Measurement and Monitoring of Emerging Contaminants: 1,4-Dioxane, N-Nitrosodimethylamine, Perchlorate, Perfluorooctane Sulfonate, Perfluorooctanoic Acid, Polybromated Biphenyls, Polybrominated Diphenyl Ethers, and 1,2,3-Trichloropropane

This literature search was focused on measurement methods and characterization approaches for a group of “emerging” contaminants. By emerging it is meant that they have not, or have not until recently, been seen as chemicals of concern for the Agency remedial action programs. For many of them, analysis by standard Contract Laboratory Program or SW 846 methods is unlikely to detect them or to detect them at levels of concern.

1,4-dioxane is a large production chemical that is miscible in water and resistant to biodegradation. A solvent in its own right, it has also been used as a stabilizer for chlorinated ethanes. Normal volatile purge-and-trap methods produce a very high method detection limit for 1,4-dioxane, and it has often been missed in routine analysis.

N-Nitrosodimethylamine (NDMA) has become of increasing concern because it is formed during the process of treating water before delivery and is a potent carcinogen, with a theoretical 10^{-6} lifetime cancer risk level at exposures of 0.7 ng/L. Water treatment is not the only source of NDMA, however, as it is associated with production of rocket fuel, rubber manufacture, and tanneries. While standard methods are available (SW 846 methods 8070 and 8270), the former is not routine and the latter has a high detection limit relative to the risk level. Unless present at a relatively high concentration, NDMA would not likely be reported under routine GC or GC/MS scans, and it is not a target compound under Superfund’s CLP program.

Perchlorate (ammonium) production first began in the United States in the mid-1940s. Today, ammonium perchlorate and the other perchlorate salts are used in a wide range of applications, including pyrotechnics and fireworks, blasting agents, matches, lubricating oils, textile dye fixing, nuclear reactors, electronic tubes, tanning and finishing leather, rubber manufacturing, electroplating, aluminum refinishing, automobile air bag inflators, paint and enamel production, and pharmaceuticals. The most common use for ammonium perchlorate is in explosives and rocket propellant. Because it was not analyzed for, it is only recently come to the attention of regulators who have found it in a number of drinking water supplies and at sites associated with rocket propellants.

Perfluorooctane sulfonate (PFOS) is persistent, bioaccumulative, and toxic to mammalian species. Uses for PFOS and related chemicals include fixing agents, flame retardants and fire preventing agents, foaming agents, impregnation agents, solvents, and intermediates. The essential uses reported by individual European countries for PFOS and related chemicals are as ingredients in fire fighting foams (Class B fires), aircraft hydraulic fluids, chromium plating (mist suppressants), anti-reflective or photoresist agents in semiconductor photolithography, and anti-static, surfactant or adhesion control agents in photographic processes. PFOS is being found more and more often in environmental settings and is not part of routine chemical analytical scans. PFOS has been found in groundwater near a fire fighting training area at Wurtsmith AFB.

Perfluorooctanoic acid (PFOA) is used to make fluoropolymers, substances with special properties that have thousands of manufacturing and industrial applications. Consumer products made with fluoropolymers include non-stick cookware and breathable, all-weather clothing. PFOA is very persistent in the environment, is found at very low levels both in the environment and in the blood of the general U.S. population, and can cause developmental and other adverse effects in laboratory animals. It is not part of routine chemical analytical scans.

Polybrominated biphenyls were at one time large production chemicals used primarily as fire retardants. Production in the US was stopped in the early 1970s following an incident involving them in Michigan. They are still produced outside the U.S., but at a very low volume. They are persistent, bioaccumulative, and classified as potential human carcinogens. They should be detectable using SW 846 Method 8270, but they are unlikely to be reported as the result of a routine scan.

Polybrominated diphenyl ethers (PBDEs) are large production chemicals used predominantly as fire retardants in plastics, upholstery fabrics, and foams and in products such as computers, televisions, furniture, and carpet pads. Prior to 2004, three products consisting primarily of penta-BDE, octa-BDE, and deca-BDE, respectively were produced. In 2004, the penta-BDE, and octa-BDE products were discontinued. PBDEs, which are persistent and bioaccumulate, are as common in the Great Lakes as PCBs and are found throughout the environment. They are not part of routine chemical scans.

1,2,3-Trichloropropane is a large volume solvent/intermediate and has had an historic use as a pesticide. It is a suspected carcinogen. While it is a targeted chemical under SW-846 method 8021B and 8060B, it is not a targeted chemical under the Superfund Contract Laboratory Program.

1,4-DIOXANE

1,4-Dioxane in Water by Selective Ion Monitoring (SIM) Gas Chromatography/Mass Spectrometry (GC/MS): EPA CLP Method OLM03.1 (1994)
U.S. EPA Region 9, 3 pp, Revised 12/17/99

Analyze water samples for 1,4-dioxane following protocols for GC/MS analysis of volatile organic compounds (VOCs) outlined in the Contract Laboratory Program (CLP) Statement of Work (SOW) OLM03.1 with the following modifications: (1) Perform GC/MS analysis using selective ion monitoring rather than full scan analysis. Monitor ions of m/e 88 +/- 0.5 and 58 +/- 0.5 for 1,4-dioxane. Monitor ions of m/e 96 +/- 0.5 and 64 +/- 0.5 for internal standard 1,4-dioxane-d8. (2) Use 25 mL aliquots of all standards, samples, and blanks. (3) Use a heated purge (50 degrees C).
http://www.epa.gov/region9/qa/pdfs/dqi/dioxane.pdf

Determination of 1,4-Dioxane in Toluene by Gas Chromatography
Cortellucci, Remi and Ed Dietz, Occidental Chemical Corporation.
Journal of High Resolution Chromatography, Vol 22 No 4, p 201-204, 1999

A gas chromatographic method for determining from 1 to 100 mg/mL 1,4-dioxane in toluene with purities ranging from commercial to high-purity grades. The method relies on extracting 1,4-dioxane from toluene into water. The water extract is analyzed for 1,4-dioxane content by gas chromatography/ flame ionization detection using splitless-injection and a capillary column coated with a bonded polyethylene glycol stationary phase. Purging extracts with nitrogen after an initial analysis is suggested as a means to confirm the identification of 1,4-dioxane and to improve baseline resolution of toluene and 1,4-dioxane when its concentration is near the method detection limit.

Determination of 1,4-Dioxane Impurity Levels in Triton X-100 Raw Material by Gas Chromatography with Mass Spectrometric Detection
Poss, M., T. Couch, A. Odufu, J. McCann, J. Mellon, B. Melnick, and D. Jenke, Baxter Healthcare Corporation, Round Lake, IL.
Journal of Chromatographic Science, Vol 41 No 8, p 410-7, Sep 2003 [Erratum in: J Chromatogr Sci.41(10):580, Nov-Dec 2003]

1,4-Dioxane is formed as a byproduct during the synthesis of Triton X-100 (octoxynol 9), a commercially available surfactant used as a solvent detergent in numerous pharmaceutical applications, including virus inactivation. The United States Pharmacopoeia (USP) contains a labor-intensive 1,4-dioxane test for Triton X-100. The method couples vacuum distillation to extract the 1,4-dioxane from the Triton X-100 matrix followed by gas chromatography (GC) using a packed column with flame-ionization detection. A headspace GC-mass spectrometry (MS) method has been developed for this application to provide a more automated and specific test methodology. Analyte quantitation is accomplished by the method of standard additions. The automated sample preparation, coupled with the specificity inherent in high-efficiency capillary column separations together with single-ion MS detection, results in an assay that is more efficient, accurate, and precise than the USP procedure. This paper contrasts the performance characteristics of the headspace GC-MS method with those of the USP method.

Determination of Organic Components in Leachates from Hazardous Waste Disposal Sites in Japan by Gas Chromatography-Mass Spectrometry
Yasuhara, A., H. Shiraishi, M. Nishikawa, T. Yamamoto, T. Uehiro, and O. Nakasugi (National Inst. for Environmental Studies, Ibaraki, Japan); T. Okumura, K. Kenmotsu, H. Fukui, M. Nagase, Y. Ono, Y. Kawagoshi, K. Baba, and Y. Noma.
Journal of Chromatography A, Vol 774 Nos 1-2, p 321-332, 1997

This paper describes an investigation of the presence and origin of organic substances in landfill leachates in Japan. The researchers used several analytical methods by which approximately 190 compounds were detected, including high amounts of organic phosphates and phthalates, 1,4-dioxane at 14 to 10,900 ng/L in most leachates, a few species of halogenated volatile organic substances, and several species of agricultural chemicals, such as pesticides.

Development and Optimization of a Mid-Infrared Hollow Waveguide Gas Sensor Combined with a Supported Capillary Membrane Sampler
de Melas, F., V.V. Pustogov, N. Croitoru, and B. Mizaikoff, Vienna Univ. of Technology, Vienna, Austria.
Applied Spectroscopy, Vol 57 No 6, p 600-606, June 2003

A gas sensor for application in water analysis was developed by combining a mid-infrared (MIR) hollow waveguide with a Fourier transform infrared (FT-IR) spectrometer and coupling the hollow waveguide gas sensor module to a supported capillary membrane sampler (SCMS) for continuous liquid-gas extraction. Different hollow waveguides were characterized to develop an optimized optical configuration. Analysis of industrially relevant compounds--dichloromethane, chloroform, and 1,4-dioxane—under simulated real-world conditions demonstrated the suitability of this spectroscopic IR sensing system for industrial applications, with limits of detection in the ppb (v/v) and ppm (v/v) concentration range for the chlorinated hydrocarbons and 1,4-dioxane, respectively.

Gas Chromatographic Determination of 1,4-Dioxane at Low Parts-per-Million Levels in Glycols
Pundlik, M.D., B. Sitharaman, and I. Kaur, Toshniwal Instruments (India) Ltd,, Satpur, Nasik, India.
Journal of Chromatographic Science, Vol 39 No 2, p 73-76, Feb 2001

1,4-Dioxane may be formed in glycols by condensation in the low parts per million in refineries where the glycols are used as dehumidifying agents. Gas chromatography (GC) can be used to identify and determine the levels of 1,4-dioxane in glycols. GC analysis can be carried out using a flame ionization detector for determination of 1,4-dioxane down to 2 ppm in glycols (and benzene).

Gas Chromatographic-Mass Spectrometric Determination of Hydrophilic Compounds in Environmental Water by Solid-Phase Extraction with Activated Carbon Fiber Felt
Kawata, K., T. Ibaraki, A. Tanabe, H. Yagoh, A. Shinoda, H. Suzuki, and A. Yasuhara.
Journal of Chromatography A, Vol 911 No 1, p 75-83, 2001

A cartridge containing activated carbon fiber felt was made for simple GC-MS determination of hydrophilic organic compounds in environmental water. The cartridge was evaluated for solid-phase extraction of various hydrophilic compounds: acrylamide, N,N-dimethylacetamide, 1,4-dioxane, N,N-dimethylformamide, N-nitrosodimethylamine (NDMA), N-nitrosodiethylamine, furfural, and furfuryl alcohol. The relative standard deviations ranged from 4.5 to 16% for the target compounds. The minimum detectable concentrations were 0.02 to 0.03 ug/L. Overall recoveries were good (80 to 100%) from groundwater and river water.

Highly Sensitive Determination of 1,4-Dioxane in Tap Water and Raw Water in Hyogo Prefecture by GC/MS Coupled with an Improved Solid-Phase Extraction-GC/MS
Yano, Miho, Tatsuhiko Kawamoto, and Nobuko Makihata, Hyogo Prefectural Inst. of Public Health and Environmental Sciences, Hyogo, Japan.
Bunseki Kagaku, Vol 54 No 9, Sep 2005

1,4-Dioxane was listed as a Standard Item in the New Water Quality Standards for Drinking Water, which was enforced as of April 1, 2004. Its regulated value was set at 0.05 mg/L. Studies of the analytical method that is used to determine 1,4-dioxane by solid phase extraction-GC/MS clarified the following: (1) 1 ml of acetone is a sufficient volume for the elution of 1,4-dioxane. Therefore, any losses of 1,4-dioxane that may accompany the concentration process can be prevented and the recovery rate is improved. (2) Blank experiments using 16 kinds of water, including purified water, re-purified water, and 14 types of mineral waters, showed that blank peaks were detected from all samples. It was also shown that the blank values of 6 of the treated mineral waters were high. Therefore, for highly sensitive analysis, the blank value from minerals should be considered. (3) The detection and quantitation limits of 1,4-dioxane by this method were 0.02 mg/L and 0.05 mg/L, respectively. Therefore, a concentration of 1/1000 of the Water Quality Standard can be quantified by this method. Using this method, the concentrations of 1,4-dioxane in raw and tap water sampled at 20 sites in Hyogo prefecture were determined. The results show that the range of concentrations that can be detected is between N.D. and 4.2 mg/L. Furthermore, tests that were conducted to compare water sources revealed that the concentration of 1,4-dioxane in ground water samples was higher than for surface waters.

Improved Purge-Trap and GC/MS/MS Techniques for the Trace-Level Determination of 1,4-Dioxane in Water

Yoo, Lee J., Orange County Water District.

The 13th Korean-American Scientists and Engineers Association South-Western Region Technology Conference & Job Fair.

Abstract not available.

Improved Purge-Trap and GC/MS/MS Techniques for the Trace-Level Determination of 1,4-Dioxane in Water

Yoo, L.J., S. Fitzsimmons, and M. Wehner.

2002 AWWA Water Quality Technology Conference.

American Water Works Association, Fountain Valley, CA.

Abstract not available.

Impurity Analysis of 1,4-Dioxane in Nonionic Surfactants and Cosmetics Using Headspace Solid-Phase Microextraction Coupled with Gas Chromatography and Gas Chromatography-Mass Spectrometry

Fuh, C.B., M. Lai, H.Y. Tsai, and C.M. Chang.

Journal of Chromatography A, Vol 1071 Nos 1-2, p 141-145, 15 Apr 2005

Impurity analysis of 1,4-dioxane in nonionic surfactants and cosmetics used headspace solid-phase microextraction coupled with gas chromatography and gas chromatography-mass spectrometry. Experimental results showed no significant difference using SPME-GC and SPME-GC-MS for analysis of 1,4-dioxane in three types of nonionic surfactants at the 95% confidence level. Conventional solvent extraction takes around 1 hour for extraction and re-concentration, but SPME takes only around 10 minutes. SPME provides better analyses of 1,4-dioxane in nonionic surfactants and cosmetics than conventional solvent extraction and head space pretreatments in term of simplicity, speed, precision, detection limit, and solvent consumption.

Nylon-Mesh Passive Samplers and 1,4-Dioxane: A Case Study in Fractured Rock in Florida

Linton, P.J. and J.C. Alonso, Blasland, Bouck and Lee, Inc., Tampa, FL.

The 15th Annual AEHS Meeting and West Coast Conference on Soils, Sediments and Water, 14-17 March 2005, San Diego, California.

Association for Environmental Health and Sciences (AEHS), poster presentation, 2005.

A new generation of passive samplers using a fine nylon mesh that allows a direct water-to-water interface has shown a potential for application to semi-volatile organic compounds and metals. At a former electronics component manufacturing facility in west-central Florida, a 1,4-dioxane/chlorinated solvent plume is present in the fractured rock aquifer beneath the site. An evaluation of the vertical distribution of contaminants in the site's open-hole rock aquifer monitoring wells was planned, using down-hole vertical and horizontal flow measurement and multiple-level sampling with nylon-mesh samplers. This paper describes the approach presented to the Florida Department of Environmental Protection in requesting implementation approval, and the results of the subsequent study.

Rapid Determination of 1,4-Dioxane in Water by Solid-Phase Extraction and Gas Chromatography-Mass Spectrometry
Song, D. and S. Zhang, Clinical Research Associates, New York, NY.
Journal of Chromatography A, Vol 787, p 283-287, 1997

Dioxane in a water sample was extracted by hexane-methylene chloride (80:20, v/v), then transferred to a C18 solid-phase extraction (SPE) cartridge and eluted by acetonitrile. An aliquot of this solution was analyzed by gas chromatography-mass spectrometry with electron impact ionization and selected ion monitoring (dioxane m/z 88) mode. The quantitative limit was set to be 0.05 ug/ml with an injection volume of 2 microliters and a sample volume of 1 milliliter. The isotopically labeled [2H8]dioxane (m/z 96) was used as internal standard. Analysis time is approximately 6 min. The authors tested various kinds of SPE cartridges in the execution of this method.

Simultaneous Determination of 22 Volatile Organic Compounds, Methyl-tert-Butyl Ether, 1,4-Dioxane, 2-Methylisoborneol and Geosmin in Water by Headspace Solid Phase Microextraction-Gas Chromatography-Mass Spectrometry
Nakamura, S. and S. Daishima, Yokogawa Analytical Systems Inc., Tokyo, Japan.
Analytica Chimica Acta, Vol 548 Nos 1-2, p 79-85, 29 Aug 2005

The authors present a method for the simultaneous determination of 22 volatile organic compounds (VOCs), methyl-tert-butyl ether (MTBE), 1,4-dioxane, 2-methylisoborneol (2-MIB), and geosmin in water by headspace solid phase microextraction (SPME)-gas chromatography-mass spectrometry (GC-MS). Three types of SPME fibers (carboxen (CAR)/polydimethylsiloxane (PDMS), divinylbenzene (DVB)/PDMS, and 100-um PDMS) were evaluated to achieve the method detection limits and linear range required in Japanese water regulation. A 100-um PDMS was found to be the best coating to obtain a wide range of linearity for the target compounds in multiple-component system. CAR/PDMS and DVB/PDMS of adsorbent type fibers showed a narrow linear range for 22 VOCs, MTBE, and 1,4-dioxane at the ug/L levels due to the limited capacity.

Solid-Phase Microextraction Method for the Determination of 1,4 Dioxane in Cosmetics
Silva, Fernando C., Cintia G. Faria, Geraldo M. Gabriel, et al.
Quimica Nova, Vol 24 No 6, p 748-750, Nov/Dec 2001

The authors present a headspace solid-phase microextraction (HS-SPME) for the determination of 1,4-dioxane in cosmetics by gas chromatography. The method utilizes a manual SPME holder with 85 um polyacrylate coating. The method shows good resolution, satisfactory linearity, a relative standard deviation of 6.3% and a detection limit of 5.00 ug/kg.

Summary: Analysis of 1,4-Dioxane by Heated Purge & Trap GC/MS
U.S. EPA Region 9, Laboratory SOP 307, Nov 2002

This Standard Operating Procedure (SOP) is for the determination of 1,4-dioxane in aqueous samples. The quantitation limit of the method is 5 ug/L. The applicability of this procedure is specific to project data quality objectives and must be assessed on a case-by-case basis. The summary describes the procedures used for the analysis of 1,4-dioxane in the Region 9 Laboratory. 1,4-Dioxane is purged from 25-ml water samples in a heated fritted sparge cell. An inert gas (helium) is bubbled through the sample in the heated sparge cell, which purges the target compound from the sample onto a trap containing an adsorbent material, which retains the analyte at ambient temperature. After the purging of

the sample is completed, the adsorbent trap is heated and back-flushed with helium to desorb the analyte onto a capillary column. The capillary column separates the analyte from potential interferences, and the effluent is swept into the mass spectrometer (MS) detector. The MS operates in the selective ion monitoring (SIM) mode, detecting specific ions. The samples are spiked with an internal standard. The target volatile organic compound is identified in the sample by analyzing standards under the exact same conditions employed for samples and comparing the resulting mass spectra and GC retention times. A response factor is established for the target compound during the initial and continuing calibrations by comparing the MS response of the primary ion produced by the target compound to the MS response for the primary ion produced by the associated internal standard. The target compound is quantitated by comparing the responses of the target compound to the internal standard in the sample, using the response factor from the most recent continuing calibration.
http://www.epa.gov/region9/lab/sops/sop307.html

Toxicological Profile for 1,4 Dioxane [Draft for Public Comment], Chapter 7: Analytical Methods
Agency for Toxic Substances and Disease Registry, p 163-172, Sep 2004

This chapter describes the analytical methods that are available for detecting, measuring, and/or monitoring 1,4-dioxane, its metabolites, and other biomarkers of exposure and effect to 1,4-dioxane. The intent is not to provide an exhaustive list of analytical methods. Rather, the intention is to identify well-established methods that are used as the standard methods of analysis. Levels of 1,4-dioxane in environmental and biological samples are determined analytically by gas chromatography-mass spectrometry (GC-MS) or gas chromatography-flame ionization detection (GCFID). The determination of 1,4-dioxane at parts-per-billion (ppb or ug/L) concentrations in samples where water is present (e.g., water, soil, sediment, and tissues) is difficult because of the high solubility of 1,4-dioxane in water. As a polar volatile organic compound (VOC), 1,4-dioxane has a low purge efficiency from water compared to non-polar VOCs. Consequently, 1,4-dioxane has a poor purge-and-trap GC-MS response. The purge-and-trap technique also suffers from interferences by some substances. 1,4-Dioxane gives poor response with headspace sample introduction due to its low volatility from water. The partition coefficients for 1,4-dioxane lead to low recoveries in single contact liquid-liquid extraction (LLE), and very large solvent-to-water ratios are needed to achieve acceptable recoveries. Because of these limitations, alternative techniques have been developed to improve the determination of 1,4-dioxane. Methods have been developed to extract 1,4-dioxane from the aqueous phase using solid-phase extraction followed by desorption with an organic solvent, heated purge-and-trap with salting out, azeotropic distillation; and continuous LLE. Isotopic dilution has also been used to correct for variability in MS instrument response.
http://www.atsdr.cdc.gov/toxprofiles/tp187.html

Trace-Level Determination of 1,4-Dioxane in Water by Isotopic Dilution GC and GC-MS
Draper, W.M., J.S. Dhoot, J.W. Remoy, and S.K. Perera, California Department of Health Services, Berkeley.
Analyst, Vol 125 No 8, p 1403-1408, Aug 2000

Investigation has established that the volatile and polar solvent 1,4-dioxane can be determined in water by various techniques, including direct aqueous injection (DAI) gas chromatography (GC) and purge-and-trap GC-mass spectrometry (MS). Because purge-and-trap GC-MS is limited by 1,4-dioxane's poor purge efficiency, resulting in detection limits up to 100 times greater than the more efficiently purged volatile organic compounds, a method based on continuous liquid-liquid extraction with dichloromethane was developed to attain the sensitivity required for monitoring drinking water. Isotope dilution was more accurate and reproducible than quantification with external standards, and the improvement in precision led to a lower method detection limit of 0.2 ug/L, using a quadrupole ion trap instrument in the electron ionization mode. Isotope dilution accuracy approached 100% at ppb.

N-NITROSODIMETHYLAMINE (NDMA)

Analysis of NDMA by Modified Method 1625 utilizing Chemical Ionization and Large Volume Injection
McLean, S., J.F. Occhialini, A. Jones, and J. Todaro, Alpha Analytical Labs, Westborough, MA.
The 15th Annual AEHS Meeting and West Coast Conference on Soils, Sediments and Water, 14-17 March 2005, San Diego, California.
Association for Environmental Health and Sciences (AEHS), poster presentation.

The authors describe a robust analytical procedure based on a modification of EPA Method 1625. This GC/MS analysis utilizes isotope-dilution, chemical ionization, and large volume injection and is capable of reaching low parts-per-trillion (ppt) reporting limits.

Analysis of Primary and Secondary Aliphatic Amines in Waste Water and Surface Water by Gas-Chromatography-Mass Spectrometry after Derivatization with 2,4-Dinitrofluorobenzene or Benzenesulfonyl Chloride
Sacher, F., S. Lenz, and H.-J. Brauch.
Journal of Chromatography A, Vol 764, 85-93, 1997

This paper presents two methods for the determination of aliphatic amines such as methylamine, dimethylamine, ethylamine, diethylamine, piperidine, pyrrolidine or morpholine in waste water and surface water at the sub-ppb level. The methods are based on a derivatization of the amines within the aqueous medium with 2,4-dinitrofluorobenzene and benzenesulfonyl chloride, respectively. In both cases the derivatives are extracted with dichloromethane and measured by GC-MS. The authors compare performance data of the two methods and discuss the application of the benzenesulfonyl chloride method to industrial wastewaters and surface waters to determine the rate of occurrence of aliphatic amines in the aquatic environment.

