoring of known environmental contaminants that have the potential to adversely affect human health, for example chlorinated dioxins, pesticides, and metals, continues. As analytical instruments evolve, detection limits improve, and new analytical methods are developed, new compounds of potential concern emerge. Table 2 summarizes some of the compounds of recent interest and the extraction and detection methods that have allowed their analyses. Some of the compounds of special interest over the past two years have included perfluorinated acids, polybrominated diphenyl ethers, phthalates, pharmaceutical compounds, perchlorate, and arsenic.

DISCLAIMER AND AUSPICES STATEMENT

not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or the University of California, and shall not be used for advertising or product endorsement purposes.

This work was performed under the auspices of the U.S. Department of Energy by University of California, Lawrence Livermore National Laboratory under Contract W-7405-Eng-48.

BIOGRAPHICAL INFORMATION

Carolyn J. Koester *is an analytical chemist working in the Forensic Science Center at the Lawrence Livermore National Laboratory. She earned a Ph.D. from Indiana University, Bloomington, Indiana, under the direction of Distinguished Professor Ronald A. Hites and performed postdoctoral work at Trent University, under the direction of Professor Raymond March, and with the Ministry of Environment, Ontario, Canada. Her current interests include the application of mass spectrometry and field-portable instrumentation to problems of environmental security and helping Casper and Wendy, two retired racing greyhounds, to enjoy their life as "40-mile-an-hour, couch potatoes" and to help them find homes for their newly-retired friends.*

Amal Moulik *is a technical information specialist working in the Library at Lawrence Livermore National Laboratory. He earned a M.S. in chemistry from the University of Michigan, Ann Arbor, Michigan and a M.L.S. from Case Western Reserve University, Cleveland, Ohio. Between his two degrees, he worked for the Gmelin Institute in*

Frankfurt, Germany and was the first inhouse author of Gmelin Handbooks written in English, covering mononuclear organometallic iron compounds. His special interests in the commercialization of technology and intellectual property led him to pursue the patent bar exam, which he passed seven years ago, being recognized as a U.S. patent agent.

LITERATURE CITED

(A1) Koester, C. J.; Simonich, S. L.; Esser, B. K. *Anal. Chem*. **2003**, *75*, 2813-2829.

(A2) Richardson, S. D. *Anal. Chem*. **2004**, *76*, 3337-3364.

(A3) Butler, O. T.; Cook, J. M.; Harrington, C. F.; Hill, S. J.; Rieuwerts, J.; Miles, D. L. *J. Anal. At. Spectrom.* **2005**, *20*, 130-157.

SAMPLE COLLECTION AND EXTRACTION METHODS

(B1) Pawliszyn, J. *Anal. Chem*. **2003**, *75*, 2543-2558.

(B2) Mayer, P.; Tolls, J.; Hermens, J. L. M.; Mackay, D. *Environ. Sci. Technol.* **2003**, *37*, 184A-191A.

(B3) Meijer, S. N.; Ockenden, W. A.; Steinnes, E.; Corrigan, B. P.; Jones, K. C. *Environ. Sci. Technol.* **2003**, *37*, 454-461.

(B4) Jaward, F. M; Farrar, N. J.; Harner, T.; Sweetman, A. J.; Jones, K. C. *Environ. Toxicol. Chem.* **2004**, *23*, 1355-1364.

(B5) Jaward, F. M; Farrar, N. J.; Harner, T.; Sweetman, A. J.; Jones, K. C. *Environ. Sci. Technol.* **2004**, *38*, 34-41.

(B6) Bartkow, M. E.; Huckins, J. N.; Müller, J. F. *Atmos. Environ*. **2004**, *38*, 5983-5990.

(B7) Söderström, H. S.; Bergqvist, P. A. *Environ. Sci. Technol.* **2004**, *38*, 4828-4834.

(B8) Harner, T.; Farrar, N. J.; Shoeib, M.; Jones, K. C.; Gobas, F. A. P. C. *Environ. Sci. Technol.* **2003**, *37*, 2486-2493.

(B9) Wania, F.; Shen, L.; Lei, Y. D.; Teixeira, C.; Muir, D. C. G. *Environ. Sci. Technol.* **2003**, *37*, 1352-1359.

(B10) Zabiegała, B.; Górecki, T.; Namieśnik, J. *Anal. Chem*. **2003**, *75*, 3182-3192.

(B11) Louch, J.; Allen, G.; Erickson, C.; Wilson, G.; Schmedding, D. *Environ. Sci. Technol.* **2003**, *37*, 1202-1207.

(B12) Hyne, R. V.; Pablo, F.; Aistrope, M.; Leonard, A. W.; Ahmad, N. *Environ. Toxicol. Chem*. **2004**, *23*, 2090-2098.

(B13) Balmer, M. E.; Poiger, T.; Droz, C.; Romanin, K.; Bergqvist, P.-A.; Müller, M. D.; Buser, H.-R. *Environ. Sci. Technol.* **2004**, *38*, 390-395.

(B14) Wang, Y.; Huang, Y. S.; Huckins, J. N.; Petty, J. D. *Environ. Sci. Technol.* **2004**, *38*, 3689-3697.

(B15) Carls, M. G.; Holland, L.G.; Short, J. W.; Heintz, R. A.; Rice, S. D. *Environ. Toxicol. Chem*. **2004**, *23*, 1416-1424.

(B16) Booij, K.; Hoedemaker, J. R.; Bakker, J. F. *Environ. Sci. Technol.* **2003**, *37*, 4213-4220.

(B17) Wennrich, L.; Vrana, B.; Popp, P.; Lorenz, W. *J. Environ. Monitoring* **2003**, *5*, 813-822.

(B18) LeBlanc, C. J.; Stallard, W. M.; Green, P. G.; Schroeder, E. D. *Environ. Sci. Technol.* **2003**, *37*, 3966-3971.

(B19) Martin, H.; Patterson, B. M.; Davis, G. B. *Environ. Sci. Technol.* **2003**, *37*, 1360-1364.

(B20) Booij, K.; Hofmans, H. E.; Fischer, C. V.; Van Weerlee, E. M. *Environ. Sci. Technol.* **2003**, *37*, 361-366.

(B21) Vinturella, A. E.; Burgess, R. M.; Coull, B. A.; Thompson, K. M.; Shine, J. P. *Environ. Sci. Technol*. **2004**, *38*, 1154-1160.

(B22) Lyytikainen, M.; Hirva, P.; Minkkinen, P.; Hamalainen, H.; Rantalainen, A. L.; Mikkelson, P.; Paasivirta, J.; Kukkonen, J. V. K. *Environ. Sci. Technol.* **2003**, *37*, 3926-3934.