An Approach to the Determination of N-Nitrosodimethylamine at Part-per-Quadrillion Levels Using Positive Chemical Ionization and Large-Volume Injection
Prest, Harry F. (Hewlett-Packard Company, Palo Alto, CA); Richard E. Herrmann (APEX Technologies, Inc., Cincinnati, OH).
Hewlett-Packard Company, HP 5973 MSD, 5 pp, 1999

Concentration and recovery factors for NDMA using present published methodologies suggest effective preconcentration of NDMA in samples to be on the order of 500, e.g., 60 to 70% recovery of NDMA in extraction of a 1-liter water sample. This suggests that the low 20-fg/ul NDMA standard corresponds to a sample concentration of 40 pg/L, or 40 parts per quadrillion. Alternatively, to quantitate NDMA at 0.5 ppt in water, which is 4 times lower than the California DHS limit and slightly lower than the EPA regulated limit, quantitating at 20 fg/ul is equivalent to requiring the extraction of only 80 ml of water even if recoveries are still only 50%. Extracting small volumes presents a

significant simplification of the process and offers savings in solvent and related materials, and in processing time. With NDMA eluting in about 5.5 minutes, the analysis is fast, and the run-to-run cycle time is short—less than 13 minutes between injections. The method can be further optimized for even more rapid analysis. The 5973 MSD provides very stable ratios for the confirming ion that can be optimized for quantitative purposes as described. In contrast to EI, in which many possible interfering fragment ions are possible that may distort the ratio of the target and confirming ion(s), PCI with ammonia is unlikely to cause fragmentation-induced interferences due to the relatively gentle nature of ammonia reagent gas. Interferences could occur involving compounds with molecular weights of 74 or 91 g/mole eluting at the same retention time, but that is unlikely scenario. The high degree of reproducibility in the injections, even at very low NDMA concentrations, demonstrates the robustness of large-volume injections using the APEX ProSep with the HP 6890/5973 MSD. It should be emphasized that the reproducibility of 2.4% for the replicate 50-ul injections of the 20-fg/ul standard reported here was for the absolute response. Use of an internal standard should further lower the deviation in response and improve quantitation. Using this approach it should now be possible to satisfy the 2 ppt action level for NDMA set by the State of California and the 700 ppq regulatory standard promulgated by the U.S. EPA.
http://www.bst.com.au/resources/5968-6036E.pdf

Attenuation Mechanisms of N-Nitrosodimethylamine at an Operating Intercept and Treat Groundwater Remediation System
Gunnison, D, M.E. Zappi, C. Teeter, J.C. Pennington, and R. Bajpai, U.S. Army Environmental Research and Development Center, Waterways Experiment Station, Vicksburg, MS.
Journal of Hazardous Materials, Vol 73 No 2, p 179-197, 3 Apr 2000

The North Boundary Containment System (NBCS) at Rocky Mountain Arsenal (RMA), Commerce City, CO, is designed to intercept and remove low-level organic contaminants from a groundwater plume exiting RMA. N-nitrosodimethylamine (NDMA) was detected in groundwater collected from the dewatering and recharge zones of the NBCS system. An investigation was undertaken to evaluate potential attenuation mechanisms for NDMA within the alluvial aquifer system and within the NBCS itself. Groundwater, soil, and granular activated carbon (GAC) samples were taken from key locations in the NBCS system. NDMA biodegradation experiments were conducted by following (14)CO2 evolution from (14)C-labeled NDMA in soils and GAC samples under aerobic and anaerobic conditions. The sorptive capacity of the site soils for NDMA was insignificant, and the little soil adsorption of the NDMA was almost completely reversible. Evaluation of the degradation potential of the native microbial consortia indicated a high level of NDMA mineralization when measured using bench-scale microcosms. The native consortia were able to mineralize the NDMA under both aerobic and anaerobic incubations. Tests of the local groundwater chemistry revealed that the area of the aquifer of interest was microaerobic and neutral in pH. These conditions were optimal for NDMA removal. While sorption was insignificant, degradation was a significant attenuation mechanism, which may be the reason that no NDMA has migrated off-site. This gives rise to the potential of a long-term sink for attenuating NDMA within the recharge zone of the treatment system.

Automated Solid-Phase Extraction and High-Performance Liquid Chromatographic Determination of Nitrosamines Using Post-Column Photolysis and tris(2,2'-bipyridyl) Ruthenium(III) Chemiluminescence.
Perez-Ruiz, T., C. Martinez-Lozano, V. Tomas, and J. Martin, Univ. of Murcia, Murcia, Spain.
Journal of Chromatography A, Vol 1077 No 1, p 49-56, 3 June 2005

This paper presents a sensitive and selective post-column detection system for nitrosamines. The principle upon which the detector works is that UV irradiation of aqueous solutions of nitrosamines leads to cleavage of the N-NO bond; the amine thus generated is detected by chemiluminescence using tris(2,2'-bipyridyl) ruthenium(III), which is generated on line by photooxidation of the ruthenium(II) complex in the presence of peroxydisulfate. This detection system was tested for N-nitrosodimethylamine, N-nitrosodiethylamine, N-nitrosomorpholine, An automated solid-phase extraction (SPE) system was used in conjunction with HPLC to determine nitrosamine residues in waters. Detection limits within the range 0.10 to 3.0 ng/L were achieved for only 250 ml of sample.

Characterization and Fate of N-Nitrosodimethylamine Precursors in Municipal Wastewater Treatment Plants
Mitch, W.A. and D.L. Sedlak, Univ. of California, Berkeley.
Environmental Science & Technology, Vol 38 No 5, p 1445-1454, 1 Mar 2004

N-nitrosodimethylamine (NDMA) is a carcinogen produced during disinfection of municipal wastewater effluent from the reaction of monochloramine and organic nitrogen-containing precursors. NDMA formation was measured after extended chloramination of both model precursors and samples from conventional and advanced wastewater treatment plants to delineate the sources and fate of NDMA precursors during treatment. Only dimethylamine, tertiary amines with dimethylamine functional groups, and dimethylamides formed significant NDMA concentrations upon chloramination. Though biological treatment effectively removed the known NDMA precursor dimethylamine, biological treatment was less effective at removing other dissolved NDMA precursors, even after extended biological treatment. The authors discuss effective strategies for the prevention of NDMA formation during wastewater chlorination.

Comparison of Alternative Nitrosoamine Analyses for Water Reuse Samples
Cheng, R.C. and C. Andrews-Tate (Long Beach Water Department); C.J. Hwang and Y. Guo (Metropolitan Water District of Southern California); J.E. Grebel and I.H. Suffet (Univ of California, Los Angeles).
Water Recycling: Realizing California's Potential, 27 February - 1 March 2005, San Diego, California. 15 pp, 2005

The methods tested in this paper are derivations or refinements of existing methods, including liquid-liquid extraction (LLE) and solid-phase extraction (SPE). One project goal was to evaluate the capabilities of multiple methods for a variety of water matrices, matrices that test the durability of the methods over a wide range of concentrations expected in various water matrices, including recycled waters. It was found through the round-robin testing that the Ambersorb(R) 572- Envicarb (Amb-Envi) cartridge SPE, Ambersorb(R) 572 SPE (Amb SPE), and the traditional LLE methods (coupled with gas chromatography/mass spectrometry (GC/MS)) were all able to report NDMA to a minimum level of approximately 2 ng/L and other nitrosamines to a level of between 2 to 4 ng/L across a broad range of sample matrices. The micro-LLE technique developed in this study, which uses a sample volume of 100 ml, also appears to be effective at analyzing a broad range of sample matrices, though the reporting level for this method is somewhat higher than the other methods (7 ng/L for NDMA, 5 to 12 ng/L for the other nitrosamines). Solid phase microextraction (SPME) was also evaluated as an alternative extraction method for nitrosamine analyses, and proved to be effective for higher concentration samples (> 30 ng/L NDMA). While NDMA was the only nitrosamine analyzed in detectable concentrations in potable water and tertiary wastewater effluent treated through reverse osmosis membranes, the two wastewater treatment plant effluent samples (secondary and tertiary effluent) contained detectable

concentrations of nitrosodiethylamine (NDEA), nitrosopyrrolidine (NPYR), nitrosomorpholine (NMOR), nitrosopiperidine (NPIP), and nitrosodi-n-butylamine (NDBA).
http://www.watereuse.org/ca/2005conf/papers/A1_rcheng.pdf

A Competitive ELISA Detecting 7-Methylguanosine Adduct Induced by N-Nitrosodimethylamine Exposure
Niot-Mansart, V, A. Muhamedi, J.P. Arnould, Univ. de Picardie Jules Verne, Amiens, France.
Human & Experimental Toxicology, Vol 24 No 2, p 89-94, Feb 2005

The authors discuss the development and validation of a competitive enzyme-linked immunosorbent assay to detect the adduct 7-methylguanosine (a methylating nucleic acid) in DNA exposed to N-nitrosodimethylamine in vitro or in vivo. This assay is reproducible, can be routinely performed, and is sensitive enough to detect 7-methylguanosine adduct in DNA samples from human exposed to N-nitrosodimethylamine.

Degradation of N-Nitrosodimethylamine (NDMA) in Landscape Soils
Yang, W.C., J. Gan, W.P. Liu, and R. Green, Univ. of California, Riverside.
Journal of Environmental Quality, Vol 34 No 1, p 336-341, Jan-Feb 2005

N-nitrosodimethylamine (NDMA), a potential carcinogen, can be found in treated wastewater as a byproduct of chlorination. Where treated water is used for landscape irrigation, it is possible for NDMA to leach into soils. In adsorption and incubation experiments conducted using landscape soils planted with turfgrass, ground cover, and trees, adsorption of NDMA was weak in all soils, indicating that NDMA has a high potential for moving with percolating water in these soils. Degradation of NDMA occurred at different rates among these soils. At 21 degrees C, the half-life of NDMA was 4.1 d for the ground cover soil, 5.6 d for the turfgrass soil, and 22.5 d for the tree soil. The persistence was substantially prolonged after autoclaving or when incubated at 10 degrees C. The rate of degradation was not significantly affected by the initial NDMA concentration or addition of organic and inorganic nutrient sources.

Detecting N-Nitrosamines in Drinking Water at Nanogram per Liter Levels Using Ammonia Positive Chemical Ionization
Charrois, J.W., M.W. Arend, K.L. Froese, S.E. Hrudey, Univ. of Alberta, Edmonton, Alberta, Canada.
Environmental Science & Technology, Vol 38 No 18, p 4835-4841, 15 Sep 2004

Researchers seeking a selective, sensitive, and affordable benchtop analytical method for eight N-nitrosamines at relevant drinking water concentrations have developed a solid-phase extraction method using Ambersorb 572 and LiChrolut EN in conjunction with GC/MS ammonia positive chemical ionization (PCI). Method detection limits for all investigated N-nitrosamines ranged from 0.4 to 1.6 ng/L. Applying the extraction method to authentic drinking water samples with dissolved organic carbon concentrations of 9 mg/L detected N-nitrosodimethylamine (2 to 180 ng/L), N-nitrosopyrrolidine (2 to 4 ng/L), and N-nitrosomorpholine (1 ng/L). With high recoveries of standards and analytes, the described internal standard method offers a valuable new approach for investigating several N-nitroso compounds at ultratrace levels in drinking water.

Determination of N-Nitrosodimethylamine at Part-per-Trillion Levels in Drinking Waters and Contaminated Groundwaters
Tomkins, B.A., W.H. Griest, and C.E. Higgins, Oak Ridge National Laboratory, Oak Ridge, TN.
Analytical Chemistry, Vol 67 No 23, p 4387-4395, 1 Dec 1995

N-nitrosodimethylamine (NDMA) can be quantitated routinely at ultratrace (ng/L) levels in drinking water or contaminated groundwater when the aqueous sample is passed through a preconditioned Empore C18 filter disk to remove neutral nonpolar species and then extracted continuously overnight with highest purity dichloromethane. The latter is then concentrated to 1 ml, and a large aliquot (up to 200 μl) is loaded onto a dual-stage carbon sorbent trap, after which the solvent is removed with ultrapure helium. The concentrated residues are then injected onto a gas chromatographic column using a short-path thermal desorber. NDMA is selectively detected using a chemiluminescent nitrogen detector (CLND) operated in its nitrosamine-selective mode, with a reporting limit of 2 ng of NDMA/L. A related procedure, employing an automatic sampler instead of the short-path thermal desorber, provides convenient analysis of heavily contaminated samples and exhibits a reporting limit (under the same protocols) of 110 ng of NDMA/L. When the two methods are used together in a "two-tiered" protocol, NDMA concentrations spanning ng/L to μg/L levels can be measured routinely.
http://www.osti.gov/bridge/servlets/purl/164458-mLXhMz/webviewable/164458.pdf

Determinations of N-Nitrosodimethylamine at Part-per-Trillion Concentrations in Contaminated Groundwaters and Drinking Waters Featuring Carbon-Based Membrane Extraction Disks
Tomkins, B.A. and W.H. Griest.
Analytical Chemistry, Vol 68 No 15, p 2533-2540, 1 Aug 1996

N-nitrosodimethylamine (NDMA) can be analyzed at part-per-trillion (ng/L) concentrations in aqueous samples using a solid-phase extraction procedure implementing a C18 (reversed-phase) membrane extraction disk layered over a recently introduced carbon-based extraction disk. The reversed-phase disk removes nonpolar water-insoluble neutrals and is set aside; the carbon-based disk is extracted with a small volume of dichloromethane. NDMA is quantified in the organic extract using a gas chromatograph equipped with both a short-path thermal desorber and a chemiluminescent nitrogen detector. The detection limit for the procedure is 3 ng of NDMA/L; the analyte recovery is approximately 57%. A related procedure substitutes a standard automatic sampler for the short-path thermal desorber and is suitable for determining NDMA in heavily contaminated (> 300 ng of NDMA/L) aqueous samples. The detection limit for the procedure, calculated in the same manner as above, is 300 ng of NDMA/L, with an analyte recovery of approximately 64%. These newer procedures offer a 50-fold saving in extraction time and a 100-fold reduction in dichloromethane consumed per sample while maintaining the wide range (3 to 4 orders of magnitude concentrations of NDMA) observed for the original procedures used together.
http://www.osti.gov/bridge/servlets/purl/261102-7RdzjS/webviewable/261102.pdf

Determination of N-Nitrosodimethylamine by HPLC, with Fluorescence Detection: A Survey of N-Nitrosodimethylamine in Commercial Beers
Cadenes, L., J.H. Ayala, V. Gonzalez, A.M. Afonso, Univ, of La Laguna, La Laguna, Spain.
Journal of Liquid Chromatography & Related Technologies, Vol 25 No 6, p 977-984, 2002

This paper describes a new method for the determination of N-nitrosodimethylamine (NDMA) in beers. The method involves extraction with diethyl ether containing 25% 2-propanol. The extract is denitrosated by hydrobromic acid-acetic acid to produce secondary amines, which are then subjected to microwave-assisted reaction with dansyl chloride. The reaction mixture is analyzed by HPLC on a C 18 column with acetonitrile-water as mobile phase with fluorimetric detection at 531 nm. The method detection limit is 0.04 ug/L. NDMA was found in 20% of the beer samples at levels ranging from 0.04 to 0.50 ug/L.

Determination of N-Nitrosodimethylamine in Artificial Gastric Juice by Gas Chromatography-Mass Spectrometry and by Gas Chromatography-Thermal Energy Analysis
Dallinga, J,W,, C.A. Krul, A. Tenfelde, E.J. Moonen, I.T. Vermeer, D. van Doorn, R.C. Schothorst, Maastricht Univ., The Netherlands.
European Journal of Cancer Prevention, Vol 10 No 3, p 265-268, June 2001

The thermal energy analyzer (TEA) is considered to be the gold standard for the determination of nitrosamines; however, many laboratories cannot justify the use of such a very specific detection system. With regard to alternative detection methods, while standard gas chromatography (GC) detectors lack the selectivity of the TEA detector, mass spectrometry (MS) seems to be the method of choice to combine GC separation with mass selective detection. The detection limits of the GC-MS assay in general use are about 4 times lower than those of the GC-TEA assay. The authors compare GC-MS and GC-TEA data on N-nitrosodimethylamine determinations, showing a strong correlation between the two assays and demonstrating the exchangeability of these methods.

Determination of N-Nitrosodimethylamine in Environmental Aqueous Samples by Isotope-Dilution GC/MS-SIM
Raksit, A. and S. Johri, ENTECH-Agri-Service Laboratory, Inc., Mississauga, ON, Canada.
Journal of the AOAC International, Vol 84 No 5, p 1413-1419, Sep-Oct 2001

A new analytical method for the determination of N-nitrosodimethylamine in environmental aqueous samples uses isotope dilution gas chromatography/mass spectrometry in the selected ion monitoring mode (GC/MS-SIM). After deuterated N-nitrosodimethylamine as surrogate standard is added to the samples, the analytes are extracted with methylene chloride, dried with anhydrous sodium sulfate, and concentrated in a rotary evaporator. The concentrated extracts are analyzed by GC/MS-SIM after adding N-nitrosodiethylamine as an internal standard. The tested method detection limit was 0.003 pg/uL, validated by an analysis of a fortified water sample.

Dimethylnitrosamine
OSHA Method 06, May 1979

Dimethylnitrosamine is an OSHA-regulated carcinogen. This standard applies to all solid or liquid mixtures that contain more than 1.0% dimethylnitrosamine by weight or volume.
http://www.osha-slc.gov/dts/sltc/methods/organic/org006/org006.html

Effect of Ultraviolet (UV) Disinfection on the Fate of NDMA and Cyanide
Jalali, Y., S.-J. Huitric, J. Kuo, C.-C. Tang, M.H. Nellor, S. Thompson, A. Garcia, R.W. Horvath, and J.F. Stahl, Los Angeles County Sanitation Districts, Whittier, CA.
Water Recycling: Realizing California's Potential, 27 February - 1 March 2005, San Diego, California. 15 pp, 2005

Because the chloramination process in wastewater treatment has been discovered to produce N-nitrosodimethylamine (NDMA) and cyanide as byproducts, the Los Angeles County Sanitation Districts are evaluating alternative disinfection technologies to replace chloramination. The authors describe an investigation of the effects of UV disinfection on NDMA and cyanide concentrations in filtered secondary effluent. The scope of work included characterizing NDMA and cyanide concentrations in the secondary effluent and tertiary filtered effluent, conducting laboratory collimated beam testing, and verifying the laboratory testing results with pilot-scale UV testing. http://www.watereuse.org/ca/2005conf/papers/A1_yjalali.pdf

Fast Microwave-Assisted Dansylation of N-Nitrosamines: Analysis by High-Performance Liquid Chromatography with Fluorescence Detection
Cardenes, L., J.H. Ayala, V. Gonzalez, A.M. Afonso, Univ. of La Laguna, Spain.
Journal of Chromatography A, Vol 946 No 1-2, p 133-140, 8 Feb 2002

A fast microwave-assisted dansylation procedure has been developed for the derivatization of N-nitrosamines prior to high-performance liquid chromatography determination. N-Nitrosomorpholine, N-nitrosodimethylamine, N-nitrosodiethylamine, N-nitrosopyrrolidine and N-nitrosopiperidine are first denitrosated by hydrobromic acid-acetic acid to produce secondary amines, which are then quantitatively dansylated in 5 min using radiation power of 378 W and a maximum pressure of 1.4 bar inside the reactor. The reaction mixture is separated on a C18 column with acetonitrile-water (55:45, v/v) as mobile phase with fluorimetric detection at 531 nm (excitation at 339 nm). The detection limits range from 8 to 75 pg for N-nitrosomorpholine and N-nitrosodiethylamine, respectively. The method was applied to study the recoveries of N-nitrosamines in beer and their determination in cigarette smoke.

Formation of N-Nitrosodimethylamine (NDMA) from Dimethylamine During Chlorination
Mitch, W.A. and D.L. Sedlak, Univ. of California, Berkeley.
Environmental Science & Technology, Vol 36 No 4, p 588-595, 15 Feb 2002

Lab experiments with potential N-nitrosodimethylamine (NDMA) precursors indicate that NDMA formation can form during the chlorination of dimethylamine and other secondary amines. The formation of NDMA during chlorination may involve the slow formation of 1,1-dimethylhydrazine by the reaction of monochloramine and dimethylamine, followed by its rapid oxidation to NDMA and other products, including dimethylcyanamide and dimethylformamide. Other pathways also lead to NDMA formation during chlorination, such as the reaction of sodium hypochlorite with dimethylamine. The authors suggest that it may be possible to reduce NDMA formation during chlorination by removing ammonia prior to chlorination, by breakpoint chlorination, or by avoidance of the use of monochloramine for drinking water disinfection.

Formation of N-Nitrosodimethylamine (NDMA) from Reaction of Monochloramine: a New Disinfection By-product
Choi, J. and R.L. Valentine, Univ. of Iowa, Iowa City
Water Research, Vol 36 No 4, p 817-824, Feb 2002

Experiments undertaken to investigate the hypothesis that N-nitrosodimethylamine (NDMA) can be produced by reactions involving monochloramine were conducted using dimethylamine (DMA) as a model precursor. NDMA was formed from the reaction between DMA and monochloramine, indicating that it should be considered a potential disinfection byproduct. The formation of NDMA increased with increased monochloramine concentration and showed maximum in yield when DMA was varied at fixed monochloramine concentrations. The mass spectra of the NDMA formed from DMA and 15N isotope-labeled monochloramine ($15NH_2Cl$) showed that the source of one of the nitrogen atoms in the nitroso group in NDMA was from monochloramine. Addition of 0.05 and 0.5

mM of preformed monochloramine to a secondarily treated wastewater at pH 7.2 also resulted in the formation of 3.6 and 111 ng/L of NDMA, respectively, showing that this is indeed an environmentally relevant NDMA formation pathway.

Free Radical Destruction of N-Nitrosodimethylamine in Water
Mezyk, S.P., W.J. Cooper, K.P. Madden, and D.M. Bartels, California State Univ. at Long Beach.
Environmental Science & Technology, Vol 38 No 11, p 3161-3167, 1 June 2004

Absolute rate constants for the reactions of the hydroxyl radical, hydrated electron, and hydrogen atom with N-nitrosodimethylamine (NDMA) in water at room temperature have been determined using electron pulse radiolysis and transient absorption spectroscopy and EPR free induction decay attenuation measurements. DMPO spin-trapping experiments demonstrated that the hydroxyl radical reaction with NDMA occurs by hydrogen atom abstraction from a methyl group. The relatively slow rate constant implies that regeneration of the parent nitrosoamine from the oxidized transient could occur in natural waters containing dissolved organic compounds. The reaction of the hydrated electron with NDMA was to form a transient adduct anion, which could subsequently transfer this excess electron to regenerate the parent chemical. Such regeneration reactions would significantly reduce the effectiveness of any applied advanced oxidation technology remediation effort on NDMA-contaminated natural waters.

Gas Chromatographic-Mass Spectrometric Determination of Hydrophilic Compounds in Environmental Water by Solid-Phase Extraction with Activated Carbon Fiber Felt
Kawata, K., T. Ibaraki, A. Tanabe, H. Yagoh, A. Shinoda, J. Suzuki, and A. Yasuhara.
Journal of Chromatography A, Vol 911 No 1, p 75-83, 9 Mar 2001

Simple gas chromatographic-mass spectrometric determination of hydrophilic organic compounds in environmental water was developed. A cartridge containing activated carbon fiber felt was devised and evaluated for solid-phase extraction of the following compounds in water: acrylamide, N,N-dimethylacetamide, N,N-dimethylformamide, 1,4-dioxane, furfural, furfuryl alcohol, N-nitrosodiethylamine, and N-nitrosodimethylamine. Overall recoveries from groundwater and river water were good (80 to 100%). The relative standard deviations ranged from 4.5 to 16% for the target compounds, and the minimum detectable concentrations were 0.02 to 0.03 ug/L.

Influence of the Order of Reagent Addition on NDMA Formation During Chloramination
Schreiber, I.M. and W.A. Mitch, Yale Univ., New Haven, CT.
Environmental Science & Technology, Vol 39 No 10, p 3811-3818, 15 May 2005

The formation of the carcinogen N-nitrosodimethylamine (NDMA) during chlorine disinfection in drinking water or wastewater treatment is of significant concern. Contrary to the importance of monochloramine indicated by previous studies, other work shows that hypochlorite forms an order of magnitude more NDMA than monochloramine when applied to a secondary municipal wastewater effluent containing excess ammonia. Experiments involving variation of the order that each reagent (i.e., hypochlorite, ammonium chloride, and dimethylamine) was added to solution suggest that the chlorination state of organic nitrogen precursors and the partial formation of dichloramine may be more important for NDMA formation than the presence of monochloramine. Chloramination strategies are suggested that may reduce NDMA formation by nearly an order of magnitude.

A Kinetic Model of N-Nitrosodimethylamine (NDMA) Formation During Water Chlorination/Chloramination.
Choi J. and R.L. Valentine, University of Iowa, Iowa City.
Water Science Technology, Vol 46 No 3, p 65-71, 2002

During experiments conducted to investigate the hypothesis that N-nitrosodimethylamine (NDMA) is a potential disinfection byproduct, NDMA was formed by the reaction of dimethylamine (DMA) with monochloramine and also with free chlorine in the presence of ammonia. The researchers proposed a mechanism for NDMA formation that does not require the presence of nitrite. The critical NDMA formation reactions consist of the formation of monochloramine by combination of free chlorine with ammonia, the formation of 1,1-dimethylhydrazine (UDMH) intermediate from the reaction of DMA with monochloramine, followed by the oxidation of UDMH by monochloramine to NDMA, and the reversible chlorine transfer reaction between free chlorine/monochloramine and DMA. A kinetic model was developed to validate the proposed mechanism.