(B23) Huckins, J. N.; Prest, H. F.; Petty, J. D.; Lebo, J. A.; Hodgins, M. M.; Clark, R. C.; Alvarez, D. A.; Gala, W. R.; Steen, A.; Gale, R.; Ingersoll, C. G. *Environ. Toxicol. Chem.* **2004**, *23*, 1617-1628.

(B24) Wenzel, K.-D.; Vrana, B.; Hubert, A.; Schüürmann, G. *Anal. Chem*. **2004**, *76*, 5503-5509.

(B25) Liu, M. M.; Zeng, Z. R.; Wang, C. L.; Tan, Y. J.; Liu, H. *Chromatographia,* **2003**, *58*, 597-605.

(B26) Davoli, E.; Gangai, M. L.; Morselli, L.; Tonelli, D. *Chemosphere*, **2003**, *51*, 357-368.

(B27) Ferrari, F.; Sanusi, A.; Millet, M.; Montury, M. *Anal. Bioanal. Chem*. **2004**, *379*, 476-483.

(B28) Isetun, S.; Nilsson, U.; Colmsjö, A. *Anal. Bioanal. Chem*. **2004**, *380*, 319-324.

(B29) Chen, Y.; Pawliszyn, J. *Anal. Chem*. **2003**, *75*, 2004-2010.

(B30) Lestremau, F.; Andersson, F. A. T.; Desauziers, V.; Fanlo, J.-L. *Anal. Chem*. **2003**, *75*, 2626-2632.

(B31) Chen, Y.; Pawliszyn, J. *Anal. Chem*. **2004**, *76*, 6823-6828.

(B32) Xiong, G. H.; Chen, Y.; Pawliszyn, J. *J. Chromatogr. A*, **2003**, *999*, 43-50.

(B33) Tuduri, L.; Desauziers, V.; Fanlo, J. L. *Analyst*, **2003**, *128*, 1028-1032.

(B34) Koziel, J. A.; Martos, P. A.; Pawliszyn, J. *J. Chromatogr. A*, **2004**, *1025*, 3-9.

(B35) Diaz, A.; Ventura, F.; Galceran, T. *J. Chromatogr. A*, **2005**, *1064*, 97-106.

(B36) Blasco, C.; Font, G.; Mañes, J.; Picó, Y. *Anal. Chem*. **2003**, *75*, 3606-3615.

(B37) Polo, M.; Gómez-Noya, G.; Quintana, J. B.; Llompart, M; García-Jares, C.; Cela, R. *Anal. Chem*. **2004**, *76*, 1054-1062.

(B38) Conder, J. M.; La Point, T. W.; Lotufo, G.; Steevens, J. A. *Environ. Sci. Technol.* **2003**, *37*, 1625-1632.

(B39) Zeng, E. Y.; Tsukada, D.; Diehl, D. W. *Environ. Sci. Technol*. **2004**, *38*, 5737-5743.

(B40) Cho, H. J.; Baek, K.; Lee, H. H.; Lee, S. H.; Yang, J. W. *J. Chromatogr. A*, **2003**, *988*, 177-184.

(B41) Chou, C. C.; Lee, M. R. *J. Chromatogr. A*, **2005**, *1064*, 1-8.

(B42) Tsai, S. W.; Chang, C. M. *J. Chromatogr. A*, **2003**, *1015*, 143-150.

(B43) Zimmermann, T.; Ensinger, W. J.; Schmidt, T. C. *Anal. Chem*. **2004**, *76*, 1028-1038.

(B44) Wei, M. C.; Jen, J. F. *J. Chromatogr. A*, **2003**, *1012*, 111-118.

(B45) Heringa, M. B.; Hermens, J. L. M. *TRAC-Trends Anal. Chem*. **2003**, *22*, 575-587.

(B46) Lee, S.; Gan, J.; Liu, W. P.; Anderson, M. A. *Environ. Sci. Technol.* **2003**, *37*, 5597-5602.

(B47) Van der Wal, L.; Jager, T.; Fleuren, R. H. L. J.; Barendregt, A.; Sinnige, T. L.; Van Gestel, C. A. M.; Hermens, J. L. M. *Environ. Sci. Technol*. **2004**, *38*, 4842-4848.

(B48) Rasmussen, K. E.; Pedersen-Bjergaard, S. *TRAC-Trends Anal. Chem*. **2004**, *23*, 1-10.

(B49) Basheer, C.; Balasubramanian, R.; Lee, H. K. *J. Chromatogr. A*, **2003**, *1016*, 11-20.

(B50) Jiang, X.; Lee, H. K. *Anal. Chem***. 2004**, *76*, 5591-5596.

(B51) Cai, Y.; Jiang, G.; Liu, J.; Zhou, Q. *Anal. Chem*. **2003**, *75*, 2517-2521.

(B52) Haupt, K. *Anal. Chem*. **2003**, *75*, 377A-383A.

(B53) Sandau, C. D.; Sjödin, A.; Davis, M. D.; Barr, J. R.; Maggio, V. L.; Waterman, A. L.; Preston, K. E.; Preau, J. L. Jr.; Barr, D. B.; Needham, L. L.; Patterson, D. J. Jr. *Anal. Chem.* **2003**, *75*, 71-77.

(B54) Paleologos, E. K.; Kontominas, M. G. *Anal. Chem*. **2004**, *76*, 1289-1294.

(B55) Bruzzoniti, M. C.; Sarzanini, C.; Mentasti, E. *J. Chromatogr. A*, **2000**, *902*, 289-309.

(B56) Rao, T. P.; Praveen, R. S.; Daniel, S. *Crit. Rev. Anal. Chem*. **2004**, *34*, 177-193.

(B57) Gazda, D. B.; Fritz, J. S.; Porter, M. D. *Anal. Chem*. **2004**, *76*, 4881-4887.

(B58) Rao, T. P.; Daniel, S.; Gladis, J. M. *TRAC-Trends Anal. Chem*. **2004**, *24*, 28-35.

(B59) Lu, Y.-K.; Yan, X.-P. *Anal. Chem*. **2004**, *76*, 453-457.

IMPORTANT SEPARATION AND DETECTION TECHNIQUES

(C1) Anderson, J. L.; Armstrong, D. W. *Anal. Chem*. **2003**, *75*, 4851-4858.

(C2) Ding, J.; Welton, T.; Armstrong, D. W. *Anal. Chem*. **2004**, *76*, 6819-6822.

(C3) Miller, S. *Anal. Chem*. **2004**, *76*, 99A-101A.

(C4) Lee, W. Y.; Iannucci-Berger, W. A.; Eitzer, B. D.; White, J. C.; Mattina, M. I. *Chemosphere* **2003**, *53*, 111-121.

(C5) Wong, C. S.; Mabury, S. A.; Whittle, D. M.; Backus, S. M.; Teixeira, C.; DeVault, D. S.; Bronte, C. R.; Muir, D. C. G. *Environ. Sci. Technol*. **2004**, *38*, 84-92.