Low Level Determination of N-Nitrosodimethylamine by GC/MS with Large Volume Injection
Grindstaff, Jeff, Jerry Peterson, and Carl Degner, Columbia Analytical Services, Inc., Kelso, WA.
The 15th Annual AEHS Meeting and West Coast Conference on Soils, Sediments and Water, 14-17 March 2005, San Diego, California.
Association for Environmental Health and Sciences (AEHS), 2005

A method has been developed to detect N-nitrosodimethylamine (NDMA) at low part-per-trillion (ppt) levels using a separatory funnel extraction designed to minimize analytical interference. The extracts are subsequently analyzed using a large volume injector in conjunction with gas chromatography and mass spectroscopy (GC/MS) running in the selected ion monitoring mode and quantified by isotope dilution techniques. An alternate method using chemical ionization GC/MS was also developed to confirm the presence of NDMA in samples with severe matrix interferences, potentially attaining method detection limits at sub-ppt levels.

Mechanistic Studies of N-Nitrosodimethylamine (NDMA) Formation in Chlorinated Drinking Water
Choi, J., S.E. Duirk, and R.L. Valentine, Univ. of Iowa, Iowa City.
Journal of Environmental Monitoring, Vol 4 No 2, p 249-52, Apr 2002

In studies conducted to investigate the hypothesis that N-nitrosodimethylamine (NDMA) is a potential disinfection byproduct specifically produced during chlorination or chloramination, experiments were conducted using dimethylamine (DMA) as a model precursor. NDMA was formed by the reaction of DMA with free chlorine in the presence of ammonia and also with monochloramine. A mechanism for NDMA formation in chlorinated or chloraminated water does not require nitrite, as in N-nitrosation. The critical NDMA formation reactions consist of the formation of monochloramine by combination of free chlorine with ammonia, the formation of 1,1-dimethylhydrazine (UDMH) intermediate from the reaction of DMA with monochloramine, followed by the oxidation of UDMH by monochloramine to NDMA, and the reversible chlorine transfer reaction between free chlorine/monochloramine and DMA. A kinetic model validates the proposed mechanism.

Method 521: Determination of Nitrosamines in Drinking Water by Solid Phase Extraction and Capillary Column Gas Chromatography with Large Volume Injection and Chemical Ionization Tandem Mass Spectrometry (MS/MS), Version 1.0
Munch, J.W. and M.V. Bassett, U.S. EPA, National Exposure Research Laboratory, Chemical Exposure Research Branch, Cincinnati, OH.
EPA 600-R-05-054, 47 pp, Sep 2004

This method provides procedures for the determination of nitrosamines in finished drinking water. The method may be applicable to untreated source waters and other types of water samples, but it has not been evaluated for these uses. The method is applicable to nitrosamines that are efficiently partitioned from the water sample onto a solid phase extraction (SPE) sorbent, and sufficiently volatile and thermally stable for gas chromatography. The method covers N-nitrosodimethylamine (NDMA), N-nitrosomethylethylamine (NMEA), N-nitrosodiethylamine (NDEA), N-nitrosodi-n-propylamine (NDPA), N-nitrosodi-n-butylamine (NDBA), N-nitrosopyrollidine (NPYR), and N-nitrosopiperidine (NPIP).
http://www.epa.gov/nerlcwww/m_521.pdf

Method Development for the Determination of N-Nitrosodimethylamine (NDMA) in Drinking Water
U.S. EPA, National Exposure Research Laboratory - FY04 Research Abstract.

NDMA is an emerging drinking water contaminant that is of interest to EPA and the environmental community. Its presence in drinking water is a potential health concern, because EPA's IRIS database lists the concentration of NDMA required to result in a one-in-one-million lifetime cancer risk to be only 0.7 ng/L. Existing methods for measuring NDMA in water are expensive and labor intensive, and some require the use of very large amounts of toxic solvents such as methylene chloride, and the sensitivity of some existing methods is insufficient for conducting low-level monitoring. EPA Method 521 was developed for inclusion in EPA's Unregulated Contaminant Monitoring Rule, scheduled for proposal in 2005, in order for the EPA Office of Water to collect nationwide occurrence data on nitrosamines in drinking water and make a regulatory determination. If NDMA or other nitrosamines become regulated drinking water contaminants in the future, the method could also be used for compliance monitoring. The research goal was to develop a sensitive, selective and cost-effective method for measuring NDMA (and other additional nitrosamines.) This research note briefly describes the approach to the development of EPA Method 521 and its potential regulatory impact.
http://www.epa.gov/nerl/research/2004/g2-6.pdf

Methods for Emerging Contaminant Groups: Explosives and Nitrosamines
Munch, J.W. and M.V. Bassett.
Proceedings: American Water Works Water Quality Technology Conference, Philadelphia, PA, November 3, 2003.

The interest in developing a method for nitrosamines began with the information that N-nitrosodimethylamine (NDMA) is a likely drinking water disinfection byproduct. This is of concern to EPA because NDMA is a potent carcinogen, with a theoretical 10(-6) lifetime cancer risk level at exposures of 0.7 ng/L. The decision was made to start a method development effort because of its emerging importance as a drinking water contaminant. In addition to NDMA, it was decided to try to include seven additional nitrosamines that are on EPA's RCRA Groundwater Monitoring List to the method. Other sources of NDMA and other nitrosamines in the environment are: production of rocket

fuel, rubber manufacture, and tanneries. Analytical challenges associated with developing a method for NDMA centered around two issues. The first issue is that NDMA is miscible with water in all proportions, and therefore very difficult to extract from water efficiently. The approach to solving that issue was to investigate the use of carbon as an SPE sorbent. The second issue is the need for an extremely low detection limit combined with the need for very specific detection. In light of the fact that NDMA and other nitrosamines are very insensitive to conventional electron ionization MS, a less conventional approach was needed. The initial approach to detection was chemical ionization (CI) GC/MS using methanol as the CI reagent. As development progressed, it became clear that the molecular ion for NDMA (m/z 75) may not be specific enough to preclude false positives. At this point, tandem mass spectrometry (MS/MS) was investigated as a possible option. Although at the time of this writing method development is still in progress, the preliminary extraction and detection procedures are summarized.
http://oaspub.epa.gov/eims/xmlreport.display?deid=62563&z_chk=2633

Monitoring Airborne Genotoxicants in the Rubber Industry Using Genotoxicity Tests and Chemical Analyses
Monarca, S., D. Feretti, A. Zanardini, M. Moretti, M. Villarini, B. Spiegelhalder, I. Zerbini, U. Gelatti, E. Lebbolo, Univ. of Brescia, Brescia, Italy.
Mutation Research, Vol 490 No 2, p 159-169, 20 Feb 2001

This paper describes research designed to examine the presence of mutagenic/carcinogenic compounds in airborne pollutants in the rubber industry using an integrated chemical/biological approach. Inhalable airborne particulate matter was collected in four rubber factories using a high-volume sampler equipped with a cascade impactor for particle fractionation. The organic extracts were examined for mutagenicity with the Ames test and for in vitro DNA-damaging activity in human leukocytes by single-cell microgel electrophoresis (Comet assay). The extracts were also studied by gas chromatography/mass spectrometry (GC/MS) for polycyclic aromatic hydrocarbon (PAH) content. Nitrosamines in ambient air were sampled on cartridges and analyzed by GC with a thermal energy analyser (TEA) detector. Airborne volatile genotoxins were monitored in situ using a clastogenicity plant test (Tradescantia/micronuclei test). The results showed that airborne particulates were mainly very fine (<0.5 microm) and that trace amounts of genotoxic nitrosamines (N-nitrosodimethylamine, N-nitrosomorpholine, and PAH) were present in air samples. The study results showed the applicability of this integrated chemical/biological approach for detecting volatile and non-volatile genotoxins and for monitoring genotoxic hazards in the rubber industry.

N-Nitrosodimethylamine: a Disinfectant Byproduct and its Occurrence in Wastewater
Siddiqui, M. and K.Z. Atasi, Tetra Tech MPS, Detroit, MI.
Water Environment Research, Vol 76 No 4, p 316-26, July-Aug 2004

This paper provides a comprehensive synthesis of information pertinent to N-nitrosodimethylamine (NDMA) to help utility professionals develop confidence toward controlling NDMA during wastewater treatment. Given the increased probability of the formation of NDMA using current wastewater treatment technologies and also in the complex matrices of the wastewaters subjected to UV treatment, the investigation of occurrence pathways and means of suppression of NDMA formation before and after treatment needs to be investigated. This paper summarizes treatment and practice strategies for NDMA control.

N-Nitrosodimethylamine (NDMA) as a Drinking Water Contaminant: A Review
Mitch, W.A. (Yale Univ., New Haven, CT); J.O. Sharp (Univ. of California, Berkeley); R.R. Trussell (Montgomery Watson Harza, Inc., Pasadena, CA); R.L. Valentine (Univ. of Iowa, Iowa City); L. Alvarez-Cohen and D.L. Sedlak (Univ. of California, Berkeley).
Environmental Engineering Science, Vol 20 No 5, p 389-404, 2003

N-Nitrosodimethylamine (NDMA) is a member of a family of extremely potent carcinogens, the N-nitrosamines. Current concern focuses on NDMA as a drinking water contaminant resulting from reactions occurring during chlorination or via direct industrial contamination. This review covers NDMA sources, occurrence, analysis, and treatment.
http://superfund.berkeley.edu/pdfs/03_mitch_1.pdf

N-Nitrosodimethylamine Content of US and Canadian Beers
Scanlan, R.A. and J.F. Barbour.
IARC Sci Publ. Vol 105, 242-243, 1991

A total of 194 beers (148 U.S. and 46 Canadian) were analyzed for volatile N-nitrosamines. N-Nitrosodimethylamine (NDMA), the only volatile N-nitrosamine detected, was found in 56% of the beers (detection level, 0.05 ug/kg), at a mean level of 0.074 ug/kg. The results indicate that NMDA levels in present-day U.S. and Canadian beers are approximately 1 to 5% of what they were a decade ago.

N-Nitrosodimethylamine Formation by Free-Chlorine-Enhanced Nitrosation of Dimethylamine
Choi, J. and R.L. Valentine, Univ. of Iowa, Iowa City.
Environmental Science & Technology, Vol 37 21, p 4871-4876, 1 Nov 2003

The formation of N-nitrosodimethylamine (NDMA) by the nitrosation of dimethylamine (DMA) is greatly enhanced by the presence of free chlorine (HOCl). The effect of HOCl appears at first to be contrary because HOCl rapidly oxidizes nitrite and hence should reduce NDMA formation from a mechanism involving classical nitrosation. The enhanced nitrosation by the presence of HOCl is, however, consistent with a mechanism that involves the formation of a highly reactive nitrosating intermediate such as dinitrogen tetroxide (N2O4) formed during the oxidation of nitrite to nitrate. This mechanism is quite unlike another recently proposed NDMA formation pathway involving the rate-limiting oxidation of DMA directly by monochloramine. The mechanism described here suggests the potential involvement of other nitrogen redox reactions that may produce reactive intermediates leading to the indirect and incidental formation of NDMA in the presence of appropriate organic nitrogen precursors.

A N-Nitrosodimethylamine (NDMA) Precursor Analysis for Chlorination of Water and Wastewater
Mitch, W.A., A.C. Gerecke, and D.L. Sedlak, Univ. of California, Berkeley.
Water Research, Vol 37 No 15, p 3733-3741, Sep 2003

N-nitrosodimethylamine (NDMA) is a potent carcinogen formed during chloramination of water and wastewater treatment plant effluents. A procedure is described for quantifying the concentration of the organic precursors of NDMA that could be formed during chlorination of wastewaters and natural waters. The method involves applying a high dose of monochloramine to a pH-buffered sample, followed by a 10-day contact period, during which the monochloramine decays at a rate unrelated to the composition of the sample. Analyses of samples of municipal wastewater effluents and surface waters indicate that the method provides a robust and reproducible measurement of NDMA precursors over a wide range of conditions. A sensitive GC/CI/MS/MS analytical procedure for dimethylamine also is described and used to demonstrate that NDMA formation during chlorination of wastewater and natural waters cannot be explained by dimethylamine concentrations alone.

NDMA: Analytical Methods Options for a New Disinfection Byproduct?
Eaton, Andrew and Mike Briggs, Montgomery Watson Laboratories, Pasadena, CA.
AWWA Water Quality Technology Conference, Nov 2000, Salt Lake City, Utah. 12 pp, 2000

Establishing the extent to which N-nitrosodimethylamine (NDMA) occurs is critical for assessing disinfection alternatives. In order to establish occurrence, it is necessary to have reliable analytical methods. Because the levels of interest for NDMA are extremely low (ppt), it is a greater challenge to ensure reliability than with contaminants occurring at higher levels. This paper describes the authors' experience in developing and validating a rugged technique for low-level NDMA and some of the issues that are critical in the analysis.
http://www.mwhlabs.com/files/papers/NDMA-Analysis%20of%20a%20new%20DBP.pdf

Occurrence of Preformed Volatile Nitrosamines in Preparations of Some Nigerian Medicinal Plants: a Preliminary Report.
Atawodi, S.E., Ahmadu Bello Univ., Zaria, Nigeria.
Food Chemistry & Toxicology, Vol 41 No 4, p 551-554, Apr 2003

Preparations of some tropical plants of medicinal importance were analyzed for preformed volatile N-nitrosamines. N-nitrosamines were analyzed by chemiluminescence detection on a thermal energy analyzer (TEA) following gas chromatographic (GC) separation. N-nitrosodimethylamine (NDMA) in the range of 1.2 to 3.4 ug/kg was detected in only four of the 29 sample preparations. These preliminary data suggest that medicinal plant preparations may be subject to microbial contamination, contributing to N-nitroso compound burden in many developing countries where ethnomedicine in still widely practiced.

Sources and Fate of Nitrosodimethylamine and its Precursors in Municipal Wastewater Treatment Plants
Sedlak, D.L., R.A. Deeb, E.L. Hawley, W.A. Mitch, T.D. Durbin, S. Mowbray, and S. Carr, Univ. of California, Berkeley.
Water Environment Research, Vol 77 No 1, p 32-39, Jan-Feb 2005

To assess the occurrence and fate of nitrosodimethylamine (NDMA) and its precursors, samples from wastewater treatment plants and industrial sources were analyzed for NDMA, total NDMA precursors, and dimethylamine (DMA). The median concentration of NDMA in untreated wastewater was approximately 80 ng/L, with maximum concentrations up to 790 ng/L. Concentrations of DMA in untreated wastewater ranged from approximately 50 to 120 ug/L and accounted for a majority of the NDMA precursors. While the removal of NDMA during secondary biological treatment exhibited considerable variability by ranging from 0 to 75%, removal of NDMA precursors and DMA generally exceeded 70%. Though DMA was removed during secondary treatment, other NDMA precursors in wastewater effluent will result in formation of additional NDMA upon disinfection with chloramines.

Supercritical Fluid Extraction of Volatile N-Nitrosamines in Fried Bacon and its Drippings: Method Comparison
Fiddler, W. and J.W. Pensabene.
Journal of the AOAC International, Vol 79 No 4, p 895-901, July-Aug 1996

Because the known carcinogens N-nitrosopyrrolidine (NPYR) and N-nitrosodimethylamine (NDMA) are consistently formed in bacon during frying, commercial bacon has been subject to regulatory monitoring and compliance for the past 20 years to ensure that N-nitrosamines do not exceed the 10 ppb volatile level. Investigators use time-consuming distillation-solvent extraction and solid-phase extraction (SPE) methods for this purpose. The authors have investigated supercritical fluid extraction (SFE) using supercritical carbon dioxide (SC-CO2) for isolation of volatile nitrosamines common to fried bacon. Eighteen fried bacon samples were analyzed for NPYR and NDMA by SFE, SPE, mineral oil distillation (MOD), and low-temperature vacuum distillation (LTVD) methods, using the same gas chromatographic-chemiluminescence detection (thermal energy analyzer) conditions. Overall, SFE was superior to the other methods with the highest recoveries, best repeatability, rapidity of analysis, and solvent-sparing characteristics.

Toxicological Profile for N-Nitrosodimethylamine, Chapter 6: Analytical Methods
Agency for Toxic Substances and Disease Registry, p 77-82, Dec 1989

Discusses analytical methods for biological materials and environmental samples.
http://www.atsdr.cdc.gov/toxprofiles/tp141.html

UV Photolytic Mechanism of N-Nitrosodimethylamine in Water: Dual Pathways to Methylamine Versus Dimethylamine
Lee, C., W. Choi, Y.G. Kim, J. Yoon, Seoul National Univ., Seoul, Korea.
Environmental Science & Technology, Vol 39 No 7, p 2101-2106, 1 Apr 2005

The direct ultraviolet (UV) photolysis of the carcinogen N-nitrosodimethylamine (NDMA) was investigated in aqueous solution, with its degradation products analyzed quantitatively. NDMA is known to be photolyzed either to dimethylamine (DMA) or to methylamine (MA) by two distinct pathways. A new mechanistic pathway of NDMA photolysis to DMA has been revealed by identifying the factors influencing the photolysis pathway. The two pathways of NDMA photolysis were found to be strongly dependent on the initial NDMA concentration and solution pH. Increasing the initial NDMA concentration clearly favored the DMA formation path. DMA production was optimized in the region of pH 4 to 5. The observed photolytic behaviors of NDMA photolysis could be successfully explained in terms of the mechanism involving the role of the nitrite ion, which is a key reagent in directing the NDMA photolysis toward DMA production.

PERCHLORATE

35Cl and 37Cl Magic-Angle Spinning NMR Spectroscopy in the Characterization of Inorganic Perchlorates
Skibsted, Jrgen; Hans J. Jakobsen, Instrument Centre for Solid-State NMR Spectroscopy, Dept. of Chemistry, Univ. of Aarhus, Aarhus, Denmark. Inorganic Chemistry, Vol 38 No 8, p 1806-1813, 1999

35Cl quadrupole coupling constants (CQ), asymmetry parameters (Q), and isotropic chemical shifts (iso) have been determined for a series of inorganic perchlorates from 35Cl magic-angle spinning (MAS) NMR spectra at 14.1 T. Illustrative 37Cl MAS NMR spectra are obtained and analyzed for some of the samples. For perchlorate anions with quadrupolar couplings less than about 1 MHz, the 35Cl/37Cl NMR parameters are most precisely determined from the full manifold of spinning sidebands observed for the satellite transitions while line-shape analysis of the central transition is employed for the somewhat larger quadrupolar couplings. The environments for the individual perchlorate anions are best characterized by the quadrupole coupling parameters (e.g., CQ ranges from 0.3 to 3.0 MHz), while the dispersion in the isotropic 35Cl chemical shifts is small (1029 ppm < iso < 1049 ppm) for the perchlorates studied. Due to the variation in quadrupole coupling parameters, 35Cl MAS NMR may conveniently be employed for identification of anhydrous and hydrated phases of perchlorates, in studies of phase transitions, hydration reactions, and the composition of mixed phases. The perchlorates studied include the anhydrous and the anhydrous and/or hydrated forms.

Accelerated Solvent Extraction (ASE) as a Sample Extraction Technique for Perchlorate in Solid Matrices
Richter, B.E., S. Henderson, and D. Later, Dionex Corp.
PITTCON 2004, 7-12 March 2004, Chicago, Illinois.

Several approaches for sample extractions are being explored as part of the overall analytical scheme to isolate perchlorate. Accelerated solvent extraction (ASE) is an extraction technique that uses organic or aqueous-based solvent for fast and efficient extractions. The use of elevated temperatures and pressures allow extractions to be done very quickly and with very little solvent. ASE fulfills the requirements of Method 3545A for the extraction of organic contaminants from solid waste samples. Aqueous solvent systems are widely used in ASE, which allows the extraction of very polar compounds. This presentation centers on the use of ASE as an extraction method prior to perchlorate determination using ion chromatography (IC) with suppressed conductivity or mass spectrometry for detection in the recovery of perchlorate from soils and vegetable samples.

Accelerated Solvent Extraction (ASE) as a Sample Extraction Technique for Perchlorate in Solid Matrices
Richter, Bruce, Sheldon Henderson, Doug Later, and Rosanne Slingsby, Dionex, Salt Lake City, UT.
NEMC 2004: The 20th Annual National Environmental Monitoring Conference, 19-23 July 2004, Washington, DC. Book of Abstracts, No. 30.

Accelerated solvent extraction (ASE) is an extraction technique that uses organic or aqueous-based solvent for fast and efficient extractions. The use of elevated temperatures and pressures allow extractions to be done quickly and with little solvent. ASE with chelating agents has been used for the extraction of metals from soils, and the method also has been used for ionic materials like chloride, sulfate, phosphate, bromate, and perchlorate. This presentation addresses the use of ASE as an extraction method prior to perchlorate determination using ion chromatography (IC) with suppressed conductivity or mass spectrometry for detection in soils and vegetation samples.

Advanced Perchlorate-Tracking Technology to Be Applied to Area Groundwater by NASA Team
NASA Jet Propulsion Laboratory Bilingual Newsletter, p 3, Mar 2005

Advanced isotopic analysis techniques similar to those being developed in the search for water on Mars are being applied to NASA's ground-water cleanup project at the Jet Propulsion Laboratory (JPL). NASA has been cleaning up volatile organic compounds (VOCs) and, more recently, perchlorate in ground water known to be related to past activities at the JPL site. While cleanup efforts continue and progress has been achieved, additional off-site groundwater investigation is still needed to determine the complete extent of travel of chemicals in ground water from historic JPL activities. With recent

detections of perchlorate in additional groundwater wells downgradient of JPL but not thought to be related to historic JPL activities, NASA is seeking a better understanding of groundwater flow patterns and possible sources of the perchlorate. Isotopic analysis may be one way of getting the information needed. All isotopes of an element contain the same number of protons, but different isotopes of the same element have different numbers of neutrons in their atoms--thus the compounds that those elements create have a unique chemical "fingerprint." Isotopic analysis is a way of fingerprinting the perchlorate in ground water by comparing the ratio of certain chemical isotopes present in or accompanying the perchlorate. For example, naturally occurring perchlorate has a higher value of the oxygen-17 isotope (an oxygen atom with eight protons and nine neutrons in its nucleus) but a lower chlorine-37 value (a chlorine atom with 17 protons and 20 neutrons in the nucleus) when compared to synthetic or manufactured samples of perchlorate. Perchlorate isotopic analyses may help distinguish between natural and man-made perchlorate and even improve the ability to distinguish among various man-made perchlorate sources, especially if each source's unique isotopic fingerprint can be determined. It could also provide clues as to whether off-site groundwater problems originated from beneath the JPL facility. The new analyses might also help in determining flow patterns of the groundwater near JPL. NASA intends to analyze isotopes of chlorine, oxygen, hydrogen, helium, and strontium in the groundwater and has assembled a team of national experts to conduct the analyses. Initial results are expected within a year.
http://jplwater.nasa.gov/NMOWeb/Adminrecord/docs_nonadmin/March%20Newsletter.pdf

Advances in the Determination of Inorganic Ions in Potable Waters by Ion Chromatography
Jackson, Peter E. and Kirk Chassaniol, Dionex Corporation, Sunnyvale, CA.
Journal of Environmental Monitoring, Vol 4 No 1, p 10-15, 2002

The authors discuss recent developments in the field of ion chromatography, such as the use of higher capacity columns, larger loop injections, more complex sample preparation and detection schemes. These advances allow the determination of contaminants, such as common inorganic anions, bromate, perchlorate, and chromate, at trace levels in potable waters using ion chromatography.

Advances in The Determination of Perchlorate in Drinking Water and Ground Water Using IC and IC/MS Methods
Joyce, Robert J. (Dionex Corporation, Sunnyvale, CA), D.W. Later, R. Slingsby, D.H. Thomas. The Pittsburgh Conference: PITTCON 2003, Presentation 2060-3.

Using IC with an MSQ mass spectrometric (MS) detector equipped with an enhanced low mass option (ELMO), perchlorate can be determined with an MDL of 0.05 ug/l. This exceptionally low MDL, combined with the unique mass selective detection that MS offers, makes IC/MS a good choice for accurate and sensitive ultra-low level perchlorate determinations. The effect of high concentrations of total dissolved solids on both IC and IC/MS methods are discussed.

Analysis of Hydroponic Fertilizer Matrixes for Perchlorate: Comparison of Analytical Techniques
Collette, T.W. (U.S. EPA, Athens, GA), T.L. Williams, E.T. Urbansky, M.L. Magnuson, G.N. Hebert, and S.H. Strauss.
Analyst, Vol 128 No 1, p 88-97, 2003

Seven retail hydroponic nitrate fertilizer products, two liquid and five solid, were comparatively analyzed for the perchlorate anion by ion chromatography (IC) with suppressed conductivity detection, complexation electrospray ionization mass spectrometry (cESI-MS), normal Raman spectroscopy, and infrared spectroscopy using an attenuated total reflectance crystal (ATR-FTIR) coated with a thin film of an organometallic ion-exchange compound. Three of the five solid products were found by all techniques to contain perchlorate ranging from 100 to 350 mg/kg. The remaining products did not contain perchlorate above the detection level of any of the techniques. Comparative analysis using several analytical techniques that depend on different properties of perchlorate allow for a high degree of certainty in both the qualitative and quantitative determinations, particularly in complex matrices.

Analysis of Perchlorate in Drinking Water, Groundwater, Saline Water, Soil, and Biota by LC/MS
Di Rienzo, Robert P. (DataChem Laboratories, Inc., Salt Lake City, UT); Kham Lin; Thomas T. McKay; Richard W. Wade. NEMC 2004: The 20th Annual National Environmental Monitoring Conference, 19-23 July 2004, Washington, DC. Book of Abstracts, No. 31.

A method has been developed and validated for the determination of perchlorate in drinking water, groundwater, saline water, soil, and biota using liquid chromatography/mass spectrometry (LC/MS) without sample pretreatment. This new method uses a newly developed commercially available peptides-impregnated reverse-phase liquid chromatography column (KP-RPPX series columns) developed by K'(Prime) Technologies, Inc. By using this column in an Agilent 1100 LC/MSD system, the technique separates perchlorate from known interferences in difficult matrices and can detect the chemical in matrices that are unacceptable for analysis by method 314.0. Mass spectrometry is used to monitor perchlorate at mass 83. An 83/85 isotopic ratio is used for additional identification of perchlorate, with statistical process control limits to assess the validity of the detection. An Internal Standard of Oxygen-18-labeled perchlorate is used to enhance the analysis. The method can achieve a method detection limit in aqueous samples of 0.05 ppb and can easily quantify perchlorate at 0.2 ppb in environmental sample matrices. Analysis is accomplished in less than 13 minutes and up to 20 samples can be processed in an eight-hour sequence with appropriate QC. The method eliminates matrix interference, high dissolved solids, and conductivity.

Analysis of Perchlorate in Groundwater by Electrospray Ionization Mass Spectrometry/Mass Spectrometry
Koester, C.J.; H.R. Beller*; R.U. Halden Lawrence Livermore National Laboratory, Livermore, CA
Environmental Science & Technology, Vol 34 No 9, p 1862-1864, 2000

An electrospray ionization mass spectrometry/mass spectrometry (ESI/MS/MS) method was developed to measure part-per-billion (µg/L) concentrations of perchlorate in ground water. Selective and sensitive perchlorate detection was achieved by operating the mass spectrometer in the negative ionization mode and by using MS/MS to monitor the ClO4- to ClO3- transition. The method of standard additions was used to address the considerable signal suppression caused by anions that are typically present in ground water, such as bicarbonate and sulfate. ESI/MS/MS analysis was rapid, accurate, reproducible, and provided a detection limit of 0.5 µg/L perchlorate in ground water. Accuracy and precision of the ESI/MS/MS method were assessed by analyzing performance evaluation samples in a ground water matrix (4.5-75 µg/L perchlorate) and by comparing ion chromatography (IC) and ESI/MS/MS results for local ground water samples (<0.5-35 µg/L perchlorate). Results for the performance evaluation samples differed from the certified values by 4-13%, and precision ranged from 3 to 10% (relative standard deviation). The IC and ESI/MS/MS results were statistically indistinguishable ($P > 0.05$) for perchlorate concentrations above the detection limits of both methods.

Analysis of Perchlorate in Human Urine Using Ion Chromatography and Electrospray Tandem Mass Spectrometry
Valentin-Blasini, L., J.P. Mauldin, D. Maple, and B.C. Blount, Centers for Disease Control and Prevention, Atlanta, GA.
Analytical Chemistry, Vol 77 No 8, p 2475-2481, 15 Apr 2005

A sensitive and selective method for quantifying perchlorate in human urine uses ion chromatography coupled with electrospray ionization tandem mass spectrometry. Perchlorate is quantified using a stable isotope-labeled internal standard with excellent assay precision. Selective chromatography and tandem mass spectrometry reduce the need for sample cleanup, resulting in a rugged and rapid method capable of routinely analyzing 75 samples/day. The lowest reportable level (0.025 ng/ml) is sufficiently sensitive to detect perchlorate in all human urine samples evaluated to date, with a linear response range from 0.025 to 100 ng/ml.

Analysis of Perchlorate in Water and Soil by Electrospray LC/MS/MS
Winkler, P. (Time Solutions Corporation, Golden, CO); M. Minteer (Analytical Quality Associates, Albuquerque, NM); J. Willey (General Engineering Laboratories, Charleston, SC).
Analytical Chemistry, Vol 76 No 2, p 469-473, 15 Jan 2004

A method has been developed for the determination of perchlorate in water and soil matrices using electrospray liquid chromatography/mass spectrometry/mass spectrometry. Perchlorate is quantitated by monitoring the ion signal from mass 83, which is formed by a loss of an oxygen atom from the perchlorate molecular ion. The aqueous method detection limit (MDL) is 0.05 ug/L as determined using an actual groundwater matrix. The soil MDL is 0.5 ug/kg as determined using Ottawa sand. The stability study was performed by spiking water samples at 0.25, 10, and 20 ug/L and analyzing them 50 days later. The procedure exhibited no significant suppression effects when tested at high salt levels. Calibration, quality control sample, field sample, and suppression study data were combined to examine isotope ratio reliability. The results of that work show that chlorine isotope ratios can be used to define statistical process control limits for use as an additional analyte identification tool.

Analysis of Perchlorate in Water by Reversed-Phase LC/ESI-MS/MS Using an Internal Standard Technique
Li, Y. and E.J. George, Underwriters Laboratories Inc., South Bend, IN.
Analytical Chemistry, Vol 77 No 14, p 4453-4458, 15 July 2005

A rapid, accurate, and reproducible method was developed for the analysis of perchlorate (ClO_4^-) in water using reversed-phase liquid chromatograhy/electrospray ionization-mass spectrometry/mass spectrometry (LC/ESI-MS/MS) in the negative ESI mode. Selective and sensitive perchlorate detection was obtained by monitoring the $35ClO_4^- > 35ClO_3^-$ and $37ClO_4^- > 37ClO_3^-$ mass transitions. Sample pretreatment for the removal of major common anions and dissolved metal ions along with internal standard quantitation compensated for ion suppression caused by the matrix. The method sensitivity, accuracy, and precision were investigated by analyzing fortified blank samples, field samples, and performance evaluation samples. The calculated method detection limits were 0.007 ug/L for deionized reagent water and 0.009 ug/L for synthesized reagent water, respectively. The minimum reporting limit was conservatively set to 0.05 ug/L.

The Analysis of Perchlorate in Well Water by Suppressor Based Ion Chromatography
Kildew, Brian R. (Alltech Associates, Deerfield, IL); Raaidah Sarri-Nordhaus. Pittcon 2000: Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy [50th], 12-17 March 2000, New Orleans, LA

The analysis of perchlorate in well water is simple and accurate by suppressor-based ion chromatography. The methacrylate-based anion exchanger column with either carbonate/bicarbonate or carbonate/bicarbonate in p-cyanophenol provides good peak shape with a short retention time for perchlorate. The detection limit for perchlorate can be reduced to the low parts-per-billion range using the methacrylate-based anion exchanger column with these mobile phases.

Application of an Ion Chromatography Method for Perchlorate Determination in Difficult Matrices
Canas, J., K. Tian, and T. Anderson, Texas Tech Univ., Lubbock. 24th Annual Meeting of the Society of Environmental Toxicology and Chemistry, 9-13 November 2003, Austin, Texas. Abstract 247, 2003

Due to matrix interferences, little progress has been made in the analysis of perchlorate in non-water samples, but recently an online preconcentration and pre-elution (PC/PE) ion chromatography method has been developed to remove matrix interferences in these difficult samples. Detection limits with this method are comparable to if not lower than those achieved using EPA Method 314.0. The PC/PE method has been applied to the analysis of perchlorate in fertilizers with detection limits ranging from 420 to 870 µg/kg (ppb) and also can be applied to other sample matrices, such as plant tissues, urine, and citrus fruits and juices.

Application of Capillary Electrophoresis for the Determination of Inorganic Ions in Trace Explosives and Explosive Residues
Kishi, T.; J. Nakamura; H. Arai, Natl. Res. Inst. Police Sci., Tokyo, Japan Electrophoresis, Vol 19 No 1, p 3-5, Jan 1998

Trace perchlorate explosives on a pair of cotton gloves were extracted with H2O and analyzed by capillary electrophoresis in a fused-silica capillary, with detection of chloride, nitrate and perchlorate. Residue from a homemade chlorate explosive (potassium chlorate plus fuel) was dissolved in H2O and analyzed in a similar manner, as was an aqueous extract of a residue from an emulsion explosive.

Application Note: Analysis of Low Concentrations of Perchlorate in Drinking Water and Ground Water by Ion Chromatography
Dionex Corp., Sunnyvale, CA Application Note 121, 4 pp, Jul 2000

According to a Dionex application note, perchlorate was determined in drinking water down to ~2.5 g/l levels by ion chromatography. Sample (1000 l) was analyzed on an IonPac AS11 analytical column (25 cm x 4 mm i.d.) equipped with an IonPac AG11 guard column (5 cm x 4 mm i.d.) with 100mM-NaOH as eluent (1 ml/min) over 12 minutes and suppressed conductivity detection. The calibration graph was linear up to 100 g/l with a detection limit of 2.5 g/l. The note contains chromatograms.

Assessment of Perchlorate Releases in Launch Operations
Lang, V.I.; K.R. Bohman; J.T. Tooley; E.W. Fournier; B.B. Brady, Aerospace Corp., El Segundo, CA.
Report No: TR-2001(1306)-3, NTIS: ADA396842. 44 pp, Oct 2001
Associated Needs Area: Remote optical sensing for fence-line monitoring for fugitive emissions/enforcement activities

An overall approach to the assessment of potential perchlorate releases from launch operations is presented. Two particular aspects of the assessment have been addressed to date. Laboratory studies to determine the effects of salinity and temperature on the chemical kinetics of perchlorate release from solid rocket motor propellant were conducted. The results showed an increase in the rate of perchlorate loss with increasing temperature and a decrease in the rate with increasing salinity. Second, a methodology developed for evaluating solid rocket motor propellant dispersal in the event of a catastrophic failure was applied to several failed historic launches, as well as to Delta IV and Atlas V cases.

More Info: http://handle.dtic.mil/100.2/ADA396842

ATR-FTIR Detection and Quantification of Low Concentrations of Aqueous Anions
Hebert, G. N., M. A. Odom, S. C. Bowman, and S. H. Strauss
Analytical Chemistry, Vol 76 No 3, 781-787, 1 Feb 2004

Evaporated thin-film coatings of anion-selective tetraalkylated ferrocenium salts were applied to the surface of attenuated total reflectance (ATR) crystals, which enabled anion detection limits to be lowered 23,000-fold below those achieved using a commercially available spectrometer with identical uncoated ATR crystals. Linear calibration curves based on d(absorbance)/dt, which is related to the rate of anion exchange in the thin film, were established in the 0.04 to 30 uM range. Using the thin-film coatings, limits of detection (10-min analyses) for perchlorate, chlorate, trifluoromethanesulfonate, perfluoro-n-butanesulfonate, perfluoro-n-octanesulfonate, tetrafluoroborate, hexafluorophosphate, and pinacolylmethylphosphonate in aqueous solution were 0.03, 0.2, 0.05, 0.07, 0.06, 0.06, 0.6, and 0.7 uM, respectively. This simple detection/quantification method using FTIR spectroscopy affords good reproducibility with relatively fast detection times.

ATR-FTIR Detection of [less than or equal to] 25 ug/L Aqueous Cyanide, Perchlorate, and Perfluorooctylsulfonate
Strauss, S.H.; M.A. Odom; G.N. Hebert; B.J. Clapsaddle,
Journal AWWA, Vol 94 No 2, p 109-115, 2002

Until recently, ion chromatography or mass spectrometry were the only ways to detect microgram-per-liter concentrations of anions such as cyanide, perchlorate, or perfluorooctylsulfonate (PFOS). Researchers at the University of Colorado have discovered that Fourier transform infrared (FTIR), a common and potentially portable spectroscopic technique, can be used to detect and identify certain aqueous anions of concern at small concentrations in favorable cases, even when competing anions are present. The reported method does not require pretreatment of the aqueous samples for the detection and identification of the three substances. Using the modified crystal and after 60-min analyses, detection limits for cyanide, perchlorate, and PFOS were 5, 3, and 25 ug/L, respectively. Previously, a commercial IR spectrometer could detect these anions only at concentrations 4,000 to 100,000 times higher. Though the new method was not ready for field or plant use at the time of this report, the authors describe a discovery that will be studied in other laboratories and pursued to develop new instruments that will provide a more robust and potentially far less expensive device for determining concentrations of cyanide, perchlorate, PFOS, and other substances at extremely low levels.

Automatic Liquid-Liquid Extraction Flow Injection Analysis Determination of Trace Amounts of Perchlorate With Spectrophotometric Detection
Ensafi, Ali A.; B. Rezaei, College of Chemistry, Isfahan University of Technology, Isfahan, Iran
Analytical Letters, Vol 31 No 1, p 167-177, 1998

The authors propose an extractive flow injection analysis for rapid, sensitive, and selective determination of perchlorate by spectrophotometric detection. The method is based on the extraction of perchlorate with Brilliant Cresyl Blue on methyl isobutyl ketone at pH 6.0. Perchlorate can be determined in the range of 0.008-1.00 µg/ml with a limit of detection of 0.003 µg/ml and rate of 30 ± 5 samples/hour. The effects of reagent concentration, pH, manifold variables, and diverse ions are completely studied. The method was tested for the determination of perchlorate in salt samples.

Available and Emerging Analytical and Sampling Techniques, Methods, and Tools for Perchlorate, and the Importance of Data Quality
Sample, Jacqueline H., U.S. Navy, Naval Sea Systems Command, Charleston, SC. SERDP/ESTCP Partners in Environmental Technology Technical Symposium & Workshop, 2-4 December 2003, Washington, DC. Technical Abstracts, p 85, 2003

At this time, the only EPA-approved method for the analysis of perchlorate is Method 314.0, which was developed and validated for use in potable water (drinking water) samples. The method reporting level (MRL), (i.e., the lowest concentration at which perchlorate measurements are reliable and repeatable within defined criteria) for Method 314.0 in pure drinking water is 4ppb, but it will not be possible to meet this MRL in all drinking water samples or in other environmental media, because Method 314.0 is a "non-specific" method, subject to false positive results due to interferences from numerous sources. Alternative analytical methods are commercially available on a limited basis, but none has yet been published or approved for use by EPA. The DoD Environmental Data Quality Workgroup (EDQW) and the Intergovernmental Data Quality Task Force are collaborating on an initiative, the Perchlorate Roundtable discussion (October 2003), to examine problems and limitations with current perchlorate sampling and testing methods, discuss emerging technology, and recommend a path forward for developing, validating, and publishing improved, performance-based perchlorate sampling and analysis methods. In addition, the EDQW is in the process of developing detailed guidance for the characterization of perchlorate across DoD, expected to be issued late in FY04. The guidance will address the development and design of sampling programs, as well as specific sampling and testing methodology.

Catalytic Determination of Perchlorate Using a Modified Carbon Paste Electrode
Neuhold, C.G.; K. Kalcher; X. Cai; G. Raber Analytical Letters, Vol 29, p 1685-1704, 1996

A carbon paste electrode chemically modified with the liquid anion exchanger Amberlite LA2 was used for the voltammetric determination of nitrate and perchlorate in aqueous solutions, based on the catalytic effect of both species on the voltammetric current responses of thallium. Thallium (III) can be accumulated as $TlCl4$ externally under open circuit conditions from an acidic solution onto the surface of the modified carbon paste electrode, giving a reduction signal at -0.88 V vs. SCE, and reoxidation signal at -0.7 V vs. SCE in cyclic voltammetry. Both signals are enhanced catalytically upon addition of nitrate or perchlorate to the preconcentration solution. The peak increase of the re-oxidation signal was exploited for quantitative purposes with differential pulse voltammetry. A procedure for the quantitative determination of both analytes is described. The influence of various parameters affecting the results, such as pH value of the measurement and analyte solution is discussed. The dependence of the peak increase on accumulation time and concentration of nitrate or perchlorate is shown. The detection limits were found to be 0.5 mg/L for nitrate and 0.05 mg/L for perchlorate respectively. The applicability of the method for the determination of the analyte species in various samples was studied

Challenges Encountered in Extending the Sensitivity of U.S. Environmental Protection Agency Method 314.0 for Perchlorate in Drinking Water

Wagner, H.P., F.X. Suarez, B.V. Pepich, D.P. Hautman, and D.J. Munch, EFFEX Analytical Services, Las Vegas, NV.

Journal of Chromatography A, Vol 1039 No 1-2, p 97-104, 11 June 2004

Researchers used 2-mm columns (the Dionex TAC LP-1 and a new Dionex high-capacity Cryptand concentrator column) with a large-loop direct injection method, a column concentration technique, and the concentration technique plus a background reduction step to increase the sensitivity for the analysis of trace levels of perchlorate in high ionic strength matrices. A surrogate was used to monitor trapping efficiency for the concentration technique, as well as confirmational columns to minimize the potential for false positives. The large-loop direct injection method and the column concentration methods provided acceptable data when the samples were pre-treated with solid phase pretreatment cartridges. The background reduction technique did not provide acceptable data with either of the concentrator columns.

Characterization of Perchlorate Exposure Using a Preconcentration Ion Chromatography Method Developed for Complex Matrices

Canas, J., K. Tian, T. Anderson, Texas Tech Univ., Lubbock Fourth SETAC World Congress, 25th Annual Meeting in North America, 14-18 November 2004, Portland, Oregon. Society of Environmental Toxicology and Chemistry, Pensacola, FL. Abstract 163, 2004

Due to matrix interferences, little progress has been made in the analysis of perchlorate in non-water matrices. An online preconcentration and preelution (PC/PE) ion chromatography method has been developed to remove matrix interferences in these complex samples. This new method has been used to characterize exposure in organisms by analyzing for perchlorate in fish, amphibians, avian eggs, biological tissues, vegetation, and hydroponic fertilizers. Preliminary work also indicates the effectiveness of the new method to deal with matrix interferences commonly found in citrus fruits and juices. PC/PE perchlorate detection limits in fertilizers range from 130 to 190 µg/kg (ppb) depending on fertilizer type, compared to a Method 314.0 detection limit of approximately 30 mg/kg (ppm).

Construction and Evaluation of Ion Selective Electrodes for Perchlorate with a Summing Operational Amplifier: Application to Pyrotechnics Mixtures Analysis

Pérez-Olmos, Ricardo; Ainoa Rios; María P. Martín; Rui A.S. Lapa; José L.F.C. Lima The Analyst, Vol 124 No 1, p 97-100, Jan 1999

An ion selective-electrode (ISE) for perchlorate was fabricated by applying four separate but identical membranes on to a conductive graphite/epoxy support. The membranes were prepared from

PVC, o-nitrophenyl octyl ether, dibutyl phthalate, and tetra-octylammonium chloride. When the use of the ISE for the direct potentiometric determination of perchlorate was evaluated, the lower linear response limit was 5.1 M perchlorate and the detection limit was 1.2 M, with a response time of 13-15 seconds. The sensor was applied to propellants and pyrotechnic mixtures and had a life of more than 10 months.

Detection and Measurement of Explosives in Groundwater Using In Situ Electrochemical Sensors
Olsen, Khris B. (Pacific Northwest National Lab., Richland, WA); Joseph Wang. Partners in Environmental Technology: 2002 SERDP & ESTCP Symposium & Workshop, 3-5 December 2002, Washington, DC. Poster Abstracts, p 41, 2002

During the course of this 2001 SEED Strategic Environmental Research and Development Program (SERDP) project, various working electrode materials and voltammetric waveforms were compared, and relevant experimental parameters were optimized. Based on this initial testing a submersible electrochemical probe was developed using a carbon-fiber electrode assembly connected to a 50-foot-long shielded cable, for the real-time monitoring of nitro-organic explosives in natural water. The facile reduction of the nitro moiety group allowed convenient and rapid square-wave voltammetric measurements at trace levels of nitroaromatic explosives (TNT, TNB, and Tetryl) down to levels of 50 to 100 ppb. A newly developed background subtraction algorithm was used to minimize background contributions. A highly stable response (with relative standard deviations of 1.0 to1.5%) was observed for prolonged (10 hour) operations in natural water samples, with no apparent surface fouling. Detection limits for nitroamine explosives (HMX and RDX) and nitrocellulose were in the range of 1 to 2 ppm. The peak potentials for nitroamine explosives are directly superimposed onto the oxygen peak in the voltammogram, resulting in significant increase in detection limits. This interference, caused by the presence of oxygen, complicates the procedures required to measure nitroamine explosives in ground water. To successfully measure nitroamine compounds, oxygen removal will be required. With oxygen removal, detection limits for nitroamine explosives should approach those of the nitroaromatic explosives. Several potential interferences were investigated including mono- and di-nitrotoluene, 4-amino-2,6-dinitrotoluene, trichloroethene (TCE), nitrates, chromate, and perchlorate. Laboratory studies determined only degradation products of nitroaromatic explosives that still contain a nitro group interfere with the measurement of the nitroaromatic parent explosive. Other common co-contaminates did not interfere with the measurements.

Detection and Quantification of Sub-Micromolar Concentrations of Aqueous Anions Using Infrared Spectroscopy and Mass Spectrometry
Hebert, Gretchen N., Ph.D. dissertation, Colorado State University.
University Microfilm, Pub No AAT 3131676, ISBN: 0-496-78917-5, 273 pp, 2004

Two different techniques—electrospray ionization mass spectrometry (ESIMS) and attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectroscopy—were used for the detection and quantification of low concentrations of aqueous anions, such as perfluoroalkanesulfonates (PFAS), perchlorate, phosphonates, and cyanide. PFAS anions were quantified in aqueous solution by ESIMS with a detection limit for perfluoro-n-octanesulfonate (PFOS) of 6 nM. Quantification of PFOS in the groundwater from wells at a fire-training area at Wurtsmith Air Force Base (WAFB), Oscoda, MI, was possible using the method of standard additions as well as linear calibration curves that ranged from 0.01 to 5 uM PFOS. Concentrations of PFAS anions up to 0.6 uM were detected in the groundwater despite a minimum of five years since active fire-fighting activity ceased at WAFB. A new ATR-FTIR method was developed for the detection and identification of low concentrations of aqueous polyatomic anions. The technique involves coating the surface of an ATR crystal with a thin-film coating of an organometallic ion-exchange extractant, which enabled anion detection limits to be lowered up to 23,000—fold below those achieved using the commercially available ATR-FTIR spectrometer with an uncoated ATR crystal. Detection limits for 10-minute analyses of perchlorate, chlorate, trifluoromethanesulfonate, perfluoro-n-butanesulfonate, PFOS, pinacolylmethylphosphonate, and cyanide were 0.03, 0.2, 0.05, 0.07, 0.06, 0.7, and 0.09 uM, respectively, using coated ATR crystals. Linear calibration curves based on d(absorbance)/dt, which is related to the rate of anion exchange, were established in the 0.04-30 uM range. Several complex matrixes—synthetic tap water, simulated seawater, and hydroponic fertilizers—were examined. Using the method of standard additions, trace quantities of perchlorate were detected in hydroponic nitrate fertilizers where the nitrate-to-perchlorate concentration ratios were as high as 9,000. This simple ATR-FTIR detection/quantification method afforded good reproducibility with relatively fast (10-minute) detection times.

Detection of Cyanide, Perchlorate, and Other Terrorist Weapons at ppb Levels in Water by FTIR Spectroscopy
Strauss, Steven H., Colorado State Univ., Fort Collins. PITTCON 2003, March 9-14, Orlando, Florida. Abstract 1550-4.

A particular commercially-available silicon ATR-FTIR probe can be used to detect aqueous perchlorate ion down to 80 ppm with 60 minutes of signal averaging. When the same probe was coated with a redox-recyclable ion-exchange compound, the detection limit for aqueous perchlorate was lowered to 3 ppb at 30 minutes of contact time, an improvement in detection limit by a factor of more than 25,000. In another case, the detection limit for aqueous cyanide (pH 10) with a bare probe was 26 ppm with 60 minutes of signal averaging. When the probe was coated with a different ion-exchange compound, the detection limit decreased by a factor of 10,000 times to 2.6 ppb at 45 minutes of contact time. The author discusses this methodology and relates progress in lowering the detection limit of G-type nerve-agent hydrolysis products from the ppm to the ppb range.

Determination of Nanomolar Levels of Perchlorate in Water by ESI-FAIMS-MS
Handy, Russell; David A. Barnett; Randy W. Purves; Gary Horlick; Roger Guevremont Journal of Analytical Atomic Spectrometry, Vol 15 No 8, p 907-911, Aug 2000

Electrospray ionization (ESI) was used to generate gas-phase anions that were subsequently separated by high-field asymmetric waveform ion mobility spectrometry (FAIMS) and detected by quadrupole mass spectrometry (MS). ESI-FAIMS-MS provided selective and sensitive determination of perchlorate at low nanomolar levels, relatively free from the interferences commonly observed for this analysis using conventional ESI-MS. For instance, the gas-phase separation of ions in FAIMS eliminated isobaric overlaps of bisulfate and dihydrogen phosphate with perchlorate. Using the FAIMS interface, analysis yielded a signal-to-background ratio (S/B) improvement of over four orders of magnitude compared with ESI-MS. The detection limit for perchlorate was 1 nM (~ 0.1 ppb).