(C6) Gotsch, A.; Mariussen, E.; von der Recke, R.; Herzke, D.; Berger, U.; Vetter, W. *J. Chromatogr. A*, **2005**, *1063*, 193-199.

(C7) Larsson, C.; Norström, K.; Athanansiadis, I.; Bignert, A.; König, W. A. *Environ. Sci. Technol.* **2004**, *38*, 4950-4955.

(C8) Liu, W. P.; Gan, J. J. *J. Agricult. Food Chem.* **2004**, *52*, 755-761.

(C9) Hashimoto, S.; Yoshimoto, T.; Nakao, M.; Omura, H.; Yamashita, N.; Kannan, K.; Giesy, J. P. *J. Separation Sci. 2003*, *26*, 903-907.

(C10) Li, Z. Y.; Zhang, Z. C.; Zhou, Q. L.; Wang, Q. M.; Gao, R. Y.; Wang, Q. S. *J. AOAC International*, **2003**, *86*, 521-528.

(C11) Mancini, F.; Fiori, J.; Bertucci, C.; Cavrini, V.; Bragieri, M.; Zanotti, M. C.; Liverani, A.; Borzatta, V.; Andrisano, V. *J. Chromatogr. A*, **2004**, *1046*, 67-73.

(C12) Desai, M. J.; Armstrong, D. W. *J. Chromatogr. Sci*. **2004**, *1035*, 203-210.

(C13) Anigbogu, V. C.; Woldeab, H.; Garrison, A. W.; Avants, J. K. *Int. J. Environ. Anal. Chem.* **2003**, *83*, 89-100.

(C14) Gong, Y.; Lee, H. K. *Anal. Chem*. **2003**, *75*, 1348-1354.

(C15) Dalluge, J.; Beens, J.; Brinkman, U. A. T. *J. Chromatogr. A*, **2003**, *1000*, 69-108.

(C16) Reichenbach, S. E.; Ni, M. T.; Kottapalli, V.; Visvanathan, A. *Chemometrics Intelligent Lab. Systems*, **2004**, *71*, 107-120.

(C17) Welthagen, W.; Schnelle-Kreis, J.; Zimmermann, R. *J. Chromatogr. A*, **2003**, *1019*, 233-249.

(C18) Xu, X.; van Stee, L. L. P.; Williams, J.; Beens, J.; Adahchour, M.; Vreuls, R. J. J.; Brinkman, U. A. T.; Lelieveld, J. *Atmos. Chem. Phys*. **2003**, *3*, 665-682.

(C19) Korytár, P.; van Stee, L. L. P.; Leonards, P. E. G.; de Boer, J.; Brinkman, U. A. T. *J. Chromatogr. A*, **2003**, *994*, 179-189.

(C20) Frysinger, G. S.; Gaines, R. B.; Xu, L.; Reddy, C. M. *Environ. Sci. Technol*. **2003**, *37*, 1653-1662.

(C21) Focant, J. F.; Sjödin, A.; Turner, W. E.; Patterson, D. G. *Anal. Chem*. **2004**, *76*, 6313-6312.

(C22) Focant, J. F.; Reiner, E. J.; MacPherson, K.; Kolic, T.; Sjödin, A.; Patterson, D. G. Jr.; Reese, S. L.; Dorman, F. L.; Cochran, J. *Talanta* **2004**, *63*, 1231-1240.

(C23) Korytár, P.; Danielsson, C.; Leonards, P. E. G.; Haglund, P.; de Boer, J.; Brinkman, U. A. T. *J. Chromatogr. A,* **2004**, *1038*, 189-199.

(C24) Kallio, M.; Hyötyläinen, T.; Lehtonen, M.; Jussila, M.; Hartonen, K.; Shimmo, M.; Riekkola, M. L. *J. Chromatogr. A*, **2003**, *1019*, 251-260.

(C25) van Stee, L. L. R.; Beens, J.; Vreuls, R. J. J.; Brinkman, U. A. T. *J. Chromatogr. A*, **2003**, *1019*, 89-99.

(C26) Shellie, R.; Marriott, P.; Leus, M.; Dufour, J. P.; Mondello, L.; Dugo, G.; Sun, K.; Winniford, B.; Griffith, J.; Luong, J. *J. Chromatogr. A*, **2003**, *1019*, 273-278.

(C27) Shellie, R.; Marriott, P.; Morrison, P.; Mondello, L. *J. Separation Sci.* **2004**, *27*, 504-512.

(C28) Gaines, R. B.; Frysinger, G. S. *J. Separation Sci*. **2004**, *27*, 380-388.

(C29) Van Mispelaar, V. G.; Tas, A. C.; Smilde, A. K.; Schoenmakers, P. J. van Asten, A. C. *J. Chromatogr. A*, **2003**, *1019*, 15-29.

(C30) Harynuk, J.; Gorecki, T. *J. Separation Sci*. **2004**, *27*, 380-388.

(D1) Zwiener, C.; Frimmel, F. H. *Anal. Bioanal. Chem*. **2004**, *378*, 851-861.

(D2) Ferrer, I.; Thurman, E. M. *TRAC-Trends Anal. Chem.* **2003**, *22*, 750-756.

(D3) Thurman, E. M.; Ferrer, I.; Furlong, E. T. *Liquid Chromatography/Mass Spectrometry, MS/MS and Time-of-Flight MS (ACS Symposium Series)*, **2003**, *850*, 128-144.

(D4) Ferrer, I.; Heine, C. E.; Thurman, E. M. *Anal. Chem*. **2004**, *76*, 1437-1444.

(D5) Schauer, C.; Niessner, R.; Poschl, U. *Anal. Bioanal. Chem*. **2004**, *378*, 725-736.

(D6) Maizels, M.; Budde, W. L. *Anal. Chem*. **2004**, *76*, 1342-1351.

(D7) Eichhorn, P.; Aga, D. S. *Anal. Chem*. **2004**, *76*, 6002-6011.

(D8) Ibáñez, M.; Sancho, J. V.; Pozo, Ó. J.; Hernández, F. *Anal. Chem*. **2004**, *76*, 1328-1335.

(D9) Ibáñez, M.; Sancho, J. V.; Pozo, Ó. J.; Niessen, W.; Hernández, F. *Rapid Comm. Mass Spectrom.* **2005**, *19*, 169-178.

(D10) Stolker, A. A. M.; Niesing, W.; Hogendoorn, E. A.; Versteegh, J. F. M.; Fuchs, R.; Brinkman, U. A. T. *Anal. Bioanal. Chem*. **2004**, *378*, 955-963.

(D11) Hernández, F.; Ibáñez, M.; Sancho, J. V.; Pozo, Ó. J. *Anal. Chem*. **2004**, *76*, 4349-4357.