Determination of Perchlorate Anion in Foods by Ion Chromatography-Tandem Mass Spectrometry
Krynitsky, A.J., R.A. Niemann, and D.A. Nortrup, U.S. Food and Drug Administration, College Park, MD.
Analytical Chemistry, Vol 76 No 18, p 5518-5522, 15 Sep 2004

The authors describe a rapid, sensitive, and specific method for determining perchlorate anion in lettuce, cantaloupe, bottled water, and milk. A test portion of chopped crop homogenate was extracted with diluted nitric acid and filtered. Milk proteins were precipitated with acetonitrile, and the supernatant, after centrifugation, was cleaned up on a graphitized carbon solid-phase extraction column. Water samples were analyzed directly. All test solutions were syringe filtered and mixed with an $(18)O_4^-$ labeled perchlorate internal standard before ion chromatography-tandem mass spectrometry. A strong anion exchange column eluted with 100 mM ammonium acetate in 50:50 (v/v) acetonitrile/water was interfaced via electrospray ionization to a triple stage quadrupole mass spectrometer operated in the negative ion mode. The labeled internal standard corrected for any sample matrix effects on measured signals.

The Determination of Perchlorate Anion in High Ionic Strength Samples
Thomas, D.H.; J.S. Rohrer, Dionex Corporation. International Labmate, Vol 27 No 2, Apr 2002

Problems of perchlorate anion contamination in drinking water and ground water require a reliable and accurate means of measurement both to identify contaminated water directly and to understand the sources of the contamination. This article focuses on an application of ion chromatography with on-line eluent generation and suppressed conductivity detection for the determination of perchlorate contamination in water derived from materials such as fertilizers and inorganic salts.

More Info: http://www.product-search.co.uk/internationallabmate.com/features/april2002/dionex.shtml

The Determination of Perchlorate Anion in High Total Dissolved Solids Water Using LC/MS/MS
Krol, Jim, Waters Corp., Milford, MA. NEMC 2004: The 20th Annual National Environmental Monitoring Conference, 19-23 July 2004, Washington, DC. Book of Abstracts, P3.

Using the EPA Information Collection Rule as a data base, drinking water facilities have reported higher than anticipated concentrations of perchlorate in environmental waters in 22 states. DoD and DoE are also interested in perchlorate, an ingredient in many munitions, from a soil contamination perspective. The current EPA method 314.0 (Determination of Perchlorate Using Ion ChromatographyY) uses anion exchange chromatography with suppressed conductivity detection. This method works well but becomes limiting as the total dissolved solids concentration increases, especially sulfate. Sample preparation to remove chloride and sulfate is necessary and requires the use of a O18 perchlorate internal standard to account for recovery. This presentation describes an LC/MS/MS method for perchlorate with no requirement for sample preparation; instead, it looks at the chromatography of perchlorate relative to sulfate. As organic modifier concentration increases, perchlorate elutes faster than sulfate, allowing the chromatographer to place perchlorate baseline separated between high chloride and high sulfate. With the direct injection of 100 uL of a solution containing 1000 ppm each of bicarbonate, chloride, and sulfate, MS/MS detection can obtain a perchlorate detection limit (3:1 S/N) of 0.2 ppb.

The Determination of Perchlorate Anion in High Total Dissolved Solids Water Using LC/MS/MS
Krol, Jim, Senior Applications Chemist, Waters Corp., Milford, MA The 20th Annual International Conference on Soils, Sediments and Water, 18-21 October 2004, University of Massachusetts at Amherst.

The current EPA method 314.0 (Determination of Perchlorate Using Ion Chromatography) uses anion exchange chromatography with suppressed conductivity detection. This method works well but becomes limiting as the total dissolved solids concentration increases, especially sulfate. Sample preparation to remove chloride and sulfate is necessary and the most difficult problem, because it requires the use of an O18 perchlorate internal standard to account for recovery. This presentation describes an LC/MS/MS method for perchlorate without the requirement for sample preparation. The key to the problem is the chromatography of perchlorate relative to sulfate. As organic modifier concentration increases, perchlorate elutes faster than sulfate, allowing the chromatograph perchlorate baseline to be separated between high chloride and high sulfate. MS/MS detection can obtain a perchlorate detection limit (3:1 S/N) of 0.2 ppb with the direct injection of 100 mL of a solution containing 1000 ppm each of bicarbonate, chloride, and sulfate. Larger injection volumes can be used to increase sensitivity.

Determination of Perchlorate at Parts-Per-Billion Levels in Plants by Ion Chromatography
Ellington, J.J.; J.J. Evans Journal of Chromatography?A, Vol 898 No 2, p 193-199, 17 Nov 2000

Abstract not available.

Determination of Perchlorate at Trace Levels in Drinking Water by Ion-Pair Extraction with Electrospray Ionization Mass Spectrometry
Magnuson, Matthew L. (U.S. EPA, Cincinnati, OH); Edward T. Urbansky; Catherine A. Kelty
Analytical Chemistry, Vol 72 No 1, p 25-29, 2000

This paper describes the analysis of perchlorate in water by liquid-liquid extraction followed by flow injection electrospray mass spectrometry (ESI/MS). Alkyltrimethylammonium salts and other cationic surfactants were used to ion-pair aqueous perchlorate, forming extractable ion pairs. The cationic surfactant associates with the perchlorate ion to form a complex detectable by ESI/MS. The selectivity of the extraction and the mass spectrometric detection increases confidence in the identification of perchlorate. The method detection limit for perchlorate determined after seven replicate injections was 100 ng L-1 (parts per trillion). Perchlorate has been added to the U.S. EPA's Drinking Water Contaminant Candidate List.

Determination of Perchlorate in Drinking Water by Ion Chromatography
Saari-Nordhaus, R. (Alltech Associates, Inc., Deerfield, IL); D.R. Douglas, P. Despres. The Pittsburgh Conference: PITTCON 2001, 4-9 March 2001, New Orleans, Louisiana. Abstract 2284P, 2001

Ammonium perchlorate is used as an oxidizer in solid propellant of rockets, missiles, and fireworks. Recently, trace amount of perchlorate is found in drinking water in areas where these devices have been manufactured and tested. Perchlorate interferes with the utilization of iodine and disrupts the production of thyroid gland, so its presence in drinking water presents a health hazard. Regulatory agencies have started to develop methods for the analysis of perchlorate in drinking water. U.S. EPA method 314.0 determines perchlorate in drinking water using ion chromatography. The perchlorate ion is very hydrophobic and it usually retains very strongly on most anion exchange columns used in ion chromatography. A new column that is hydrophilic has been developed to reduce the retention time and improve the peak shape. This paper describes the analysis of perchlorate in drinking water using the new column and discusses the optimized mobile phase conditions, method detection limits, and linearity of the calibration curves.

Determination of Perchlorate in High Salinity Water: Preconcentration/Preelution IC
Tian, K., P. Dasgupta, R. Patel, and T. Anderson, Texas Tech Univ., Lubbock. 24th Annual Meeting of the Society of Environmental Toxicology and Chemistry, 9-13 November 2003, Austin, Texas.

An automated system has been developed for the determination of trace perchlorate by ion chromatography (IC) with an online preconcentration and preelution technique. The sample is preconcentrated and less strongly held ions preeluted before the analyte is transferred to the principal separation system. This approach provides low limits of detection (LOD) and is particularly robust toward the effect of high concentrations of common anions, such as those present in groundwater samples. It compares favorably with EPA Method 314.0. Experimental results with synthetic water samples, groundwater samples, and some retail hydroponic nitrate fertilizer samples show that this approach is particularly robust toward the effect of complex matrix in various samples due to its high efficiency to remove the background matrix of samples.

Determination of Perchlorate in Selected Surface Waters in the Great Lakes Basin by HPLC/MS/MS
Backus, S.M., P. Klawuun, S. Brown, I. D'sa, S. Sharp, C. Surette, and D.J. Williams, Environment Canada, Burlington, ON, Canada.
Chemosphere [proofed, corrected, and in press sometime after September 2005]

Surface water samples were collected from 55 sites in the Great Lakes Basin and analyzed for the presence of perchlorate using HPLC/MS/MS with an isotopically enriched internal standard. Detection of perchlorate at several of the sites at concentrations close to the method detection limit (0.2 ug/L) was confirmed by sample concentration and determination of the isotopic ratio of perchlorate.

Determination of Perchlorate in Tobacco Plants and Tobacco Products
Ellington, J.J., N.L. Wolfe, W. Garrison, J.J. Evans, J.K. Avantis, and Q. Teng.
Environmental Science & Technology, Vol 35 No 15, p 3213-3218, 2001

This paper contains results of preliminary investigations on the occurrence of perchlorate in tobacco plants grown in soils amended with a fertilizer whose nitrogen content is derived from naturally occurring sodium nitrate (Chile saltpeter). Ion chromatography (IC) and capillary electrophoresis (CE) were used for quantitative analysis, while nuclear magnetic resonance (NMR) spectroscopy was used for qualitative analysis of perchlorate. The results show that perchlorate is accumulated into tobacco plant leaves from soil amended with fertilizers that contain perchlorate. The presence of perchlorate can persist in the leaves even under processing, as shown by concentrations ranging from nd to 60.4 +/- 0.8 mg/kg on a wet weight basis in various off-the-shelf tobacco products (i.e., cigarettes, cigars, and pouch and plug chewing tobaccos).

Determination of the Origin and Fate of Perchlorate Using Stable Isotope Analysis
Hatzinger, Paul B. (Shaw Environmental, Inc., Lawrenceville, NJ); N.C. Sturchio; A. Beloso, Jr.; J.K. Bohlke; B. Gu; J. Horita; G.M. Brown.
Partners in Environmental Technology Technical Symposium & Workshop, 30 November - 2 December 2004, Washington, DC. Technical Program Abstracts, p 86, 2004

Isotope ratio analysis has been widely used to document the origin and geochemical behavior of both organic (e.g., chlorinated and non-chlorinated VOCs) and inorganic pollutants (e.g., nitrate and nitrous oxide). Recently, isotopic methodologies have also been developed for perchlorate. Using these techniques, the isotopic compositions of both chlorine and oxygen in the perchlorate molecule have been observed to differ significantly and consistently between naturally-occurring perchlorate and perchlorate from various anthropogenic sources. These isotopic differences, which range from approximately 8 - 15 per mil for 37Cl and 5 - 7 per mil for 18O, are readily distinguishable using isotope ratio mass spectrometry (IRMS). Recent data have also revealed that natural perchlorate is characterized by a unique 17O isotopic signature that readily differentiates it from man-made material. In addition to source identification, laboratory studies have shown that chlorine isotope analysis is a sensitive technique to document perchlorate biodegradation. Isotopic fractionation by the perchlorate-reducing isolate Dechlorosoma suillum JPLRND was observed to be as high as 60 per mil for 37Cl during active perchlorate metabolism. A smaller but significant isotopic fractionation of chlorine (approximately 2.7 per mil) was also observed during a SERDP-funded field demonstration of in situ perchlorate bioremediation. This presentation provides an overview of the application of stable isotope analysis for perchlorate forensics and bioremediation.

Determination of Trace-Level Perchlorate According to U.S. EPA Method 314.0 Using a Polyvinyl Alcohol Gel Resin

De Borba, Brian M.; Derrick W. Rowe, Metrohm-Peak, Inc., Houston, TX. American Laboratory News, p 22-24, Apr 2001

No National Primary Drinking Water Regulation (NPDWR) has been determined for perchlorate as of 2001. In 1996, perchlorate was placed on the Contaminant Candidate List, which is not currently subject to the NPDWR. Data from the U.S. EPA suggest an action level from 4 to 18 µg/L to provide adequate human health protection. Levels exceeding this range will require removal and proper treatment of the contaminated water source. In 1997, the California Department of Health Services and the Nevada Division of Environmental Protection established an action level of 18 µg/L. In 1999, Arizona and Texas set provisional action levels of 31 and 22 µg/L, respectively. This article discusses an improved method for the determination of trace levels of perchlorate that requires a large sample loop with a Metrosep A Supp 5 column, a hydroxide eluent modified with p-cyanophenol, and suppressed conductivity to quantitate down to the 2 µg/L level. Other parameters, such as calibration linearity, method detection limit, matrix conductivity threshold, and recovery of perchlorate in various matrices, are discussed also. In addition, the performance of a dedicated IC system (Metrohm 761 Compact IC, Metrohm-Peak, Inc., Houston, TX) is assessed.

More Info: http://www.iscpubs.com/articles/entirealn.html

Determination of Trace Level Perchlorate in Drinking Water and Ground Water by Ion Chromatography

Jackson, P. E.; M. Laikhtman; J.S. Rohrer, Dionex Corp., Sunnyvale, CA Presented at the International Ion Chromatography Symposium, held in Osaka, Japan, 28 Sep-1 Oct 1998 Journal of Chromatography?A, Vol 850, No 1/2, p 131-135, 30 Jul 1999

Samples were analyzed on an IonPac AG11 guard column and an IonPac AS11 analytical column with a mobile phase of 0.1M-NaOH and suppressed conductivity detection, with use of an ASRS-ULTRA suppressor at 0.3 A. Calibration graphs were linear for 2.5-100 ug/ml of perchlorate, with a detection limit of 0.3 ug/l. When seven replicates of a 2.5 ug/l standard were injected, the retention time RSD was 0.5% and the peak area RSD was 2.4%. There was no interference from 22 common anions. Tests were also carried out on a new column, the IonPac AS16, with its IonPac AG16 guard column. The AS16 was specifically developed for polarizable anions, such as perchlorate, iodide, thiosulfate and thiocyanate. The new column is more hydrophilic than the AS11, has higher capacity (allowing the analysis of samples with higher salt contents) and higher peak efficiency. An example of analysis of 5 ug/l of perchlorate in ground water is illustrated.

The Development and Application of Preconcentration/Preelution Ion Chromatography Methods for the Detection of Trace Perchlorate in Difficult Matrices
Canas, Jaclyn Elaine, Ph.D. thesis, Texas Tech University, Lubbock. 183 pp, Aug 2005

Analysis of perchlorate in biological samples by ion chromatography can be difficult because matrix components often interfere with low-level detection. A preconcentration/preelution ion chromatography method was developed in the laboratory to address such interferences in high salinity samples and was proposed for application to other matrices. This study assessed the ability of the method to remove interferences and determine lower sample background for gastrointestinal tract, kidney, liver, zebrafish, quail egg, lettuce, milk, urine, citrus, and soil matrices. Chapter I contains a review of analytical methods for perchlorate determination to provide a rationale for exploring the methodologies in this dissertation research. Chapter V contains the evaluation and development of a method for perchlorate determination in soil. Though this project was not part of the original dissertation proposal, it was conducted as part of a collaboration with EPA's Office of Solid Waste. The findings of the studies described in Chapter V will be part of the revision of EPA Method 9058 and will also be published as a manuscript on the development of an extraction method for perchlorate determination in soil.
http://etd.lib.ttu.edu/theses/available/etd-07142005-150134/unrestricted/Canas_Jaclyn_diss.pdf

Development of a Better Method to Identify and Measure Perchlorate in Drinking Water
Hedrick, E.J., D.J. Munch, and T.D. Behymer.
EPA Science Forum 2004, 1-3 June 2004, Washington, DC.

As analytical methods have improved in sensitivity, the discovery of perchlorate in drinking waters at lower and lower concentrations has increased. Collaboration between EPA's Office of Research and Development, the Office of Water and an instrument manufacturer has produced a method that is capable of identifying concentrations of perchlorate in drinking water ten times lower than previous methods. The most distinguishing feature of this method, which is not available in existing methods, is the capability to identify perchlorate by its chlorine isotope ratio. This isotopic ratio, in addition to separation of perchlorate from interferences, virtually eliminates the likelihood of mistaken identity. Should perchlorate become regulated in drinking water, this method will enable definitive identification and quantitation of perchlorate at concentrations as low as 0.1 part per billion.

Development of an IC/MS/MS Method for Low Level Determination of Perchlorate in Environmental Samples
Kurtz, Kristine (Clayton Group Services, Novi, MI) and Kem Charron. The Pittsburgh Conference: PITTCON 2003, Presentation 740-3.

For determination of perchlorate in drinking water, EPA Method 314.0 employs ion chromatography (IC) and conductivity detection, with a reporting limit of 4 ug/L and method detection limit (MDL) of 0.53 ug/L. The report limit of 4 ug/L corresponds to the minimum reporting level established by the EPA for monitoring purposes. Improved analytical methodology sensitivities for perchlorate determination are needed because the current minimum reporting limit and state action levels approach the detection and quantitation capabilities of 314.0. The authors present an IC/MS/MS method that couples IC and tandem mass spectrometry (MS/MS) for the determination of low-level perchlorate in environmental samples. Greatly improved sensitivity and selectivity provide for a calculated MDL of 0.02 ug/L in reagent water. The method is applicable to various environmental matrices, and due to the inherent sensitivity and selectivity of MS/MS detection, matrix interferences are significantly reduced for biological samples such as vegetation and animal tissue.

Development of a Surface Enhanced Raman Spectroscopy (SERS)-Based Sensor for the Long Term Monitoring of Toxic Anions
Boss, Pamela A., Space and Naval Warfare Systems Center, San Diego, CA. Partners in Environmental Technology: 2002 SERDP & ESTCP Symposium & Workshop, 3-5 December 2002, Washington, DC. Poster Abstracts, p 33, 2002

The ideal field-deployable sensor would be able to detect toxic anions reversibly in the low ppb concentration range, in situ, on site, with little or no sample preparation, and with no interferences. One technology that meets many of these criteria is Surface Enhanced Raman Spectroscopy (SERS) using cationic-coated silver substrates. SERS has advantages of specificity and sensitivity over other spectroscopic techniques. All polyatomic species will exhibit a characteristic Raman signature that can be used to both identify and quantify it, but with time, these substrates oxidize, resulting in a decrease in the SERS signal. To protect the silver or gold SERS substrates from degradation, the surface is allowed to react with a thiol to form a self-assembled monolayer. The added advantage with this approach is that thiol coatings can be chosen to attract the analytes of interest. In this SERDP-sponsored effort, detection of chromate, dichromate, perchlorate, and cyanide using cationic-coated SERS substrates has been demonstrated. Limits of detection in the ppb-ppm concentration range have been achieved. The coatings used in this investigation possess no anion recognition functionalities, other than a positive charge; consequently these coatings interact simultaneously with different anions. Means of improving selectivity have been examined, such as identifying ionophores specific for the anions and removal of the interferences using solid phase extraction, supported liquid membranes, and nanotubule technology. The electrochemical etching parameters have been optimized to lower the detection limit. A sensor module has been designed that can be used either stand-alone or inserted inside a modified, cone penetrometer sampler probe. The sensor module is used stand-alone immersed in samples obtained from monitoring wells. Inserting the sensor module inside a cone penetrometer sampler probe allows sampling of ground water at various depths. Either approach will provide monitoring data in real time without the additional cost of an outside lab.

Electrochemical Detection for Gaseous Vinyl Chloride with a Sputtered Au/Porous Alumina Substrate/Pt Electrode Assembly
Chuang, Min-Chieh; Ming-Chang Yang, National Cheng Kung Univ., Tainan, Taiwan, ROC. Electroanalysis, Vol 14 No 17, p 1209-1214, Sep 2002

A detector with a porous alumina substrate has been developed to monitor vinyl chloride gas in the concentration range of 0.5-4% at room temperature. Higher sensitivities were obtained with tetrabutylammonium perchlorate as the supporting electrolyte than with tetrabutylammonium tetrafluoborate, with the highest sensitivity of 70.9 A%-1 obtained at -2.1 V (vs. Ag/Ag+) in 50% toluene/50% DMF electrolyte. The sensing current and the sensitivity for vinyl chloride increased significantly with the porosity of the porous alumina substrate.

Electrochemical Investigation of Lead(II) in a Polymerized Crystalline Colloidal Array Sensor Material Containing Benzo-18-Crown-6-Ether
Geary, Caroline D. (Univ. of Pittsburgh, Pittsburgh, PA); S.A. Asher, C.E. Reese, S.G. Weber. PITTCON 2003, March 9-14, Orlando, Florida. Abstract 450-8.

In nanosystems research, the complexation between 18-crown-6 and lead(II) has been applied to both sensors and display devices. Electrochemical experiments have been carried out on this system with lead(II) in aqueous solution containing an excess of 18-crown-6. Using a square wave waveform with different experimental timescales, stoichiometry, binding constants, and rate constants have been determined at 25 degrees C for the system with both nitrate and perchlorate anions at a Hg/C electrode. Results indicate that there is an anion effect on the rate constants. Electrochemical experiments also have tested the binding of lead(II) with benzo-18-crown-6 immobilized in a polymerized crystalline colloidal array (PCCA) using a mercury film on gold electrode in contact with the PCCA.

Electrochemiluminescent Determination of Perchlorate by Solvent Extraction in the Presence of Ru(bpy)32+
Xu, G.; S. Dong, Lab. Electroanal. Chem., Changchun Inst. Applied Chem., Chinese Acad. Sci., Changchun, China, Electrochemistry Communications, Vol 1 No 10, p 463-466, Oct 1999

For the highly sensitive determination of perchlorate, the authors propose a method based on solvent extraction in the presence of Ru(bpy)32+ and followed by Ru(bpy)32+ electro-chemiluminescent determination. The detection limit was 50nM perchlorate and the RSD (n = 10) was 1.6%. Interference studies suggest that this method is selective for the determination of perchlorate.

Environmental Forensics of Perchlorate Origin and Biodegradation Using Stable Isotope Ratio Analysis
Gu, Baohua (Oak Ridge National Laboratory, Oak Ridge, TN); P.B. Hatzinger; J. Horita; N.C. Sturchio; J.K. Bohlke; H. Bao; A. Beloso, Jr.; G.M. Brown.
Partners in Environmental Technology Technical Symposium & Workshop, 30 November - 2 December 2004, Washington, DC. Poster Program Abstracts, p 75, 2004

Successful isolation and recovery of trace quantities of perchlorate from contaminated water and/or salt deposits has been demonstrated using novel selective ion exchange and recovery technologies. The isotopic compositions of both chlorine and oxygen in perchlorate were found to differ significantly and consistently between naturally-occurring perchlorates and those from various anthropogenic sources. Natural perchlorate derived from Atacama Desert soils has unique chlorine and oxygen isotope signatures and is readily distinguishable using isotope ratio mass spectrometry (IRMS). Natural perchlorates show a low negative 37Cl but large positive 17O anomalies in comparison with no 37Cl and 17O anomalies in man-made perchlorates. These isotope anomalies provide direct evidence of atmospheric origin of natural perchlorates and thus offer a potentially powerful tool for forensic determinations of perchlorate in the environment. In addition to source identification, laboratory studies have revealed that 37Cl isotope analysis is a sensitive technique to document perchlorate biodegradation and potentially to distinguish this process from other non-biological mechanisms leading to reduced perchlorate levels during in situ remediation efforts. For example, chlorine isotopic fractionation by the perchlorate-reducing isolate Dechlorosoma suillum JPLRND was observed to be as high as 60% during active perchlorate metabolism. These data suggest that the rate of the $35ClO_4$ reduction by this bacterium is ca. 1.3 to 1.7% faster than that of the $37ClO_4$ reduction. Recent data have also revealed a significant isotopic fractionation of chlorine (approximately 2.7%) during perchlorate biodegradation in the field. These results, which were gained during a SERDP-funded field demonstration, confirm that chlorine isotope analysis will be a sensitive technique to verify in situ bioremediation of perchlorate in groundwater.

Environmental Isotope Forensics of Perchlorate Contamination
Horita, J. (ORNL, Oak Ridge, TN); J.F. Bohlke (USGS, Reston, VA): N.C. Sturchio (Univ. Of Illinois, Chicago); B. Gu and G.M. Brown (ORNL): J.R. Batista (Univ. of Nevada, Las Vegas). Geological Society of America 2004 Denver Annual Meeting (November 7-10, 2004), Abstracts with Programs, Vol 36 No 5, p 241, 2004

The stable isotope ratios of Cl and O can potentially be used to distinguish the source(s) of perchlorate in a given location and to evaluate the extent of biodegradation. The stable isotope ratios of

Cl and O in anthropogenic perchlorate salts can be readily measured in milligram amounts, but it is difficult to extract and recover isotopically measurable amounts of perchlorate from natural waters in which the perchlorate concentrations may be on the order of ppb. The recent development of a new class of bifunctional anion exchange resins for efficient sorption and removal of perchlorate, along with a new resin regeneration technique for recovering sorbed perchlorate, provides a means for nearly quantitative recovery of perchlorate from water samples collected in the field for isotopic analysis. Using these innovative separation-recovery technologies, both developed at Oak Ridge National Laboratory, researchers have begun a systematic characterization of the stable isotope ratios of Cl and O in perchlorate from different sources, including anthropogenic perchlorate reagents, natural perchlorate-bearing salt deposits, salt-derived fertilizers, and waters from contaminated military and industrial sites. Preliminary results indicate that there are isotopic differences between various anthropogenic and natural perchlorate sources. When the data set of isotopically characterized perchlorate sources becomes sufficiently representative, stable isotope forensics of perchlorate may become useful for issues of source apportionment, natural attenuation, or remediation monitoring.