(D12) Schmidt, T. C.; Zwank, L.; Elsner, M.; Berg, M.; Mechdenstock, R. U.; Haderlein, S. B. *Anal. Bioanal. Chem*. **2004**, *378*, 283-300.

(D13) Zwank, L.; Berg, M.; Schmidt, T. C.; Haderlein, S. B. *Anal. Chem*. **2003**, *75*, 5575-5583.

(D14) Schmitt, J.; Glaser, B.; Zech, W. *Rapid Commun. Mass Spectrom*. **2003**, *17*, 970-977.

(D15) Dickhut, R. M.; Padma, T. V.; Cincinelli, A. *Environ. Sci. Technol.* **2004**, *38*, 3871-3876.

(D16) Bao, H.; Gu, B. *Environ. Sci. Technol.* **2004**, *38*, 5073-5077.

(D17) Becker, J. S. *Spectrochimica Acta Pt. B—At. Spectros*. **2003**, *58*, 1757-1784.

(D18) Heumann, K. G. *Anal. Bioanal. Chem*. **2004**, *378*, 318-329.

(D19) Profrock, D.; Leonhard, P.; Wilbur, S.; Prange, A. *J. Anal. At. Spectrom*. **2004**, *19*, 623-631.

(D20) Kim, C. S.; Kim, C. K.; Lee, K. J. *J. Anal. At. Spectrom*. **2004**, *19*, 743-750.

(D21) Vondeheide, A. P.; Zoriy, M. V.; Izmer, A. V.; Pickhardt, C.; Caruso, J. A.; Ostapczuk, P.; Hille, R.; Becker, J. S. *J. Anal. At. Spectrom*. **2004**, *19*, 675-680.

(D22) Becker, J. S.; Zoriy, M.; Halicz, L.; Teplyakov, N.; Muller, C.; Segal, I.; Pickhardt, C.; Platzner, I. T. *J. Anal. At. Spectrom*. **2004**, *19*, 1257-1261.

(D23) Novák, M.; Emmanuel, S.; Vile, M. A.; Erel, Y.; Véron, A.; Pačes, T.; Wieder, R. K.; Vaněček, M.; Štěpánová, M.; Břízová, E.; Hovorka, J. *Environ. Sci. Technol.* **2003**, *37*, 437-445.

(D24) Spiro, B.; Weiss, D. J.; Purvis, O. W.; Mikhailova, I.; Williamson, B. J.; Coles, B. J.; Udachin, V. *Environ. Sci. Technol.* **2004**, *38*, 6522-6528.

(D25) Krachler, M.; Zheng, J.; Fisher, D.; Shotyk, W. *Anal. Chem*. **2004**, *76*, 5510-5517.

(D26) Trešl, I.; de Wannemacker, G.; Quétel, C. R.; Petrov, I.; Vanhaecke, R.; Moens, L.; Taylor, P. D. P. *Environ. Sci. Technol*. **2004**, *38*, 581-586.

(D27) Christensen, J. N.; Dresel, P. E.; Conrad, M. E.; Maher, K.; Depaolo, D. L. *Environ. Sci. Technol.* **2004**, *38*, 3330-3337.

(D28) Masqué, P.; Cochran, J. K.; Hebbeln, D.; Hirschberg, D. J.; Dethleff, D.; Winkler, A. *Environ. Sci. Technol.* **2003**, *37*, 4848-4854.

(D29) Moldovan, M.; Krupp, E. M.; Holliday, A. E.; Donard, O. F. X. *J. Anal. At. Spectrom.* **2004**, *19*, 815-822.

(D30) Ray, S. J.; Andrade, F.; Gamez, G.; McClenathan, D.; Rogers, D.; Schilling, G.; Wetzel, W.; Hieftje, G. M. *J. Chromatogr. A*, **2004**, *1050*, 3-45.

(D31) Wuilloud, J. C. A.; Wuilloud, R. G.; Vonderheide, A. P.; Caruso, J. A. *Spectrochim. Acta Pt. B—At. Spectros*. **2004**, 755-792.

(D32) Yang, L.; Mester, Z.; Sturgeon, R. E. *J. Anal. At. Spectrom*. **2003**, *18*, 1365-1370.

(D33) Wahlen, R.; Wolff-Briche, C. *Anal. Bioanal. Chem*. **2003**, *377*, 140-148.

(D34) Lambertsson, L.; Bjorn, E. *Anal. Bioanal. Chem*. **2004**, *380*, 871-875.

(D35) Davis, W. C.; Vander Pol, S. S.; Schantz, M. M.; Long, S. E.; Day, R. D.; Christopher, S. J. *J. Anal. At. Spectrom*. **2004**, *19*, 1546-1551.

(D36) Jitaru, P.; Infante H. G.; Adams, F. C. *J. Anal. At. Spectrom*. **2004**, *19*, 867-875.

(D37) Monperrus, M.; Martin-Doimeadios, R. C. R.; Scancar, J.; Amouroux, D.; Donard, O. F. X. *Anal. Chem*. **2003**, *75*, 4095-4102

(D38) B'Hymer, C.; Caruso, J. A. *J. Chromatogr. A*, **2004**, 1045, 1-13.

(D39) Zheng, J.; Hintelmann, H. *J. Anal. At. Spectrom*. **2004**, *19*, 191-195.

(D40) Karthikeyan, S.; Hirata, S. *Appl. Organomet. Chem*. **2004**, *18*, 323-330.

(D41) Chatterjee, A.; Shibata, Y.; Tao, H.; Tanaka, A.; Morita, M. *J. Chromatogr. A*, **2004**, *1042*, 99-106.

(D42) Nischwitz, V.; Michalke, B.; Kettrup, A. *J. Chromatogr. A*, **2003**, *1016*, 223-234.

(D43) Barnes, J. H.; Schilling, G. D.; Hieftje, G. M.; Sperline, R. P.; Denton, M. B.; Barinaga, C. J.; Koppenaal, D. W. *J. Amer. Soc. Mass Spectrom.* **2004**, *15*, 769-776.

(D44) Crowe, S. A.; Fryer, B. J.; Samson, I. M.; Gagnon, J. E. *J. Anal. At. Spectrom*. **2003**, *18*, 1331-1338.

(D45) Seltzer, M. D. *Appl. Spectros*. **2003**, *57*, 1173-1177.

(D46) Boulyga, S. F.; Tibi, M.; Heumann, K. G. *Anal. Bioanal. Chem*. **2004**, *378*, 342-347.

(E1) Buddrus, J.; Burba, P.; Lambert, J.; Herzog, H. *Anal. Chem*. **1989**, *61*, 628-631.

(E2) Cardoza, L. A.; Korir, A. K.; Otto, W. H.; Wurrey, C. J.; Larive, C. K. *Progress in Nuclear Magnetic Resonance Spectroscopy,* **2004**, *45*, 209-238.