Evaluation of Perchlorate Biodegradation Using Chlorine Isotope Analysis
Hatzinger, P.B. (Shaw Environmental, Inc., Lawrenceville, NJ); N.C. Sturchio; M.D. Arkins; C. Suh; L.J. Heraty. SERDP/ESTCP Partners in Environmental Technology Technical Symposium & Workshop, 2-4 December 2003, Washington, DC. Poster Session Abstracts, p 170, 2003

When evaluating the biological degradation of perchlorate in the field, evaluating the performance of in situ bioremediation is complicated by the difficulty of distinguishing chemical loss due to biodegradation from abiotic loss mechanisms, such as dilution and adsorption. In addition, it is often difficult to document slow biodegradation processes that are occurring naturally over time (i.e., intrinsic bioremediation). Stable isotope analysis of light elements (e.g., H, C, N, Cl) has been used to successfully differentiate biodegradation of common pollutants, such as chlorinated solvents, gasoline constituents, and nitrate, and from other non-biological loss mechanisms for these compounds, but little information exists concerning the application of this technique for evaluating perchlorate biodegradation. Researchers quantified chlorine isotope fractionation during perchlorate reduction by Dechlorosoma suillum JPLRND, an isolate initially obtained from a perchlorate-contaminated groundwater source in southern California. The values of the chlorine isotopic fractionation factor were derived from two studies with this organism. The values show that the rate of the 35ClO4 reduction by this organism is ~1.3-1.7% faster than that of the 37ClO4 reduction. This large isotope effect suggests that chlorine isotope analysis will be a sensitive technique to document in situ bioremediation of perchlorate in groundwater. Additional studies are underway to evaluate chlorine isotope fractionation during microbial perchlorate reduction in a field setting and to evaluate the use of isotope analysis to distinguish perchlorate sources.

Experimentally Determined Holding Times for Environmental Samples Containing Low Levels of Perchlorate
Stetson, S. and R. Wanty (USGS, Denver, CO); D. Macalady (Colorado School of Mines, Golden). Fourth SETAC World Congress, 25th Annual Meeting in North America, 14-18 November 2004, Portland, Oregon. Society of Environmental Toxicology and Chemistry, Pensacola, FL. Poster PH010, 2004

The stability of perchlorate in water samples has not been thoroughly examined, which means that scientifically defensible holding times of perchlorate-bearing samples and standards have yet to be determined. This paper details a study to determine the long-term stability of perchlorate standards in deionized water and in a common water matrix. Sets of samples containing 1000, 100, 10, and 0 g/L perchlorate in deionized water and in local tap water were formulated. These samples were analyzed for perchlorate concentration against freshly prepared standards every 24 hours for the first seven days, biweekly for the next four weeks, and weekly after that for a total of 25 weeks. The results from this 6-month study are presented with a recommendation for maximum holding times of perchlorate samples after collection.

Field Screening Method for Perchlorate
Thorne, Philip G., Applied Research Associates, Inc., South Royalton, VT. Partners in Environmental Technology: 2002 SERDP & ESTCP Symposium & Workshop, 3-5 December 2002, Washington, DC. Poster Abstracts, p 34, 2002

A simple, reliable, and inexpensive colorimetric method for perchlorate in water has been developed and tested with surface water, well water, and bioreactor effluent. The detection limit is 1ug/L. A 0.5 L sample is passed through a solid-phase extraction cartridge that has been conditioned with a perchlorate-specific ion-pair reagent. Perchlorate is retained, as well as small quantities of chlorate and major ions. A rinse step removes the interferences and the perchlorate is eluted into an ion-pairing dye in a 15mL test tube. A layer of xylene is added, the tube is shaken, and the dye-pair extracts into the xylene that separates into a layer lying in the beam of a standard portable spectrophotometer. Results from nearly 100 well water and bioreactor samples show excellent agreement with EPA Method 314 over the range of 1-300 ug/L (slope = 1.15, R2=0.96). Some false positives were encountered in some wells. The method is being adapted to an automated on-line monitor that will be operational and in field trials by next June.

Field Screening Method for Perchlorate in Water and Soil
Thorne, Philip G., Applied Research Associates, South Royalton, VT. Report No: ERDC/CRREL Technical Report 04-8, 36 pp, Apr 2004

Federal and state regulatory agencies are concerned about the possible adverse effects of perchlorate (ClO4-) contamination in drinking water, as the anion is known to target the human thyroid gland and its metabolic hormone-producing function. A reliable and inexpensive colorimetric method for perchlorate in water and soil extracts has been developed and tested with surface water, well water, bioreactor effluent, and soil extracts. The detection limit for water is 1 mg/L and 0.3 mg/g for spiked soils. A 0.5-L sample of water or a 1-mL sample of aqueous soil extract is passed through a solid-phase extraction cartridge that has been conditioned with a perchlorate-specific ion-pair reagent. Perchlorate, as well as small quantities of chlorate and major ions, is retained. A rinse step removes the interferences and the perchlorate is eluted into an ion-pairing dye in a 13 x 100-mm test tube. A 1-mL aliquot of xylene is added, the tube is shaken, and the dye pair extracts into the xylene that separates into a layer lying in the light path of a standard portable spectrophotometer. Results from nearly 100 well-water and bioreactor samples show excellent agreement with EPA Method 314 over the range of 1 to 225 mg/L (slope = 1.11, R2 = 0.913). Some false positives were encountered in some wells. A cleanup method was developed that can eliminate false positives due to humic substances. The colorimetric method is being adapted to an automated on-line monitor.
More Info: http://www.crrel.usace.army.mil/techpub/CRREL_Reports/reports/TR04-8.pdf

Gas-Phase Ion Association Provides Increased Selectivity and Sensitivity for Measuring Perchlorate by Mass Spectrometry
Martinelango, P.K., J.L. Anderson, P.K. Dasgupta, D.W. Armstrong, R.S. Al-Horr, and R.W. Slingsby, Texas Tech Univ., Lubbock.
Analytical Chemistry, Vol 77 No 15, p 4829-4835, 1 Aug 2005

This paper reports an ion chromatography-ion association-electrospray ionization-mass spectrometry (IC/IA-ESI-MS) method for measuring perchlorate (ClO_4^-) that is more selective and sensitive than other available single-stage MS approaches. A long chain dipositive cationic agent (D(2+)) is added postcolumn in low concentration. This ion associates with perchlorate, even in the gas phase, thus detecting it as $DClO_4^+$ in the positive ion mode at an m/z value between 300 and 400 (depending on the choice of D(2+)). The authors show results for various dicationic agents that vary in their selectivity and affinity for perchlorate. For a 100-ul injected standard, limits of detection are as good as 25 ng/L on a single quadrupole mass spectrometer.

Improved Method for the Determination of Trace Perchlorate in Ground and Drinking Waters by Ion Chromatography
Jackson, P.E.; S. Gokhale; T. Streib; J.S. Rohrer; C.A. Pohl, Dionex Corp., Sunnyvale, CA Journal of Chromatography?A, Vol 888 No 1/2, p 151-158, 4 Aug 2000

An improved ion chromatographic method has been developed for the determination of low g/l levels of perchlorate in ground and drinking waters based on a Dionex IonPac AS16 column, a hydroxide eluent generated using an EG40 automated eluent generator, large loop (1 ml) injection, and suppressed conductivity detection. The method is free of interferences from common inorganic anions, linear over the range of 2-100 g/l perchlorate, and quantitative recoveries are obtained for low g/l levels of perchlorate in spiked ground- and drinking-water samples. The method has a detection limit of 0.15 g/l.

Ion Chromatographic Analysis of Food for Perchlorate by Suppressed Conductivity Compared to Tandem Mass Spectrometry
Niemann, R.A. and A.J. Krynitsky, U.S. Food and Drug Administration, College Park, MD.
The 230th ACS National Meeting, Washington, DC, Aug 28-Sept 1, 2005. ENVR 212.

An inexpensive but chemically identity-deficient conductivity detector (CD) was compared against highly specific and sensitive mass spectrometry (MS)/MS detection for determination of perchlorate anion in edible portions of cantaloupe, carrots, lettuce, and spinach. A sample test portion was blended with dilute nitric acid, the extract was vacuum filtered, and the volume was measured. Tandem MS with electrospray interface to an anion exchange column was used to analyze, by fixed volume injection, extract diluted 9:10 with NaCl18O4 internal standard solution. Another portion of extract was acidified to pH ~2 by addition of cation exchange resin; several mLs was passed through a graphitized carbon cleanup column; and an aliquot of the collected fraction was pushed through a short anion exchange precolumn for anion extraction, enrichment, and subsequent injection onto an analytical column by valve switching. Experimental details and comparative data are presented.

Ion Chromatographic Determination of Perchlorate in Vegetation Using Accelerated Solvent Extraction (ASE) With Integrated Clean-Up
Richter, B.E., S.E. Henderson, and B. Murphy, Dionex Corporation, Salt Lake City, UT.
The 230th ACS National Meeting, Washington, DC, Aug 28-Sept 1, 2005. ENVR 213.

This presentation centers on the use of accelerated solvent extraction (ASE) as an extraction method prior to perchlorate determination using ion chromatography (IC) with suppressed conductivity or mass spectrometry. Vegetation extracts generally require significant column cleanup steps prior to IC analysis. The authors have found that by placing the proper sorbent material in the exit of an ASE extraction cell, extracts that are essentially free from interferences can be obtained from plant samples. These samples can be analyzed by IC without any additional cleanup steps. This presentation discusses ASE precision and accuracy results for the determination of perchlorate from various milk, fruit, and vegetable sample types and addresses how the various operating parameters affect analyte recovery.

Low Level (Subppb) Analysis of Perchlorate
Medina, V.F. (U.S. Army Corps of Engineers, Engineer Research and Development Center, Vicksburg, MS); A. Bednar; A. Weathersby. SERDP/ESTCP Partners in Environmental Technology Technical Symposium & Workshop, 2-4 December 2003, Washington, DC. Poster Session Abstracts, p 167, 2003

Long-term monitoring (LTM) associated with subsurface contamination sites is a key element of Long Term Stewardship and Legacy Management across the DOE complex; however, LTM is an expensive endeavor, often exceeding the costs of the remediation phase of a cleanup project. The primary contributors to LTM costs are associated with labor. Sample collection, storage, preparation, analysis, and reporting can add a significant financial burden to project expense when extended over many years. Development of unattended in situ monitoring networks capable of providing quantitative data satisfactory to regulatory concerns has the potential to significantly reduce LTM costs. But survival and dependable operation in a difficult environment is a common obstacle because deploying almost any sensor in the subsurface for extended periods of time will expose it to chemical and microbial degradation. Frequent replacement or servicing (cleaning) of sensors is expensive and labor-intensive, offsetting most, if not all, of the cost savings realized with unattended in situ sensors. To enable facile, remote monitoring of contaminants and other subsurface parameters over prolonged periods, Applied Research Associates, Inc has been working to develop an advanced LTM sensor network consisting of three key elements: (1) an anti-fouling sensor chamber that can accommodate a variety of chemical and physical measurement devices based on electrochemical, optical and other techniques; (2) two rapid, cost-effective, and gentle means of emplacing sensor packages either at precise locations directly in the subsurface or in pre-existing monitoring wells; and (3) a web browser-based data acquisition and control system (WebDACS) utilizing field-networked microprocessor-controlled smart sensors housed in anti-fouling sensor chambers. The monitoring network is highly versatile and can be applied to a variety of subsurface sensing scenarios in different media. The project is initially focused on monitoring water quality parameters of pH, conductivity, oxidation-reduction potential, and temperature in groundwater.

Low-Level Perchlorate Detection Method Shows Promise
Los Alamos National Laboratories News Release, 18 July 2003

A Los Alamos National Laboratory evaluation of a relatively new method to detect minuscule amounts of perchlorate in water indicates that the detection method holds promise in detecting perchlorate at concentrations of less than one part per billion, which could further strengthen and improve the Laboratory's environmental surveillance capabilities. The study--done in conjunction with personnel from the New Mexico Environment Department and DOE--also indicates that Northern New Mexico waters may have trace concentrations of perchlorate that are well below any proposed safe drinking water standard. EPA currently has one approved method (EPA Method 314) for perchlorate detection, but the method is reliable only for concentrations of four parts per billion (ppb) or greater. In 2003, Los Alamos researchers began a rigorous scientific evaluation of Liquid Chromatography/Mass Spectrometry/Mass Spectrometry (LC/MS/M) to detect ultra-low concentrations of perchlorate. In tests, the LC/MS/MS method seemed to be able to reliably detect perchlorate in the pure water samples that had been spiked with a known concentration of the chemical, but when used to test drinking water and groundwater samples, the LC/MS/MS method seemed less reliable--perhaps due to the presence of salts and minerals commonly found in groundwater. The study suggested the presence of minuscule traces of perchlorate in all drinking water samples tested with the LC/MS/MS method; concentrations potentially ranged from 0.1 to 0.3 ppb. The results of this study suggest that trace levels of perchlorate may be widespread in the environment, but this hypothesis must be further tested. Greater quality control and calibration procedures are necessary at laboratories that use the LC/MS/MS method to test water before the method can be deemed reliable and accurate.

Measurement of Perchlorate in Water by Use of an 18O-Enriched Isotopic Standard and Ion Chromatography with Mass Spectrometric Detection
Hedrick, E. and D. Munch, U.S. EPA, Cincinnati, OH.
Journal of Chromatography A, Vol 1039 No 1-2, p 83-88, 11 June 2004

Although the most promising analytical methodology currently available for low-level determination and confirmation of perchlorate in drinking water is ion chromatography followed by electrospray ionization mass spectrometric detection (IC-ESI-MS), there are still potentially limiting situations that must be considered when analyzing real world samples by IC-ESI-MS. These limitations consist of (1) co-elution of contaminants with fragment ions having the same m/z as perchlorate, (2) high background counts at the m/z of interest leading to a subsequent decrease in signal-to-noise, (3) gradual loss of sensitivity occurring over time as the sampling cone and/or ion optics of the mass spectrometer are fouled, and (4) suppression of gas phase ion formation (ionization suppression) that can occur if high concentrations of contaminants co-elute with perchlorate. The authors discuss the evaluation of commercially available sodium perchlorate enriched with oxygen-18 for its potential as an internal standard that may offset some of the limitations of perchlorate analysis.

Metabolic Primers for the Detection of (Per)chlorate-Reducing Bacteria in the Environment and Phylogenetic Analysis of cld Gene Sequences
Bender, K.S., M.R. Rice, & W.H. Fugate, J.D. Coates, L.A. Achenbach
Applied & Environmental Microbiology, Vol 70 No 9, p 5651-5658, Sep 2004

Natural attenuation of perchlorate is dependent on the presence and activity of dissimilatory (per)chlorate-reducing bacteria (DPRB) within a target site. Researchers have developed and optimized two degenerate primer sets targeting the chlorite dismutase (cld) gene to detect DPRB in the environment. A nested PCR approach increases the sensitivity of the molecular detection method. Screening of environmental samples indicated that all products amplified by this method were cld gene sequences. The use of these primer sets represents a direct and sensitive molecular method for the qualitative detection of (per)chlorate-reducing bacteria in the environment, thus offering another tool for monitoring natural attenuation.
More Info: http://www.science.siu.edu/microbiology/achenbach/CDprimers.pdf

Method 314.0: Determination of Perchlorate in Drinking Water Using Ion Chromatography, Rev 1.0
Hautman, D.P., D. Munch, A.D. Eaton, and A.W. Haghani, U.S. EPA, Cincinnati, OH.
EPA 815-B-99-003, 49 pp, 1999

This U.S. EPA method covers the determination of perchlorate in reagent water, surface water, groundwater, and finished drinking water using ion chromatography.
http://www.epa.gov/OGWDW/methods/met314.pdf

Method 314.1: Determination of Perchlorate in Drinking Water Using Inline Column Concentration/Matrix Elimination Ion Chromatography with Suppressed Conductivity Detection, Revision 1.0
Wagner, H.P. (Lakeshore Engineering Services, Inc.); B.V. Pepich (Shaw Environmental, Inc.); C. Pohl, D. Later, R. Joyce, K. Srinivasan, B. DeBorba, D. Thomas, and A. Woodruff (Dionex, Inc., Sunnyvale, CA); D.J. Munch (U.S. EPA, OGWDW).
EPA 815-R-05-009, 38 pp, May 2005

This is a sample pre-concentration, matrix elimination ion chromatographic (IC) method using suppressed conductivity detection for the determination of perchlorate in raw and finished drinking waters. This method requires the use of a confirmation column to validate all perchlorate concentrations reported at or above the MRL on the primary column. Precision and accuracy data have been generated for perchlorate, with both the primary and confirmation columns, in reagent water, finished groundwater, surface water and a laboratory fortified synthetic sample matrix. The single laboratory lowest concentration minimum reporting level has also been determined in reagent water.
http://www.epa.gov/safewater/methods/sourcalt.html

Method 331.0: Determination of Perchlorate in Drinking Water by Liquid Chromatography Electrospray Ionization Mass Spectrometry, Rev. 1.0
Wendelken, S.C. and D.J. Munch (U.S. EPA, OGWDW); B.V. Pepich (Shaw Environmental, Inc.); D.W. Later and C.A. Pohl (Dionex, Inc. Sunnyvale, CA).
EPA 815-R-05-007, 34 pp, January 2005

This is a liquid chromatography electrospray ionization mass spectrometry (LC/ESI/MS) method for the determination of perchlorate in raw and finished drinking waters. This method can be used to acquire data with either selected ion monitoring (SIM) or multiple reaction monitoring (MRM) detection. Based on known interferences, MRM detection is recommended; however, SIM detection may be used if all of the criteria outlined in Section 9.1 are met. Precision and accuracy data have been generated for both SIM and MRM detection of perchlorate in reagent water, finished groundwater, finished surface water, and a synthetic high ionic strength matrix. The single laboratory lowest concentration minimum reporting level (LCMRL) has also been determined for both detection modes in reagent water.
http://www.epa.gov/safewater/methods/sourcalt.html

Method 332.0 Determination of Perchlorate in Drinking Water by Ion Chromatography with Suppressed Conductivity and Electrospray Ionization Mass Spectrometry, Revision 1.0
Hedrick, E. and T. Behymer, R. Slingsby, and D. Munch.
EPA 600-R-05-049, 48 pp, Mar 2005

Method 332.0 (formerly to have been designated 330.0) describes the instrumentation and procedures necessary to identify and quantify low levels of perchlorate (ClO_4^-) in drinking waters using IC-ESI/MS. Drinking water samples are collected using a sterile filtration technique. A small volume of

sample is injected into an ion chromatograph. Using an anion exchange column, perchlorate is separated from constituent cations and anions in the sample using a potassium hydroxide mobile phase. Due to the use of a non-volatile mobile phase, the eluate from the column is passed through a conductivity suppressor to remove the potassium (K+) ions of the mobile phase and to remove the analyte counter cations prior to the eluate entering the mass spectrometer. An 18O-enriched (35)Cl(18)O_4^- internal standard (m/z 107) is used for quantitation to improve accuracy and ruggedness of the method. Identification is made by verifying the relative retention time of the two predominant ClO_4^- ions with respect to the internal standard. Qualitative confirmation of perchlorate is made by confirming that the m/z 99/101 area count ratio is within a specified range. If these conditions are met, along with passing all other QC requirements defined in Section 9, then the concentration obtained using the m/z 101 quantitation ion is reported.
http://www.epa.gov/nerlcwww/m_332_0.pdf

Method 6850: Determination of Perchlorate Using High Performance Liquid Chromatography/Mass Spectrometry (LC/MS)
Di Rienzo, R.P. (DataChem Laboratories, Inc., Salt Lake City, UT); Kham Lin (K' (Prime) Technologies, Inc., Calgary, AB, Canada).
The 230th ACS National Meeting, in Washington, DC, Aug 28-Sept 1, 2005. ENVR 210.

DataChem Laboratories, Inc. in conjunction with K'(Prime) Technologies, Inc. has developed a new method for the detection and confirmation of perchlorate that relies on liquid chromatography to separate perchlorate from interferences and mass spectrometry to confirm and quantify. Method 6850 for the determination of perchlorate uses a newly developed, commercially available liquid chromatography column in an Agilent 1100 LC/MSD system to separate perchlorate from known interferences in difficult matrices. The method can detect perchlorate not only in drinking water, but in matrices that are unacceptable for analysis by drinking water methods, such as soil and biota samples. Method 6850 can quantify perchlorate at 0.2 ppb in environmental sample matrices and use simple determinative techniques available to current LC/MS technologies, with no systematic pretreatment of samples required prior to analysis. U.S. EPA is currently evaluating method SW-846 Method 6850 with an inter-laboratory validation study.

Methods Development to Improve Low-Level Perchlorate Detection in Drinking Water by Conductivity and Mass Spectrometry: Issues and Impact
Hedrick, E.J.
Severn Trent 4th Annual Analytical Program Compliance, 17-18 June 2003, Louisville, KY.

U.S. EPA is working on a method for the determination of sub-ppb concentrations of the perchlorate anion in ground and surface drinking waters. To date, ion chromatography using a KOH mobile phase, electrolytic conductivity suppression and electrospray ionization mass spectrometric detection has been explored. There is an urgent need to be able to confirm and quantify perchlorate at lower concentrations than is allowed by the currently approved EPA method, which uses ion chromatography with suppressed conductivity detection. This work demonstrates sub-ppb quantitation of perchlorate in drinking waters and contaminated ground waters using ion chromatography with electrolytic conductivity suppression electrospray ionization mass spectrometry (IC-ESI-MS).

Microscale Extraction of Perchlorate in Drinking Water with Low Level Detection by Electrospray Mass Spectrometry
Magnuson, M.L.; E.T. Urbansky; C.A. Kelty, U.S. EPA, Water Supply and Resources Div., Cincinnati, OH Talanta, Vol 52 No 2, p 285-291, 21 Jun 2000

Perchlorate in drinking water has been determined at sub-microgram/l levels by extraction of the ion-pair formed between the perchlorate ion and a cationic surfactant with electrospray mass spectrometry detection, a technique that compared favorably with results determined by ion chromatography. Confidence in the selective quantification of the perchlorate ion is increased through both the use of the mass based detection as well as the selectivity of the ion pair. This study investigates several extraction solvents and experimental work-up procedures in order to achieve high sample throughput. The method detection limit for perchlorate was 300 ng/l (parts-per-trillion) for methylene chloride extraction and 270 ng/l for IBMK extraction. Extraction with methylene chloride produces linear calibration curves, enabling standard addition to be used to quantify perchlorate in drinking water.

Miniaturized Reference Electrode Based on Perchlorate-Sensitive Field Effect Transistor
Pöötter, W.; C. Dumschat; K. Cammann Analytical Chemistry, Vol 67 No 24, 4586-4588, 1995

Abstract not available.

A Model Describing the Biodegradation Kinetics of Perchlorate In the Presence of Competing Electron Acceptors
Hatzinger, P.B. (Shaw Environmental, Inc.); Y.H. Farhan; M. Goltz; J. Huang; P. Chosa.
Partners in Environmental Technology Technical Symposium & Workshop, 30 November - 2 December 2004, Washington, DC. Poster Program Abstracts, p 84, 2004

A mathematical model was developed to describe the biodegradation kinetics of perchlorate in the presence of alternate electron acceptors. The model links the rate of perchlorate degradation to the rate of biomass growth and electron donor utilization. Inhibition coefficients are incorporated to describe the influence of alternate electron acceptors (oxygen and nitrate) on the rate of perchlorate degradation. Model parameter values were determined by fitting model simulations to data obtained from a series of batch biodegradation experiments conducted using Dechlorosoma suillum JPLRND, a perchlorate-degrading strain isolated from groundwater in southern California. The fitted values for the maximum specific growth rate and half-saturation constant for the bacterium when utilizing either perchlorate or nitrate were 0.155 per hr and 158 mg acetate/L, respectively. These parameters were different when the strain was utilizing oxygen as an electron acceptor. Cell yield and cell decay were not distinctly different for the three electron acceptors. Experiments evaluating competitive inhibition confirmed that nitrate inhibits perchlorate degradation by the test strain. Using pre-determined parameters and a fitted inhibition coefficient value of 25 mg nitrate/L, the model successfully described perchlorate and nitrate degradation data in pure culture studies. Based on this success, the biodegradation model has recently been incorporated into a fate and transport model developed at the Air Force Institute of Technology. The coupled model will be used during ESTCP Project CU-0425 to describe perchlorate biodegradation in the field during in situ treatment using a horizontal flow treatment well (HFTW) system.