(E3) Kaiser, E.; Simpson, A. J.; Dria, K. J.; Sulzberger, B.; Hatcher, P. G. *Environ. Sci.Technol.* **2003**, *37*, 2929-2935.

(E4) Khalaf, M.; Kohl, S. D.; Klumpp, E.; Rice, J. A.; Tombácz, E. *Environ. Sci. Technol*. **2003**, *37*, 2855-2960.

(E5) Repeta, D. J.; Hartman, N. T.; John, S.; Jones, A. D.; Goericke, R. *Environ. Sci. Technol*. **2004**, *38*, 5373-5378.

(E6) Cook, R. L.; McIntyre, D. D.; Langford, C. H.; Vogel, H. J. *Environ. Sci. Technol*. **2003**, *37*, 3935-3944.

(E7) Mao, J.-D.; Hundal, L. S.; Schmidt-Rohr, K.; Thompson, M. L. *Environ. Sci. Technol.* **2003**, *37*, 1751-1757.

(E8) Simpson, A. J.; Tseng, L. H.; Simpson, M. J.; Spraul, M.; Braumann, U.; Kingery, W. L.; Kelleher, B. P.; Hayes, M. H. B. *Analyst*, **2004**, *129*, 1216-1222.

(E9) Meier, U. C. *Anal. Chem*. **2004**, *76*, 392-398.

(E10) Turner, B. L.; Leytem, A. B. *Environ. Sci. Technol.* **2004**, *38*, 6101-6108.

(E11) Hunger, S.; Cho, H.; Sims, J. T.; Sparks, D. L. *Environ. Sci. Technol.* **2004**, *38*, 674-681.

(E12) Lukens, W. W.; Shuh, D. K.; Schroeder, N. C.; Ashley, K. R. *Environ. Sci. Technol.* **2004**, *38*, 229-233.

(E13) Strynar, M.; Dec, J.; Benesi, A.; Jones, A. D.; Fry, R. A.; Bollag, J.-M. *Environ. Sci. Technol.* **2004**, *38*, 6645-6655.

(E14) Gunasekara, A. S.; Simpson, M. J.; Xing, B. *Environ. Sci. Technol*. **2003**, *37*, 852-858.

(E15) Viant, M. R.; Rosenblum, E. S.; Tjeerdema, R. S. *Environ. Sci. Technol*. **2003**, *37*, 4982-4989.

(E16) Bundy, J. G.; Spurgeon, D. J.; Svendsen, C.; Hankard, P. K.; Weeks, J. M.; Osborn, D.; Lindon, J. C.; Nicholson, J. K. *Ecotoxicology* **2004**, *13*, 797-806.

EMERGING DETECTION TECHNIQUES

(F1) Skipperud, L.; Oughton, D. H. *Environ. International*, **2004**, *30*, 815-825.

(F2) Marchetti, A. A.; Brown, T. A.; Cox, C. C.; Hamilton, T. F.; Martinelli, R. E. *J. Radioanal. Nuc. Chem.* **2005**, *263*, 483-487.

(F3) Borretzen, P.; Standring, W. J. F.; Oughton, D. H.; Dowdall, M.; Fifield, L. K. *Environ. Sci. Technol.* **2005**, *39*, 92-97.

(F4) Alfimov, V.; Aldahan, A.; Possnert, G.; Winsor, P. *Marine Pollut. Bull*. **2004**, *49*, 1097-1104.

(F5) Kanke, H.; Uchida, M.; Okuda, T.; Yoneda, M.; Takada, H.; Shibata, Y.; Morita, M. *Nuc. Instrum. Methods Phys. Res. Sect. B-Beam Interactions with Materials and Atoms*, **2004**, *223-224*, 545-554.

(F6) Reddy, C. M.; Xu, L.; O'Neil, G. W.; Nelson, R. K.; Eglington, T. I.; Faulkner, D. J.; Norstrom, R.; Ross, P. S.; Tittlemier, S. A. *Environ. Sci. Technol*. **2004**, *38*, 1992-1997.

(F7) Guevremont, R. *J. Chromatogr. A*, **2004**, *1058*, 3-19.

(F8) Gabryelski, W.; Froese, K. L. *Anal. Chem*. **2003**, *75*, 4612-4623.

(F9) McSheehy, S.; Mester, Z. *J. Anal. At. Spectrom*. **2004**, *19*, 373-380.

(F10) Gabryelski, W.; Wu, F. W.; Froese, K. L. *Anal. Chem*. **2003**, *75*, 2478-2486.

(F11) Shoji, R.; Takeuchi, T.; Kubo, I. *Anal. Chem*. **2003**, *75*, 4882-4986.

(F12) Marx, S.; Zaltsman, A.; Turyan, I.; Mandler, D. *Anal. Chem*. **2004**, *76*, 120-126.

(F13) Meyer, M.; Schieffer, G. M.; Moeker, E. K.; Brodersen, J. J.; Swenson, O. F.; Borgerding, A. J. *Anal. Chem*. **2004**, *76*, 1702-1707.

(F14) Emmenegger, C.; Kalberer, M.; Morrical, B.; Zenobi, R. *Anal. Chem*. **2003**, *75*, 4508-4513.

(F15) Kalberer, M.; Henne, S.; Prevot, A. S. H.; Steinbacher, M. *Atmos. Environ*. **2004**, *38*, 6447-6456.

(F16) Whiteaker, J. R.; Prather, K. A. *Anal. Chem*. **2003**, *75*, 49-56.

ANALYTES OF EMERGING INTEREST

(G1) Andreu, V.; Picó, Y. *Anal. Chem*. **2004**, *76*, 2878-2885.

(G2) Ali, I.; Jain, C. K. *International J. Environ. Anal. Chem*. **2004**, *84*, 947-964.

(G3) Sloth, J. J.; Larsen, E. H.; Julshamn, K. *Rapid Commun. Mass Spectrom*. **2005**, *19*, 227-235.

(G4) Richardson, S. D.; Thruston, A. D. Jr., Rav-Acha, C.; Groisman, L.; Popilevsky, I.; Juraev, O.; Glezer, V.; McKague, A. B.; Plewa, M. J.; Wagner, E. D. *Environ. Sci. Technol*. **2003**, *37*, 3782-3793.

(G5) Morris, S.; Allchin, C. R.; Zegers, B. N.; Haftka, J. J. H.; Boon, J. P.; Belpaire, C.; Leonards, P. E. G.; Van Leeuwen, S. P. J.; de Boer, J. *Environ. Sci. Technol*. **2004**, *38*, 5497-5504.

(G6) Benijts, T.; Lambert, W.; De Leenheer, A. *Anal. Chem*. **2004**, *76*, 704-711.

(G7) Rodriguez-Mozaz, S.; Lopez de Alda, M. J.; Barceló, D. *Anal. Chem*. **2004**, *76*, 6998-7006.

(G8) Plewa, M. J.; Wagner, E. D.; Jazwierska, P.; Richardson, S. D.; Chen, P. H.; McKague, A. B. *Environ. Sci. Technol*. **2004**, *38*, 62-68.

(G9) Plewa, M. J.; Wagner, E. D.; Richardson, S. D.; Thruston, A. D. Jr.; Woo, Y.-T.; McKague, A. B. *Environ. Sci. Technol*. **2004**, *38*, 4713-4722.

(G10) Schwikowski, M.; Barbante, C.; Doering, T.; Gaeggeler, H. W.; Boutron, C.; Schotterer, U.; Tobler, L.; van de Velde, K.; Ferrari, C.; Cozzi, G.; Rosman, K.; Cescon, P. *Environ. Sci. Technol*. **2004**, *38*, 957-964.

(G11) Rahman, G. M. M.; Kingston, H. M. *Anal. Chem*. **2004**, *76*, 3548-3555.

(G12) Peck, A M.; Hornbuckle, K. C. *Environ. Sci. Technol*. **2004**, *38*, 368-372.

(G13) Charrios, J. W.; Arend, M. W.; Froese, K. L.; Hrudey, S. E. *Environ. Sci. Technol*. **2004**, *38*, 4835-4841.

(G14) Loyo-Rosales, J. E.; Schmitz-Afonso, I.; Rice, C. P.; Torrents, A. *Anal. Chem*. **2003**, *75*, 4811-4817.

(G15) Krynitsky, A. J.; Niemann, R. A.; Nortrup, D. A. *Anal. Chem*. **2004**, *76*, 5518-5522.

(G16) Kärrman, A.; van Bavel, B.; Järnberg, U.; Hardell, L.; Lindström, G. *Anal. Chem*. **2005**, *77*, 864-870.

(G17) Yamashita, N.; Kannan, K.; Taniyasu, S.; Horii, Y.; Okazawa, T.; Petrick, G.; Gamo, T. *Environ. Sci. Technol*. **2004**, *38*, 5522-5528.

(G18) Yu, K.; Krol, K.; Balogh, M.; Monks, I. *Anal. Chem*. **2003**, *75*, 4103-4112.

(G19) Cahill, J. D.; Furlong, E. T.; Burkhardt, M. R.; Koplin, D.; Anderson, L. G. *J. Chromatogr. A*, **2004**, *1041*, 171-180.

(G20) Zuehlke, S.; Duennbier, U.; Heberer, T. *Anal. Chem*. **2004**, *76*, 6548-6554.

(G21) Vanderford, B. J.; Pearson, R. A.; Rexing, D. J.; Snyder, S. A. *Anal. Chem*. **2003**, *75*, 6265-6274.

(G22) Lin, Z.-P.; Ikonomou, M. G.; Jing, H.; Mackintosh, C.; Gobas, F. A. P. C. *Environ. Sci. Technol*. **2003**, *37*, 2100-2108.

(G23) Rauch, S.; Hemond, H. F.; Peucker-Ehrenbrink, B. *Environ. Sci. Technol*. **2004**, *38*, 396-402.

(G24) Söderström, G.; Marklund, S. *Environ. Sci. Technol.* **2004**, *83*, 825-830.

(G25) Wang, D. L.; Cai, Z. W.; Jiang, G. B.; Wong, M. H.; Wong, W. K. *Rapid Commun. Mass Spectrom*. **2005**, *19*, 83-89.

(G26) Sellström, U.; Bignert, A.; Kierkegaard, A.; Häggberg, L.; de Wit, C. A.; Olsson, M.; Jansson, B. *Environ. Sci. Technol*. **2003**, *37*, 5496-5501.

(G27) Sjödin, A.; McGahee, E. E. III; Focant, J.-F.; Jones, R. S.; Lapeza, C. R.; Zhang, Y.; Patterson, D. G. Jr. *Anal. Chem*. **2004**, *76*, 4508-4514.

(G28) Helm, P. A.; Bidleman, T. F.; Li, H. H.; Fellin, P. *Environ. Sci. Technol*. **2004**, *38*, 5514-5521.

(G29) da Silva, A. F.; Dias, L. F.; Saint'Pierre, T. D.; Curtius, A. J.; Welz, B. *J. Anal. At. Spectrom. 18*, 344-349.

(G30) Montauban, C.; Bégos, A.; Bellier, B. *Anal. Chem*. **2004**, *76*, 2791-2797.

Table 1. List of abbreviations used in this article.

1-D — one dimensional
2-D — two dimensional
AED — atomic emission detector
AMS — accelerator mass spectrometry
BTEX — benzene, toluene, ethylbenzenes, and xylenes
CERN — European Organization for Nuclear Research (Geneva, Switzerland)
CPMAS — cross-polarization magic angle spinning spectra (NMR technique)
DPB — (water) disinfection by-product
DDE — dichlorodiphenyldichloroethylene
DOM — dissolved organic matter
DRIFT — diffuse reflectance infrared Fourier transform
DVB — divinyl benzene
ECD — electron capture detector
ESI — electrospray ionization
EVA — ethylene vinyl acetate
FAIMS — high-field asymmetric waveform ion mobility spectrometry
FID — flame ionization detector
FTIR — Fourier transform infrared spectrometer
GC — gas chromatography
GC x GC — two-dimensional gas chromatography
GC/MS — gas chromatography/mass spectrometry
GFF — glass fiber filter
HCB — hexachlorobenzene
HRMS — high resolution mass spectrometry
HSQC — heteronuclear single quantum correlation (NMR technique)
HSQMBC — heteronuclear single quantum multiple bond correlation (NMR technique)
ICPMS — inductively coupled plasma mass spectrometry
IRMS — isotope ratio mass spectrometry
K_d — partition coefficient
K_{ow} — octanol-water partition coefficient
L2MS — two-step laser mass spectrometry
LC — liquid chromatograph
LC/MS — liquid chromatograph/mass spectrometry
LDPE — low density polyethylene
MAS — magic angle spinning (NMR technique)
MC-ICPMS — multiple collector inductively coupled plasma mass spectrometry
MIP — molecularly imprinted polymer
MS — mass spectrometry
MS/MS — mass spectrometry/mass spectrometry
MWNTs — multiwalled carbon nanotubes
NEMI — National Environmental Methods Index
NIOSH — National Institute for Occupational Safety and Health
NMAM — NIOSH Manual of Analytical Methods