The Molecular Detection of Perchlorate-Reducing Bacteria in Environmental Samples
Achenbach, L.A. (Southern Illinois Univ., Carbondale, IL); K.S. Bender; M.R. Rice; W.H. Fugate; J.P. Schmidt; E.J. Miller; J.D. Coates.
Partners in Environmental Technology Technical Symposium & Workshop, 30 November - 2 December 2004, Washington, DC. Poster Program Abstracts, p 95, 2004

Successful natural attenuation of perchlorate within a target site is dependent on the presence of dissimilatory perchlorate-reducing bacteria (DPRB) that can reduce perchlorate to chloride and oxygen. Due to the extreme phylogenetic diversity of DPRB, it is impossible to use 16S detection methods for the detection of organisms capable of perchlorate reduction, so lengthy isolation approaches are currently the method used most often for detecting DPRB at a given site. A fast and simple approach for the detection of bacteria capable of perchlorate reduction was developed that targets a metabolic gene that is unique to DPRB, the chlorite dismutase (cld) gene. The cld gene from a number of DPRB strains was cloned and partial sequences were aligned to design degenerate primer sets specific for this gene. These primer sets were used in a nested PCR procedure in which an extremely degenerate cld primer set was employed in the first round of amplification, followed by a second round of amplification using a more specific internal primer set. This procedure produced single amplification products when tested on both pure cultures of DPRB and environmental samples. Sequence analysis of the amplicons from pristine sites in the Antarctic and perchlorate-contaminated sites in Los Alamos, NM, verified the ability of these primer sets to detect only cld gene sequences. Multiple phylotypes were also present in many of the environmental samples, indicating the presence of more than one strain possessing the cld gene. The cld primer sets are not limited to the detection of DPRB in the environment but can also be used to quantify the number of DPRB strains present in a sample via denaturing gradient gel electrophoresis (DGGE). The number of bands resulting from DGGE analysis should correlate directly to the number of different DPRB strains present. In addition, these primer sets can be used to quickly track populations of DPRB in an enrichment scheme or in a contaminated environment to determine if the growth and activity of DPRB was successfully stimulated in a bioremediation strategy. The use of these chlorite dismutase primer sets represents a rapid, direct, and sensitive molecular method for the qualitative detection of DPRB in the environment and another technological tool for future monitored natural attenuation efforts.

Monitoring the Solid Phase Synthesis Using Ion-Selective Electrode
Pátek, Marcel (Selectide Corp., Tucson, AZ); Sylvia Bildstein; Zuzana Flegelová (Biopharm, Research Inst. of Biopharmacy and Veterinary Drugs, Jílové, Czech Republic) Tetrahedron Letters, Vol 39 No 8, p 753-756, 1998

Ion-selective electrodes (ISEs) offer another noninvasive method for monitoring and quantitative determination of basic functionalities on solid support. The ISE method is based on complete protonation of basic functionalities after treatment of the resin with a large excess of 1% $HClO_4$. After thorough washing with water, the bound anion is eluted with a suitable base providing an easily detectable perchlorate anion that can be quantified potentiomentrically with a perchlorate ion-selective electrode. Limitations of this technique include the requisite use of water-compatible solid supports and basic functionalities possessing a pKHB+ > 7.
More Info: http://www.5z.com/divinfo/procedures/ise.html

Natural Perchlorate Has a Unique Oxygen Isotope Signature
Bao, Huiming (Louisiana State Univ., Baton Rouge); Baohua Gu (Oak Ridge National Lab, Oak Ridge, TN). Environmental Science & Technology, Vol 38 No 19, p 5073 5077, 2004

The authors report the first measurement of the triple oxygen isotope ratios (18O/16O and 17O/16O) for both man made perchlorate from commercial sources and natural perchlorate extracted from Atacama Desert soils. They found that normalized 18O/16O ratios for natural perchlorate has a far wider range than does man made perchlorate. The findings from this research provide a tool for the identification and forensics of perchlorate contamination in the environment.

The New Analytical Method and Related Issues
Donnelly, Joseph. Perchlorate Issue Group Presentations, AWWA website

The California Department of Health Services (CDHS) has developed an interim analytical method protocol for perchlorate. The method detection limit of 0.7 µg/l in reagent water addresses the desired 4 µg/l detection limit in aqueous environmental matrices, and an 18 ppb action level. This ion chromatographic (IC) method has been used to detect perchlorate in water supplies in California, Arizona, and Nevada. Goals for an analytical method include that it be simple, rugged, use widely-available equipment and expertise, be cost-effective, reliable, and produce data of known and adequate quality. The CDHS method uses a strong base eluent. Strong acid is used to regenerate the column after analysis. The column is an anion-exchange type, from which perchlorate elutes relatively late (about 7.5 minutes retention time). A general conductivity detector is used. The potential for false positives and negatives should be studied. Potential analytical interferences could include iodide, bromate, iodate, thiocyanate, sulfate, and nitrate anions. The ion chromatographic retention time of perchlorate shifts with concentration. For example, one research group reported a retention time of 35 minutes for a 50 ppm solution. This time was shortened to 20 minutes for a 2 parts-per-thousand solution. Confirmatory analytical techniques would be desirable, both qualitative (identity) and quantitative (precision and accuracy). Other methods for perchlorate analysis are available, but either are not suitable or have not been optimized for trace-level environmental analysis. Capillary electrophoresis has been applied to perchlorate analysis in the ppm concentration level, with general detectors, such as ultraviolet, and with specific detectors such as Raman or mass spectrometric. Electrospray mass spectrometry has also been used to detect perchlorates. The following capabilities of the CDHS method should be defined: confirmation of analyte identity, and absence of interference (false positives, false negatives); single and multiple laboratory precision and accuracy; matrix effects such as dissolved solids/conductivity. Sample holding times and sample preservation should also be investigated. One goal for future research is to determine the stability of perchlorate in the environment, particularly aqueous ecosystems. The thermodynamics of perchlorate decomposition are favorable; it is potentially a powerful oxidizer. The kinetics are slow at ambient temperatures and in the absence of catalysis. Whether biological systems provide biochemical catalysts has not been found to date in the literature search. This question is key to answering concerns about the relative toxicity of the perchlorate anion in drinking water. In summary, several laboratory-based studies of the Cal-DHS method would be worthwhile.
More Info: http://www.awwarf.com/newprojects/percsum.html

New Cetyltrimethylammonium Methods of Determination of Perchlorate
Cyganski, A.; P. Kowalczyk; J. Krystek; B. Ptaszynski. Chemical Analysis, Vol 45 No 6, p 911-919, Nov-Dec 2000

Perchlorates form a sparingly soluble compound in the presence of cetyltrimethylammonium bromide (CTA) that analysis has shown to be cetyltrimethyl-ammonium perchlorate. The authors have worked out gravimetric, nephelometric, and turbidimetric methods of determination of perchlorates such that measurements can be made in the pH range from 1.5 to 11.5. The gravimetric method is used for 5 to 20 mg of perchlorate, and the nephelometric and turbidimetric methods can be used for 0.05 to 1.0 mg of perchlorate. The effect of foreign ions has been examined, and only large anions (e.g., MnO4-, CrO42-, Cr2O72-, J-) interfere with the determination.

New Membrane Perchlorate-Selective Electrodes Containing Polyazacycloalkanes as Carriers
Lizondo-Sabater, J., M.-J. Segui, J.M. Lloris, R. Martinez-Manez, T. Pardo, F. Sancenon, and J. Soto, GDDS, Univ. Politecnica de Valencia, Valencia, Spain. Sensors and Actuators B: Chemical, Vol 101 No 1-2, p 27-29, 15 June 2004

PVC membrane anion-selective electrodes containing synthesized polyazacycloalkanes as ionophores give a linear response in the presence of perchlorate. Researchers have determined the EMF response characteristics and selectivity coefficients of these membrane-based perchlorate-selective electrodes. The synthesized polyazacycloalkanes are
1,4,8,11-tetra(n-octyl)-1,4,8,11-tetraazacyclotetradecane,
1,4,7,10,13-penta(n-octyl)-1,4,7,10,13-pentaazacyclopentadecane, and
1,4,7,10,13,16-hexa(n-octyl)-1,4,7,10,13,16-hexaazacyclooctadecane.

New Tools for Characterization and Selective Treatment of Perchlorate Contamination Plumes
Burton, E. (Lawrence Livermore National Lab., Livermore, CA); B. Bourcier; S. Coleman; B. Daily; B. Esser; Q. Hu; B. Hudson; P. Krauter; J. Moran; K. O'Brien; D. Bishop; R. Newmark; J. Reynolds. Partners in Environmental Technology Technical Symposium & Workshop, 30 November - 2 December 2004, Washington, DC. Poster Program Abstracts, p 86, 2004

Advanced measurement capabilities in mass spectrometry at LLNL allow use of isotopic signatures to track the source and age of contaminant plumes. In particular, tritium/helium groundwater ages and isotopically-enriched introduced tracers are used to determine flow rates and dilution of contaminated water by ambient groundwater. Coupling these tools with analysis of organic and inorganic contaminants at very low concentrations and with use of PCR and other bioassay techniques results in much improved characterization of the extent and impact of contaminant plumes. These analyses are then utilized as inputs to biogeochemical-hydrologic models to assess rates of plume migration, bioremediation, and attenuation, and to predict their impacts. Perchlorate treatment technologies under development or evaluation include engineered membranes, functionalized composite materials, next-generation electrically-regenerated ion exchange systems, and wetland bioreactors.

Novel LC/MS/MS and IC/MS/MS Methods for Definitive Identification of Perchlorate in Environmental Samples
Penfold, L.E. and M. Dymerski, Severn Trent Laboratories.
PITTCON 2004, 7-12 March 2004, Chicago, Illinois.

Severn Trent has successfully used LC/MS/MS for definitive analysis of a wide variety of environmental samples that are difficult to analyze by the more commonly used IC technique of EPA method 314.0. The IC method was approved by EPA for perchlorate analysis in drinking water, but other types of environmental samples (e.g., perchlorate remediation waste waters, industrial process waters, high conductivity groundwater, soil, and biota) also require analysis. These analytically difficult samples are often successfully analyzed by LC/MS/MS without pretreatment, while many IC results are proven by LC/MS/MS to be false positives. Despite its analytical power, the LC/MS/MS method is not entirely free of interferences. Special quality control measures are required to monitor and/or correct for ionization suppression effects at the ESI interface. This presentation reports the results of recent investigations into the use of modern ion chromatography equipment combined with tandem mass spectrometry (IC/MS/MS) and its effectiveness in minimizing or eliminating interferences in the analysis of a variety of environmental samples.

Optical Chloride Sensor Based on [9]Mercuracarborand-3 with Massively Expanded Measuring Range
Xu, Chao, Yu Qin, and Eric Bakker, Auburn Univ., Auburn, AL. Talanta, Vol 63 No 1, p 180-184, 10 May 2004

By optimizing a fluorescent chloride optical sensing film based on a plasticized poly(vinyl chloride) film incorporating the halide-selective ionophore [9]mercuracarborand-3 and the H+-chromoionophore ETH 5418, researchers expanded the sensor measuring range for monovalent ions by about 6 orders of magnitude. This optimization was achieved with a recently established two-step ionophore binding mechanism. The optode shows very good selectivity, with an excellent discrimination of thiocyanate and lipophilic anions such as salicylate, nitrate, and perchlorate. The main interferences are the other halides, bromide and iodide.

ORNL System Eliminates Perchlorate, Helps Scientists Trace Source
Oak Ridge National Laboratory News Release, 21 Oct 2004

An award-winning system developed at Oak Ridge National Laboratory to clean up perchlorate pollution is helping scientists determine whether the contamination is natural or man-made. The latter application could be instrumental in tracking environmental perchlorate, finding its source, and resolving resulting liability issues. Perchlorate is produced and used to make solid rocket propellant and explosives but also occurs naturally, as in nitrate soils from Chile used to make fertilizers, making the source sometimes difficult to trace. The ORNL treatment system developed under the leadership of ORNL scientist Baohua Gu removes and breaks down perchlorate into harmless chloride and water, then recharges the resin so it can be reused many times. The process costs up to 80% less than conventional methods and is one of R&D Magazine's top 100 inventions for 2004. The developers have found another benefit: the process of removing perchlorate also purifies it, allowing the scientists to isolate trace quantities and examine the compound more closely than ever before. Using isotopic analysis, they compared naturally-occurring perchlorate from Chile's Atacama Desert to synthetic or manufactured samples and found the natural type had a much higher value of the oxygen-17 isotope (an oxygen atom with 8 protons and 9 neutrons in the nucleus) but a lower chlorine-37 value (a chlorine atom with 17 protons and 20 neutrons in the nucleus). The ORNL treatment system provides a tool for the identification and forensics of perchlorate contamination in the environment. ORNL has licensed the resin technology to the Purolite company and the regeneration and recovery technology to Calgon Carbon Corporation. The presence of natural or atmospheric perchlorate in the environment obviously has far-reaching ramifications, ranging from public health issues to liabilities that could be imposed by agricultural and environmental cleanup needs. Perchlorate has been found in lettuce and milk, which begs the questions: How is it getting there and migrating through the environment? Where is the liability? The technology could have a considerable impact on how those questions are answered. Contact: Mike Bradley, ORNL, 865-576-9553, bradleymk@ornl.gov.

Overview of a New EPA Method: Determination of Perchlorate in Drinking Water, Groundwater and High Salinity Water by Ion Chromatography, Suppressed Conductivity with Electrospray Ionization Mass Spectrometric Detection
Hedrick, E.J.
Texas Commission on Environmental Quality, Environmental Trade Fair and Conference, 3-5 May 2004, Austin, TX.

This presentation describes the analytical instrumentation and procedures necessary to qualitatively and quantitatively determine low levels of perchlorate (ClO_4^-) in drinking waters using ion chromatography with electrolytic conductivity suppression, electrospray ionization mass spectrometric detection (IC-ESI-MS). Using an anion exchange separator column, ClO_4^- is separated from constituent cations and anions in natural water samples using a potassium hydroxide mobile phase. During the time frame that ClO_4^- elutes from the column, the eluate is passed through an electrolytic conductivity suppressor to remove the K^+ ions of the mobile phase and the analyte counter ions prior to the eluate entering the mass spectrometer. The masses of interest for ClO_4^- are 99 and 101, based on the 75.53% relative abundance of the chlorine-35 isotope and 24.47% abundance of the chlorine-37 isotope, respectively. Accurate quantitation is made possible by using an oxygen-18 enriched ClO_4^- internal standard that has a mass-to-charge ratio of 107. Qualitative identification of ClO_4^- is made by retention time and mass ratio confirmation (99:101) within predetermined quality control limits. U.S. EPA type method detection limits are between 0.02 to 0.06 ppb whether quantifying on the mass 99 or mass 101 ion. The lowest concentration minimum reporting limit (LCMRL) using the mass 99 ion is 0.15 ppb. The LCMRL is defined as the lowest concentration for which the 99% prediction interval for results is within a predefined acceptance limit of 50 to 150% recovery. The method is applicable to waters containing up to 3,000 ppm total dissolved solids without sample dilution or sample pretreatment to remove the common anions chloride, sulfate or carbonate (Cl^-, SO_4^{-2}, CO_3^{-2}). Of the common anions, Cl^-, SO_4^{-2}, CO_3^{-2}, sulfate is the most problematic due to an isotope of sulfur contributing to the background at mass 99 (HSO4-). For samples containing more than 1,000 ppm sulfate, pretreatment to remove the sulfate is recommended to maintain optimal method performance. Analysis of perchlorate concentrations less than 1.0 ppb is possible in high salinity samples (>30,000 ppm TDS) by sample dilution and in some cases sample pretreatment to reduce sulfate levels.

Passive Sampling Devices as Potential Indicators of Contaminant Uptake in Plants
Yu, L. and T. Anderson, Texas Tech Univ., Lubbock. 24th Annual Meeting of the Society of Environmental Toxicology and Chemistry, 9-13 November 2003, Austin, Texas. Poster PH135, 2003

As the significance of bioavailability in ecotoxicological studies has increased, the use of surrogates to monitor contaminant exposure and uptake into biological systems has gained attention among scientists. Based on the results of previous work, perchlorate is readily accumulated into plant tissue, especially in plant tissues above ground, thus serving as a potential pathway of exposure from soil/sediment to higher-level organisms. Strong anion/cation exchange cartridges (SAX/SCX) and Nafion tubing were evaluated as potential passive sampling devices for perchlorate and metal uptake into vegetation during a one-week period. Details and results are presented.

Perchlorate Analysis Using Solid-Phase Extraction Cartridges
Medina VF, S.L. Larson, B. Extine, and A. Bednar, U.S. Army Engineer Research and Development Center, Vicksburg, MS.
Journal of Chromatographic Science, Vol 43 No 4, p 195-200, Apr 2005

Researchers investigated the use of solid-phase extraction cartridges as an alternative to large-volume injection loops to achieve low-level (µg/L) perchlorate quantitation. The method involves commercially available strong anion exchange (SAX) cartridges. Water samples are filtered (100 to 1000 ml) using the cartridge, which removes the perchlorate from the solution by anion exchange. After the desired volume is filtered, the perchlorate is extracted using 4 ml of 1% NaOH. A cleanup method was developed to remove competing anions (e.g., chloride, sulfate, and carbonate). Analyses are performed with an ion chromatograph using a 10-µl injection loop, yielding a perchlorate method detection limit (MDL) of 210 µg/L. One-liter volumes of a 2-µg/L perchlorate spiked deionized water solution are filtered with SAX SPE. Following extraction and analysis, an MDL of 0.82 µg/L is obtained.

Perchlorate Identification in Fertilizers

Susarla, S.; T.W. Collette; A.W. Garrison; N.L. Wolfe; S.C. McCutcheon, U.S. EPA,Natl. Exposure Res. Lab., Athens, GA, Environmental Science & Technology, Vol 33 No 19, p 3469-3472, 1 Oct 1999

After fertilizer samples were dispersed in H2O, centrifuged, and further diluted before analysis, ion chromatography was performed using a Dionex 500 ion chromatograph. The detection limit was 10 ug/l. Capillary electrophoresis was used as confirmation. The limit of detection was 10 ug/l perchlorate and the average RSD was 1.1%. Further confirmation was provided by Raman spectrometry. The types and configurations of the analytical instruments are detailed. Results are presented and discussed with reference to the possible action of fertilizers as sources of perchlorate in the food chain.

Perchlorate in the Environment

Perchlorate in the Environment [Papers presented at the 218th American Chemical Society symposium in the Division of Environmental Chemistry, 22-24 August 1999, New Orleans, Louisiana] Urbansky, E.T. (ed.) Plenum Publishers, New York. ISBN: 030646389X. Environmental Science Research, V. 57, 2000

These collected papers comprise the first comprehensive book to address perchlorate as a potable water contaminant. The two main topics are analytical chemistry (focusing on ion chromatography and electrospray ionization mass spectrometry), and treatment or remediation. Also included are topics such as ion exchange, phytoremediation, bacterial reduction of perchlorate, bioreactors, and in situ bioremediation. To provide complete coverage, background chapters on fundamental chemistry, toxicology, and regulatory issues are also included. The authors are environmental consultants, government researchers, industry experts, and university professors from a wide array of disciplines.

Perchlorate in Various Vegetables by IC/MS

Gandhi, Jay (Metrohm-Peak, Inc., Houston TX); Joe Hedrick (Agilent Technologies). NEMC 2004: The 20th Annual National Environmental Monitoring Conference, 19-23 July 2004, Washington, DC. Book of Abstracts, No. 32.

This paper describes successful use of IC-MS for the analysis of perchlorate in vegetable extracts to low parts per billion detection limits. Superior Suppressor technology from Metrohm IC enabled coupling an industry standard Agilent Mass Spectrometer for robust analysis without any matrix diversion or splitting. System configuration and sample results demonstrate method performance.

Perchlorate in Water: A Comparison of Methods 314.0 and 332.0
McLean, S., J.F. Occhialini, A. Jones, and J. Todaro, Alpha Analytical Labs, Westborough, MA.
The 15th Annual AEHS Meeting and West Coast Conference on Soils, Sediments and Water, 14-17 March 2005, San Diego, California.
Association for Environmental Health and Sciences (AEHS), poster presentation.

The currently accepted method for low-level perchlorate analysis, EPA 314.0, utilizes an ion chromatograph fitted with a conductivity detector and a suppressor to reduce interference from background contaminants; however, this method encounters problems in the presence of elevated sample conductivity. An alternative method, EPA 332.0, utilizes an IC fitted with an MS or MS/MS. The MS technology allows for the detection of perchlorate to sub-ppb concentrations even in the presence of high concentrations of interferents. The authors present method qualification data and real-world sample data for both methods. Comparison of real world data from samples with high conductivity demonstrate the capability of Method 332.0 to accurately and precisely quantitate perchlorate.

Perchlorate Monitoring in Groundwater
Analytical Chemistry, p 447A, 1 Jul 2000

Perchlorate can inhibit iodide uptake in humans, which reduces thyroid hormone production, and thus constitutes a public health concern. Possible sources of perchlorate contamination in ground water include fertilizers and the manufacturers of rocket propellants, missiles, and fireworks. Analytical methods are needed to determine how widespread perchlorate contamination is. The most commonly used method for determining perchlorate levels is ion chromatography (IC) with conductivity detection. Researchers at Lawrence Livermore National Laboratory now demonstrate that an electrospray ionization (ESI) MS/MS method offers superior detection limits and compound confirmation capabilities. The researchers analyzed ground-water samples from the Livermore area using the ESI/MS/MS method and sent half of each sample to an independent laboratory for analysis by the state-certified IC method. The IC and ESI/MS/ MS results were statistically indistinguishable when perchlorate concentrations were above the detection limits of both methods. ESI/MS/MS, however, provides greater accuracy at low concentrations, with a detection limit of 0.5 μg/L. In addition, ESI/MS/MS has high specificity, eliminating interferences from coeluting compounds. By operating in the negative ionization mode, selective detection of ClO4? and ClO3? can be achieved. The standard additions method helps to eliminate other interferences, such as the strong signal suppression caused by sulfate, chloride, bicarbonate, and other ions commonly found in ground water.

Perchlorate: Problems, Detection, and Solutions
Motzer, William E., Hydro-Environmental Technologies, Inc., Alameda, CA. Environmental Forensics, Vol 2 No 4, p 301-311, 2001

Most perchlorate salts have high water solubilities; concentrated solutions have densities greater than water. Once dissolved, perchlorate is extremely mobile, requiring decades to degrade. Contaminated surface and groundwater may require bioremediation and/or phytoremediation technologies. Perchlorate in groundwater is relatively unretarded and probably travels by advection. Therefore, it may be used as a tracer for hydrocarbon and metal contaminants that are significantly more retarded. Possible forensic techniques include chlorine isotopes for defining multiple or commingled perchlorate plumes.

Perchlorate Reduction on Irradiated Titanium Dioxide Studied by LITD-FTMS, XPS, and IC
Lormand, K.D. (NAWC-WD, China Lake, CA); D.P. Land and E. Pyatt (Univ. of California, Davis). The 225th ACS National Meeting, New Orleans, LA, March 23-27, 2003, Abstract ENVR 186.

Preliminary studies have shown that oxidized surfaces of titanium exposed to ultraviolet radiation effectively reduce perchlorates in aqueous solutions. This reduction has been studied using laser induced thermal desorption-Fourier transform mass spectroscopy (LITD-FTMS), x-ray photoelectron spectroscopy (XPS), and ion chromatography (IC). The work has shown that perchlorate and its oxy-chloride derivatives have fragmentation patterns too indistinct to be studied by LITD-FTMS; however, XPS and IC studies have indicated that irradiated titanium dioxide, in a thin film form, is a slow but very effective catalyst for the reduction of perchlorate.

Perchlorate Screening Study: Low Concentration Method for the Determination of Perchlorate in Aqueous Samples Using Ion Selective Electrodes. Letter Report of Findings for Method Development Studies, Interference Studies, and Split Sample Studies, Including Standard Operating Procedure
U.S. Army Corps of Engineers & U.S. EPA Region 9. 172 pp, Oct 2001

The method was found to perform well in matrices with low concentrations of anions, and is expected to be especially useful for matrices with less than 1000 mg/L chloride or 1.5 mg/L NO_3-N. Matrices with higher concentrations of these anions must be evaluated to determine if this method meets project objectives.
More Info: http://clu-in.org/programs/21m2/letter_of_findings.pdf

Perchlorate-Selective Membrane Electrode Based on a New Complex of Uranil
Ardakani, M., M. Jalayer, H. Naeimi, H.R. Zare, and L. Moradi, Yazd Univ., Yazd, Iran.
Analytical & Bioanalytical Chemistry, Vol 381 No 6, p 1186-1192, Mar 2005

A potentiometric ion-selective electrode based on a new compound, as a carrier, has been successfully developed for detection of perchlorate anion in aqueous solution. The limit of detection as determined from the intersection of the extrapolated linear segments of the calibration plot was 8.0×10^{-7} mol/L. The proposed electrode has good discriminating ability toward perchlorate ion in comparison to other anions. The sensor has a response time of $\leq$ 10 s and can be used for at least 2 months without substantial divergence in potential.

Perchlorate Selective Membrane Electrodes Based on a Phosphorus(V)-Tetraphenylporphyrin Complex
Shamsipur, M. (Razi Univ., Kermanshah, Iran); A. Soleymanpour (Shiraz Univ., Shiraz, Iran); M. Akhond; H. Sharghi; A.R. Hasaninejad. Sensors and Actuators B: Chemical, Vol 89 No 1-2, p 9-14, 1 Mar 2003

When novel polymeric membrane and coated glassy carbon perchlorate-selective electrodes based on a phosphorus(V)-tetraphenylporphyrin complex were tested, the electrodes exhibited near-Nernstian responses over a wide range of perchlorate ion concentrations and very low detection limits. The electrodes possess low resistances, very fast response times, relatively long lifetimes, and good selectivities relative to a variety of other common anions. The potentiometric response of the electrodes is independent of the pH of test solution in the pH range of 4.0 to 10.0. The sensors were used to determine perchlorate ion in water and human urine.