NMR — nuclear magnetic resonance
NPD — nitrogen phosphorus detector
PAH — polycyclic aromatic hydrocarbon
PBB — polybromined biphenyl
PBDE — polybrominated diphenyl ether
PCB — polychlorinated biphenyl
PCDD — polychlorinated dibenzodioxin
PCDE — polychlorinated diphenyl ether
PCDF — polychlorinated dibenzofuran
PCN — polychlorinated naphthalene
PDMS — poly(dimethylsiloxane)
PFOA — perfluorooctanoic Acid
PFOS — perfluorooctane sulfonate
PUF — polyurethane foam
PVC — polyvinyl chloride
QTOF/MS — quadrupole mass filter coupled with time-of-flight mass spectrometry
SF-ICPMS — sector field inductively coupled plasma mass spectrometry
SPE — solid phase extraction
SPMD — semi-permeable membrane device
SPME — solid phase microextraction
TCDD — tetrachlorodibenzodioxin
TNT — trinitrotoluene
TOF/MS — time-of-flight mass spectrometry
TRAPDOR – transfer of populations in double resonance (NMR technique)
TRIMPS — trimethyl pentane solvent
TWA — time-weighted average
UV — ultra-violet

TABLE 2. Emerging environmental contaminants and analysis techniques. Note that "dl" indicates detection/reporting limits. Although detection limits are analyte-specific, detection limits are presented as ranges so that the reader may quickly understand the order-of-magnitude concentrations at which certain compound classes have been detected. Unless otherwise noted, all GC/MS data can be assumed to have been collected in the positive, electron ionization mode and all LC/MS data can be assumed to have been collected in the positive, electrospray ionization mode. All abbreviations used in this table have been defined previously in Table 1.

Analyte	Matix	Sample Preparation Method	Detection Technique	Comment	Ref
Alkyl benzene sulfonates & degradation products	Soil	Soxhlet extraction with methanol, SPE clean-up (C_{18})	LC/ESI-MS^2 or MS^3 (negative ESI with ion trap), 4.6 mm x 50 mm, Zorbax SB-Aq, LC column	dl = 0.5-50 µg/kg (LC/MS), 2-400 µg/kg (LC/MS^2), 20-4000 µg/kg (LC/MS^3); 0.1-15 mg/kg analytes detected in soils amended with sewage sludges	G1
Arsenic (As) species	Various			Various separation (GC, LC, IC, CE) & speciation techniques reviewed	G2
Arsenic (As) species--dimethylarsinoyl- acetate, ethanol, and propionate	Various marine species		LC/ICPMS and LC/MS/MS used to elucidate structures	dl = 2-3 µg/kg; compounds reported as naturally occurring in marine samples	G3
Brominated acids, other DBPs	Water	40 L water extracted with XAD resin, most polar compounds derivatized with pentafluorobenzyl-hydroxylamine	GC/MS, GC/HRMS (electron and chemical ionization modes)	New drinking water DBPs indentified	G4
Brominated flame retardants, tetrabromobisphenol A, hexabromocyclododecane	Sewage sludge, sediments, organisms	1-g sludge Soxhlet extracted with acetone/hexane, GPC clean-up	LC/ESI-MS, 2 mm x 150 mm C_{18} LC column,	dl = 0.5-1 µg/kg; first LC/MS method reported for this compound class; total analytes in aquatic organisms varied by location and ranged from not dectected to 7000 µg/kg	G5
Cyanobaceria toxins	Water	100-mL sample adjusted to pH 10, extracted with C_{18} disks	LC/ESI-TOF/MS, 1.0 mm id x 150 mm, C_{18} LC column	dl = 1 µg/L; sample preparation and analysis time of 1 hour	D6
Endocrine disruptors	Water	500-mL sample	LC/ESI-MS/MS	dl = 0.1-20 ng/L; wide-spectrum SPE	G6

		extracted with Oasis HLB	(positive & negative ionization modes), 2 mm x 100 mm, C18, LC column	combined with 2 modes of ionization allowed determination of 35 compounds	
Estrogens	Water	250-mL sample extracted with PLRP polymer	LC/ESI-MS/MS (negative ESI), 2 mm x 125 mm, Purospher STAR-RP-18e LC column	dl = 0.02-1 ng/L; fully automated, on-line SPE-LC-ESI/MS/MS system used to determine eight compounds in 1 hour; only estrone, at 0.7 ng/L, and estrone-3-sulfate, at 0.3 ng/L, detected in river water	G7
Halonitromethanes	Drinking water	Extracted with XAD-2 & XAD-8 resins	GC/HRMS	New halonitromethanes identified as DBPs and their toxicities studied; halonitromethanes are prevalent in waters treated with ozone-chlorine & are difficult to detect because of potential degradation during analysis	G8
Iodoacid DBPs	Water	39-L samples extracted with XAD resin	Derivatized by methylation with BF_3 and methanol, analyzed by GC/HRMS	New drinking water contaminants reported and their toxicities investigated; iodoacid DBPs form in water of high bromide/iodide content that is disinfected with chloramines	G9
Lead (Pb)	Snow and ice cores	Ice melted and sample acidified in class 100 clean room	SF-ICPMS	dl = 3 pg/g (limited by Pb concentrations in blank); Pb concentrations 25-fold higher now (~3000 pg/g) than in 17^{th} century	G10
Mercury (Hg), organo-mercury	Soil, sediment	1.0-g sample extracted with HCl/ethanol (EPA Method 3200)	LC/ICP-MS, C_{18} LC column	Five methods for extraction of inorganic Hg and methyl Hg evaluated; proposed EPA Method 3200 afforded optimal extraction; non-acceptable methods converted organic Hg to inorganic Hg	G11
Musks, fragrances	Water, air	Air (60-600 m^3) collected with high volume samplers and	GC/MS (selected ion monitoring)	Eight synthetic musks from personal care products measured in Lake Michigan water at 0-5 ng/L and in the air above at	G12

		XAD-2; ~100 L water extracted with XAD-2; XAD-2 extracted with acetone/hexane and extract fractionated with silica gel column		0-14 ng/m^3; concentrations of musks in sewage treatment plant effluent were 40-1600 ng/L	
Nitrosoamine species, NDMA	Water	500-mL samples adjusted to pH=8, extracted with LiChrolut EN & Ambersorb 572	GC/MS (positive chemical ionization with NH_3)	dl = 0.4-1.6 ng/L; NDMA in drinking waters ranged from not-detected to 180 ng/L	G13
Octyl- & nonyl-phenols and ethoxylates	Water, sediment	4 L water extracted with Isoelute ENV+, 1 g sediment extracted by ASE with acetone/hexane	LC/ESI-MS/MS (both positive and negative ESI performed in single run), 4.6 mm x 150 mm, MSpak GF-310 LC column	dl = 0.04-3 ng/L in water; 0.2-13 ng/g sediment; concentrations measured in river were <8 – 200 ng/L water and <9-6700 ng/g sediment	G14
Perchlorate, $(ClO_4)^-$	Water, food	100 g food extracted with HNO_3, 5 mL milk subjected to SPE clean-up, 1-mL water sample used directly	IC/ESI-MS/MS (negative ESI), 4.6 mm x 75 mm IC-Pak Anion HR column	dl = 1µg/kg, 2 µg/kg, 0.5 µg/L, and 3 µg/L, in lettuce, cantaloupe, bottled water, and milk, respectively; $(ClO_4)^-$ in 19 lettuce samples measured at not-detected to 55 µg/kg; $^{18}O_4$-labelled perchlorate internal standard mitigated matrix effects	G15
Perfluorinated compounds, PFOS, PFOA	Blood	0.75 mL sample extracted with C_{18}	LC/ESI-MS (negative ESI) 2.1 mm x 50 mm C_{18} LC column	dl = 0.1-0.5 ng/mL; low ng/mL concentrations detected in human blood	G16
Perfluorinated compounds, PFOS, PFOA, & other fluorinated acids	Sea water	1-L grab sample collected and extracted with C_{18}	LC/ESI MS/MS (negative ESI), 2.1 mm x 50 mm, C_{18} column	dl= low pg/L; PFOS in Tokyo Bay measured 12-25 ng/L; PFOA in Tokyo Bay measured 150-190 ng/L	G17
Pesticides, carbamates	Drinking & waste water	None	LC/ESI-MS, 2.1 mm x 150 mm C_8 LC column	dl = 0.09-20 µg/L; 46 analytes screened in single run with 50 µL injection	G18

Pharmaceutical compounds	Surface waters	1-L sample extracted with Oasis HLB	LC/ESI-MS, 2.0 mm x 150 mm C18 LC column	dl ~ 0.2 µg/L; 22 different compounds detected	G19
Pharmaceutical compounds	Sewage & surface waters	250-mL sample derivatized, *in-situ,* with K_2CO_3 and acetic anhydride to form acetylated derivatives of the most polar drugs, which were subsequently extracted with C18	LC/APCI-MS/MS LC column 2.1 mm x 150 mm C12	dl = 10-20 ng/L; APCI provided matrix-independent ionization; field samples contained ~30-600 ng/L pharmaceutical compounds	G20
Pharmaceutical, steroid, & personal care compounds	Surface waters	1-L sample extracted with Oasis HLB	LC/ESI-MS/MS (positive and negative ion) and LC/MS/MS (APCI); LC column 4.6 mm x 250 mm C_{12}	dl = 1 ng/L; three MS/MS protocols needed to detect 27 analytes; compounds detected in surface waters at <1 – 100 ng/L	G21
Phthalate esters	Sediments & biota	2 g sediment or 5 g biota extracted with CH_2Cl_2/hexane and subjected to alumina column clean-up	LC/ESI-MS	Sodiated adduct ions formed with little fragmentation & used for quantitation, dl = 0.5-4 ng/g; LC/MS method afforded reliable quantitation of C_6-C_{10} isomeric mixtures, which were not reliably quantitated by GC/MS	G22
Platinum group elements (Pt, Pd, Rd -- automobile catalyst components)	Road dust	200 mg sample prepared by NiS fire assay (which exploits the Pt-group elements' affinity for sulfide), followed by clean-up and acidic dissolutions	ICP/MS	Pt, Pd, and Rh measured in sediments of urban lake; prior to 1992, Pt concentrations were 1 ng/g, after 1992, Pt concentration of 20 ng/g measured; concentrations of Pd and Rh also increase after 1992	G23
Plutonium (Pu), ^{239}Pu, ^{240}Pu, ^{237}Np	Soil, sediment, biota	1-g sample ashed at 500ºC, dissolved in HNO_3, and purified	SF-ICPMS	dl for analytes in sample extracts were 2.5, 2.1, and 0.42 pg/L for ^{237}Np, ^{239}Pu, and ^{240}Pu, respectively	D20

		with automated sequential injection system containing TEVA-Spec resin			
Polybrominated-chlorinated-dibenzo dioxins and polybrominated-chlorinated-dibenzofurans (PBCDD/PBCDF)	Combustion gas	Collected in sampling train, solvent extraction, chromatographic clean-up	GC/HRMS	PBCDD/PBCDF concentrations increased with decreasing combustion zone temperature between 250-800°C	G24
Polybrominated diphenyl ethers (PBDE)	Soil	Soxhlet extraction, column chromatographic clean-up	GC/MS/MS (ion trap)	dl = 0.1-0.2 ng/g	G25
PBDE	Bird eggs	5-10 g samples extracted with multiple solvents	GC/MS (electron-capture negative ionization mode)	Concentrations varied depending on year of sample collection & were ~10-1000 ng/g	G26
PBDE, polybrominated and chlorinated biphenyls	Breast milk	1-g sample extracted with diatomaceous earth, clean-up with acidic silica	GC/HRMS	dl = 0.1-0.9 ng/g; demonstrated use of novel, semiautomated extraction system	G27
Polychlorinated biphenyls (PCB)	Air	Collected with PUF, extracted with CH_2Cl_2, clean-up with alumina, silica gel, and GPC columns	GC/MS, selected ion monitoring	dl ~ 0.3-5 pg/m^3; total PCB measured in air samples were 20-1700 pg/m^3	B5
Polychlorinated naphthalenes (PCN)	Air	Composite samples of 1000-3600 m^3 collected with PUF and GFF and Soxhlet extracted with hexane or CH_2Cl_2 followed by	GC/MS (electron-capture negative ionization mode)	dl = 0.2 to 90 fg/m^3 (PUF) and 0.3-15 fg/m^3 (GFF); average total PCN concentrations of 0.3-0.8 pg/m^3 measured in air samples collected in Arctic during 1994-5	G28

		fractionation on silica columns			
Thallium (Tl)	Sediment	250 mg sediment digested with HNO_3 and HF, permanganate modifier added	Electrothermal vaporization ICPMS	dl = 0.07 µg/g Tl and 0.18 µg/g Hg	G29
Tin (Sn), organotins	Sediment	0.5 g digested with acetic acid and derivatizated with sodium tetraethylborate	GC-SF-ICPMS	dl ~ 0.4 ng/g for dibutyltin and tributyl tin	D32
Uranium (U)	Urine	10-mL sample digested with H_2O_2 and HNO_3 and purified with TEVA-U resin	SF-ICPMS	dl = 0.14 pg/g	D26
Vx	Soil	5 g soil mixed with alkaline buffer and sonicated with hexane/dichloromethane	GC-flame photometric detector (P-specific); GC/MS (electron and negative chemical ionization modes) to confirm identities of Vx and degradation products	Method allowed detection of Vx in soils at 10 µg/kg and suggested many standard protocols for extraction of Vx in soils are inadequate.	G30