Perchlorate-Selective MEMFETs and ISEs Based on a New Phosphadithiamacrocycle
Errachid, A.; C. Perez-Jimenez; J. Casabo; L. Escriche; J.A. Munoz; A. Bratov; J. Bausells Centre Nacional de Microelectronica, CSIC, Barcelona, Spain Sensors and Actuators B (Chemical), Vol B43 No 1-3, p 206-210, Sep 1997

A new phosphadithiamacrocycle has been synthesized and used as a neutral carrier in ion-selective PVC membranes that have been applied to the development of perchlorate-selective MEMFETs and ISEs. Both devices have shown a wide working pH range and better response and selectivity for perchlorate ions than conventional ClO4 - electrodes based on hydrophobic cations as electroactive species.

Perchlorate Sensor Development: FY01 RARE Project
U.S. EPA Region 9 Regional Science Council, 2001

Perchlorate is a contaminant showing up at an increasing number of sites. Richard Russell (RPM) and Joe Eidelberg (QA) proposed a project to develop a field sensor for detecting perchlorate in ground water and soil in support of their cleanup work at Edwards Air Force Base. An ORD sponsor has been identified; Dr. Elizabeth Hedrick of the National Exposure Research Laboratory in Cincinnati, an analytical chemist, has worked on several EPA methods development projects, and is interested in perchlorate and the issues of perchlorate contamination. Bobbye Smith, the Regional Science Liaison, will coordinate with Dr. Hedrick and provide periodic status updates. Region 9's Regional Science Council selected the project to be funded by RARE (Regional Applied Research Effort) for FY01. The project period should be less than one year.

Preconcentration/Preelution Ion Chromatography for Characterizing Exposure to Perchlorate
Anderson, T.A., P. Dasgupta, and K. Tian, Texas Tech University.
PITTCON 2004, 7-12 March 2004, Chicago, Illinois.

Due to matrix interferences, little progress has been made in the analysis of perchlorate in non-water samples. An attractive automated system for the determination of trace perchlorate by ion chromatography (IC) with an online preconcentration and preelution technique has been developed. The sample is preconcentrated and less strongly held ions preeluted before the analyte is transferred to the principal separation system. This approach provides low limits of detection and is particularly robust towards the effect of high concentrations of common anions, such as those present in groundwater samples. It compares favorably with EPA Method 314.0.

Potentiometry with Perchlorate and Fluoroborate Ion-Selective Carbon Paste Electrodes
Jezkova, J.; J. Musilova; K. Vytras, Dept. Anal. Chem., Fac. Chem. Technol., Univ. Pardubice, Pardubice, Czech Republic, Electroanalysis, Vol 9 No 18, p 1433-1436, Dec 1997

The electrodes were used for both direct potentiometric measurements and potentiometric titration with 0.1M-cetylpyridinium chloride. The electrodes had a rapid response, low resistance and limits of detection and selectivity similar to the limits of commercial membrane electrodes.

Quantitation of Perchlorate Ion by Electrospray Ionization Mass Spectrometry (ESI-MS) Using Stable Association Complexes with Organic Cations and Bases to Enhance Selectivity
Urbansky, Edward T.; Matthew L. Magnuson; David Freeman; Christopher Jelks, U.S. EPA, Cincinnati, OH Journal of Analytical Atomic Spectrometry, Vol 14 No 12, p 1861-1866, 01 Dec 1999

Although ion chromatographic methods presently offer the lowest limit of detection for quantitation of trace levels of perchlorate ion in water (~40 nM (4 ng ml-1)), chromatographic retention times are not considered to be unique identifiers and often cannot be used in legal proceedings without confirmatory testing. Mass spectrometry can provide such confirmation; however, detection capabilities can impose a practical limitation on its use. Moreover, quadrupole mass spectrometers cannot provide sufficient accuracy and precision in m/z to identify conclusively an ion as perchlorate when samples are run directly without prior chromatographic or electrophoretic separation. The authors report on the abilities of tetralkylammonium cations and minimally nucleophilic, sterically hindered organic bases to increase selectivity in the electrospray ionization mass spectrometric (ESI-MS) determination of perchlorate ion without concomitant loss of sensitivity. The chlorhexidine-perchlorate complex (m/z equals 605) can be observed even in the presence of equiformal nitrate, nitrite, hydrogen sulfate, chloride, bromide, bromate, and chlorate (all together) down to approximately 1 M; thus, the method is rugged enough to find application to systems containing multiple inorganic anions.

Quantitative Analysis of Perchlorate in Extracts of Whole Fish Homogenates by Ion Chromatography: Comparison of Suppressed Conductivity Detection and Electrospray Ionization Mass Spectrometry
Dodds, E.D., J.M. Kennish, F.A. Von Hippel, R. Bernhardt, and M.E. Hines, Univ. of Alaska, Anchorage.
Analytical and Bioanalytical Chemistry, Vol 379 No 5-6, p 881-7, July 2004

Most perchlorate analyses are currently carried out by ion chromatography (IC) with suppressed conductivity detection (SCD). While this procedure has been demonstrated to provide acceptable performance for analysis of water samples, the determination of perchlorate in high-conductivity aqueous extracts of plant or animal material is not readily accomplished by IC-SCD unless lengthy cleanup protocols are applied. With the addition of electrospray ionization mass spectrometry (ESI-MS) to IC, interference imposed by various ionic species may be significantly reduced without the need for purification, though the analysis of perchlorate in relatively unpurified extracts of biologically derived homogenates by IC-ESI-MS has not previously been described in the literature. The authors present a comparison of the capabilities of IC-SCD and IC-ESI-MS to detect perchlorate in reagent water and in crude extracts of perchlorate-exposed fish.

Quantitative Determination of Perchlorate Ion Concentrations in Urine
Richman, K., American Pacific Corp., Cedar City, UT 1999 American Industrial Hygiene Conference & Exposition, Toronto, Ontario, Canada American Industrial Hygiene Association, Fairfax, VA

Perchlorate (ClO4) concentration in water can be quantitatively analyzed using ion chromatography, and the technique has been adapted for the analysis of urine samples. Instrument parameters included a Dionex Ionpac AS11, AG11 column, elution with 100 mM NaOH, a flow rate of 1.00 mL/min, and an injection volume of 1000 mL. Suppressed conductivity was used for detection (Dionex ASRS-II, autosuppression external water mode) at a column temperature of 30 degrees C. Perchlorate ions eluted from the chromatography column in less than 10 minutes, and all urine components eluted from the column in less than 20 minutes. A practical lower limit for quantifying the perchlorate level was determined to be 0.5 parts per million (ppm).

Raman Analysis of Fertilizer and Plant Tissue Extracts for Perchlorate Contamination
Collette, T.W. and T.L. Williams, U.S. EPA.
Eastern Analytical Symposium, 1-4 October 2001, Atlantic City, NJ.

Perchlorate was found at high levels (approximately 500 to 8,000 mg/kg) in ~ 90% of 25 or more fertilizer products (primarily lawn-and-garden type) with no discernable link to mined nitrate-bearing Chilean ore, a known source of naturally occurring traces of perchlorate that is sometimes used in fertilizer production. These fertilizer products were acquired over the period of November 1998 to January 1999 at 5 locations across the U.S. Investigators subsequently analyzed more than 20 similar products acquired after May 1999. Some of these were the same products (although not the same lots) as those previously sampled. Most of these more recent products contained no detectable levels of perchlorate. These results suggest that the contamination of the earlier products was an episodic (if not singular) event; nonetheless, there is an ongoing need for robust analytical methods for rapid and definitive analysis of perchlorate in complex matrices such as extracts of fertilizers and plant materials, because some plants have been shown to take up perchlorate when it is present in soil or irrigation water. The authors describe the unique merits of analysis by Raman spectroscopy, without the need for prior chromatographic separation, to meet this need.

Raman Spectroscopic Analysis of Fertilizers and Plant Tissue for Perchlorate
Williams, Ted L.; Robert B. Martin; Timothy W. Collette, U.S. EPA, Athens, GA. Applied Spectroscopy, Vol 55 No 8, Aug 2001

This paper discusses the use of Raman spectroscopy for qualitative and quantitative analysis of 59 samples of fertilizers for perchlorate. The researchers also applied Raman spectroscopy to the qualitative identification of perchlorate in extracts of lettuce grown in a greenhouse using irrigation water spiked at 10 ppm with perchlorate, and the results were compared to results obtained via ion chromatography, which is the currently recommended method for perchlorate analysis.

Raman Spectroscopic Detection for Perchlorate at Low Concentrations
Gu, B., J. Tio, W. Wang, Y.K. Ku, and S. Dai, Oak Ridge National Laboratory, Oak Ridge, TN.
Applied Spectroscopy, Vol 58 No 6, p 741-744, June 2004

When the authors explored the use of surface-enhanced (SERS) and normal Raman spectroscopy for detecting perchlorate at low concentrations, they found that perchlorate is SERS-active, and they were able to detect, for the first time, perchlorate at concentrations as low as 10-6-10-7 M (or 10 to 100 g/L) through the application of silver SERS substrates or selective sorbents, such as bifunctional anion-exchange resins. The use of selective sorbents greatly enhanced the reproducibility and sensitivity of perchlorate detection by normal Raman spectroscopy.

Rapid and Sensitive Detection of Perchlorate at Trace Concentrations
Office of Technology Transfer and Commercialization (OTTC), California State Univ., San Bernardino, 22 July 2004

Methods for a rapid and sensitive detection of perchlorate in ground water and drinking water are strongly desired for a continuous monitoring and detection of this contaminant. A rapid and real-time detection of perchlorate at low concentrations is being developed using surface enhanced Raman spectroscopy (SERS) at Oak Ridge National Laboratory. The overall goal of this proposed project is to develop a new SERS substrate material for rapid, real-time, specific, and sensitive detection of perchlorate at a range from one part per billion (ppb = microgram per liter) to a few ppb concentrations. According to Dr. Gu, analytical time (the time required to obtain a test result) by SERS

is very rapid, on the order of a few seconds to a few minutes. Perchlorate has a very strong, characteristic Raman peak, so that this method is specific for analyzing perchlorate in water. Other common anions, such as chloride, are not Raman active, whereas nitrate, sulfate, and chlorate have different characteristic Raman peaks The presence of these anions does not interfere with the detection of perchlorate. The preliminary results indicated that the technology can achieve a detection limit of about ten ppb (sensitivity). The presence of high concentrations of other anions and organic materials in natural water may interfere or decrease the sensitivity, but it is believed that the technology will achieve greater sensitivity even in the presence of these interference anions. This new technology is expected to reduce manpower time and handling of chemicals as compared with the ion chromatographic and electron-spray mass spectroscopic techniques. The SERS substrate sensing materials could potentially be reused and may result in significant cost savings in both sample preparation and instrument analytical times. For more information:
More Info: http://www.esd.ornl.gov/~b26/

Rapid Normal Raman Spectroscopy of Sub-ppm Oxy-Anion Solutions: The Role of Electrophoretic Preconcentration
Kowalchyk, Will K.; Patrick A. Walker III; Michael D. Morris Applied Spectroscopy, Vol 49 No 8, Aug 1995

Normal Raman spectroscopy is used as an on-line detector for capillary electrophoresis to detect sub-ppm mixtures of nitrate and perchlorate in water. Field-amplified injection, a form of sample stacking, into a running electrolyte of 0.1 M KCl increases the analyte concentration at the detection window by up to 1800 times its starting value. Raman bands of nitrate (1047 cm-1) and perchlorate (934 cm-1) are measured in a total separation time of less than 3 minutes, using only 1 second integration times. The authors demonstrate the Raman spectroscopy of solutions originally 1 x 10-5 M nitrate (620 ppb) and perchlorate (1 ppm).

Recent Advances in IC and IC-MS Methods for Parts-per-Trillion Determination of Perchlorate in Environmental Water Samples
Later, D.W., B. De Borba, E. Kaiser, S. Kannan, C.A. Pohl, W. Schnute, R. Slingsby, D. Thomas, and A. Woodruff, Dionex Corp.
PITTCON 2004, 7-12 March 2004, Chicago, Illinois.

This presentation reports the achievements of Dionex chemists to improve method performance for the analytical measurement of perchlorate in support of emerging health-risk-based environmental regulations. A key to reliable ppt reporting levels is the elimination of interfering matrix anions such as chloride, carbonate and sulfate. Ion chromatographic techniques developed for matrix elimination, including sample pretreatment, pre-concentration, second column confirmation, enhanced suppression, and matrix diversion-mass spectrometric (MD-MS) detection are presented and discussed, with emphasis on the advantages of each of these analytical techniques for the accurate and precise determination of ppt levels of perchlorate.

Recent Developments in the Analysis of Perchlorate Using Ion Chromatography
Jackson, P.E.; S. Gokhale; J.S. Rohrer, Dionex Corporation, Sunnyvale, CA Abstracts of Papers - American Chemical Society, Division of Environmental Chemistry, 218th National Meeting, 22-26 August 1999, New Orleans, LA. [Session title: Perchlorate in the Environment: Toxicological, Ecological, Analytical, Water Treatment and Site Remediation Developments in Pure and Applied Science] Plenum Pub., New York. ISBN: 9-8412-3685-2. Vol 218 Pt 1, 1999

Abstract not available.

Response Characteristics of Anion-Selective Polymer Membrane Electrodes Based on Gallium(III), Indium(III) and Thallium(III) Porphyrins

Steinle, Erich D.; Ulrich Schaller; Mark E. Meyerhoff * Dept. of Chemistry, Univ. of Michigan, Ann Arbor, MI Analytical Sciences (Japan Society for Analytical Chemistry), Vol 14 No 1, Feb 1998

The researchers examined the potentiometric anion responses of ion-selective electrodes prepared with polymeric membranes doped with gallium(III), indium(III) and thallium(III) metalloporphyrins. When inserted into either octaethyl- or tetraphenyl-porphyrin derivatives and subsequently incorporated into plasticized polyvinylchloride membranes, these group XIII metals serve as anion ionophores with selectivity patterns that deviate significantly from the classical Hofmeister series for anions. The gallium(III) porphyrin-based electrodes exhibit significantly enhanced response toward fluoride, whereas the indium(III) and thallium(III) porphyrins display some preference for chloride and also effectively discriminate less hydrated anions such as perchlorate and nitrate. All of the metalloporphyrins investigated have been determined to function via a charged carrier response mechanism. This mechanism is elucidated by correlating the effect of adding lipophilic ionic sites, either cationic (quaternary ammonium) or anionic (tetraphenylborate) salts, to the observed anion selectivity and response patterns of the metalloporphyrin-based liquid /polymer membrane electrodes.

More Info: http://wwwsoc.nacsis.ac.jp/jsac/analsci/pdfs/a14_0079.pdf

Sampling Explosives in Ground Water Using the Redesigned HydraSleeve Sampler and USGS Nylon Diffusion Sampler

Parker, Louise and Denise MacMillan

Proceedings: Accelerating Site Closeout, Improving Performance, and Reducing Costs through Optimization, 15-17 June 2004, Dallas, Texas.

In recent years, there has been considerable interest in ground water sampling devices that allow one to profile the contamination within a well with depth. While these devices cannot be used for low-flow purging and sampling, they can be used for either no-purge or minimal-purge sampling, where it can be assumed that ground-water flow within the well screen is horizontal and laminar (i.e., almost exclusively in short-screened wells). Two devices designed for this type of sampling are the USGS Passive Diffusion Bag (PDB) sampler and the HydraSleeve sampler. Previous research has shown that the PDB sampler cannot be used for sampling explosives, and while the HydraSleeve sampler could be used to recover representative concentrations of some analytes, such as explosives, the up-and-down motion necessary for sampling can disturb the well and elevate turbidity. The effect the HydraSleeve device has on turbidity would prevent its use for sampling for charged species, such as metals and perchlorate, and highly hydrophobic organic compounds, such as PCBs and some pesticides. Other membranes and diffusion samplers are being examined to find one that could be used for sampling explosives. One device developed by D. Vroblesky of the USGS is a Nylon sampler. This device consists of a polypropylene jar, a 120u Nylon mesh that covers the open end of the jar, and an (open) polypropylene cap that holds the membrane in place. The HydraSleeve sampler has been substantially redesigned since its earlier evaluation. The newly designed device has a thin plastic (polyethylene) reed valve that has replaced the ball check valve. A weight can be added to the top of the device that allows the length of the (flexible) device to be compressed in the well. As a result, the sampler can be filled in a single pull, reducing concerns with turbidity substantially. This presentation reports findings from recent laboratory and field tests of these devices.

More Info: http://clu-in.org/siteopt/posters.htm

Selective Determination of Perchlorate at Sub-ppb Levels Using a Unique Stationary Phase
Bogren, Karin Pittcon 2000: Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy [50th], 12-17 March 2000, New Orleans, LA

Abstract not available.

Specific Tools for Monitoring Perchlorate Bioremediation
Coates, J.D. and S.M. O'Connor (Univ. of California, Berkeley); N.B. Sutton (Claremont McKenna College, Claremont, CA). The 19th Annual International Conference on Contaminated Soils, Sediments and Water, 20 23 October 2003, Univ. of Massachusetts at Amherst. Northeast Regional Environmental Health Center, Univ. of Massachusetts, Amherst. CD ROM, 2003

Two taxonomic groups, the Dechloromonas and the Dechlorosoma species, have been identified that represent the dominant (per)chlorate reducing bacteria (ClRB) in the environment. Chlorite dismutation is a key step in the reductive pathway common to all ClRB and is mediated by the enzyme, chlorite dismutase (CD). Biochemical and genetic analyses suggested that CD is highly conserved amongst the ClRB, which makes this enzyme makes an ideal target for a probe specific for these organisms. This paper describes efforts that have led to the development of a highly specific and sensitive immuno probe based on the commonality of the CD in ClRB. A rapid (45 min) ELISA microtiter assay has been developed to assess ClRB in environmental samples regardless of their phylogenetic affiliations. This work aims to enable the monitoring of ClRB in an engineered perchlorate bioremediation strategy.

Stable Isotope Composition of Perchlorate to Monitor Its Biodegradation, Attenuation by Other Processes, and Fingerprint Its Source
Coleman, Max (Jet Propulsion Laboratory, California Inst. of Technology, Pasadena, CA); M. Ader; A. Godon; R. Mielke; S. Chaudhuri; R. Chakraborty; J.D. Coates.
Partners in Environmental Technology Technical Symposium & Workshop, 30 November - 2 December 2004, Washington, DC. Poster Program Abstracts, p 82, 2004

Previous research has demonstrated that perchlorate is readily reduced and converted to innocuous chloride by the activity of perchlorate-reducing bacteria under anaerobic conditions. Several molecular tools have been developed to monitor the microbial populations associated with perchlorate reduction in the environment and to identify the controlling parameters that moderate the activity of these organisms. Monitoring the effectiveness of a bioremediative strategy in field environments is often difficult due to the complex nature of the environment, and results can be tainted by combining and confusing the effects of several processes. Extent of attenuation is affected by abiotic adsorption or chemical reactivity of the contaminant, as well as biodegradation. Adsorption is of concern since the contaminant may be released subsequently as conditions change. One strategy for overcoming these potential shortcomings is to monitor the stable isotope composition of the contaminant molecule. Stable isotope composition may change with extent of remediation because many bacterial processes are isotopically selective. Chlorine can exist as either of two stable isotopes, 35Cl or 37Cl, with a natural abundance of 76% and 24%, respectively. An investigation of the extent to which perchlorate-reducing bacteria could change the isotopic compositions of perchlorate and of chloride resulting from its biodegradation revealed that the perchlorate-reducing bacterium, Azospira (formally Dechlorosoma) suillum, preferentially utilizes perchlorate containing 35Cl. This process results in a significant isotopic fractionation (-150/00) of the chloride produced as the organism grows (and a complementary but opposite fractionation of the residual perchlorate). Prior to this discovery, no microbial system has been demonstrated to fractionate the chlorine isotopes of chlorine oxyanions, and abiotic fractionation is considered relatively minor. These results demonstrate that monitoring the stable isotope signature of perchlorate in a contaminated site undergoing bioremediation will allow differentiation between abiotic attenuation and biotic degradation processes affecting the removal of perchlorate. If specific isotopic signatures are associated with different perchlorate sources, it may also be possible to fingerprint these and identify the point source of perchlorate contamination in a given site.

The Status of Method Revisions by the U.S. EPA for the Low Level Determination of Perchlorate in Environmental Water Matrices
Munch, David J., U.S. EPA-OGWDW.
PITTCON 2004, 7-12 March 2004, Chicago, Illinois.

The detection limit for perchlorate analysis using EPA Method 314.0 is 0.52 µg/L with a generally accepted minimum reporting level (MRL) of 4 µg/L. U.S. EPA promulgated Method 314.0 in March 2000 for the analysis of perchlorate in support of the Unregulated Contaminant Monitoring Rule. U.S. EPA is completing development of a series of new analytical methods for the determination of perchlorate in water. These methods use either ion chromatography or liquid chromatography combined with conductivity, mass spectrometry, or mass spectrometry/mass spectrometry detection. The goal is to establish a minimum reporting level at the sub-µg/L to low-µg/L concentrations while increasing the specificity of the identification.

Studies of Perchlorate Triggered Ion-Gate Behavior of sBLM by Electrochemiluminescence and Its Application to a Sensor for Perchlorate
Han, Xiaojun, Guobao Xu; Shaojun Dong; Erkang Wang. Electroanalysis, Vol 14 No 17, p 1185-1190, Sep 2002

The authors found that a supported lipid bilayer membrane (sBLM) made of dimethyldioctadecylammonium bromide (a kind of synthetic lipid), showed ion-gate behavior for the permeation of Ru(bpy)32+ in the presence of perchlorate anion. There existed a threshold concentration (0.1 M) of perchlorate anion for ion-gate opening; below the threshold the ion gate was closed. Above the threshold, the number of opened ion-gate sites increased with the increase of perchlorate anion concentration and leveled off at concentrations higher than 1200 M. Based on these results, a new, reusable sensor for perchlorate was developed.

Surface Modified ATR FTIR Sensor Used to Detect, Identify, and Quantify Low Concentrations of Aqueous Anions
Hebert, G.N.; M.A. Odom; S.H. Strauss, Dept. of Chemistry, Colorado State Univ., Fort Collins, CO.
PITTCON 2000, Abstracts, p 2158, 2000

ATR FTIR sensors have been developed that can detect, identify, and quantify aqueous IR active anions at low concentrations. The ability to detect and quantify aqueous anions is important for ground- and surface-water testing. Commercially available silicon ATR crystals have been surface modified with highly selective thin films that enhance the sensitivity of the sensor 10,000 times. Modifications of the crystal surface with organometallic ion-exchange complexes were achieved through evaporative processes to form films of sub-micron thickness. The capability of the surface modified ATR FTIR sensor to identify the analyte by its unique IR spectrum enabled the elimination of false positive responses. Rapid quantification (Le. less than 10 minutes) has been achieved of target analytes such as cyanide, perchlorate, and fluorinated surfactants. Selectivity for the analyte was observed in the presence of at least 100 times excess of a competitor anion. Detection of 10 muM cyanide in a 1 M NaCl solution demonstrates both the sensitivity and selectivity of the sensor.

Trace Analysis of Bromate, Chlorate, Iodate, and Perchlorate in Natural and Bottled Waters
Snyder, S.A., B.J. Vanderford, and D.J. Rexing, Southern Nevada Water Authority, Henderson.
Environmental Science & Technology, Vol 39 No 12, p 4586-93, 15 June 2005

A simple and rapid method has been developed to simultaneously measure sub-µg/L quantities of the oxyhalide anions bromate, chlorate, iodate, and perchlorate in water samples. Water samples (10 ml) are passed through barium and hydronium cartridges to remove sulfate and carbonate, respectively. The method utilizes the direct injection of 10 µl volumes of water samples into a liquid chromatography-tandem triple-quadrupole mass spectrometry (LC-MS/MS) system. Ionization is accomplished using electrospray ionization in negative mode. The method detection limits were 0.021 µg/L for perchlorate, 0.045 µg/L for bromate, 0.070 µg/L for iodate, and 0.045 µg/L for chlorate anions in water. The authors compare the LC-MS/MS method described here to established EPA methods 300.1 and 317.1 for bromate analysis and EPA method 314.0 for perchlorate analysis using samples of natural and bottled waters.
http://env1.kjist.ac.kr/upload/2005-Oxyhalide-LCMS-EST.pdf

Trace Analysis of Perchlorate in Water
Vanderford, B. (Southern Nevada Water Authority, Las Vegas), P. Roefer, K. Zikmund, J. LaBounty, D. Rexing. 24th Annual Meeting of the Society of Environmental Toxicology and Chemistry, 9-13 November 2003, Austin, Texas. Abstract 242, 2003

Perchlorate levels in surface waters and groundwater are often quite low and may not be detectable by traditional analytical methodology. EPA Method 314, which has a reporting limit of 4 ug/L, is most commonly used. A novel analytical method has been developed that utilizes liquid chromatography with tandem mass spectrometry to accurately measure trace (ng/L) levels of the perchlorate anion. The method is robust, rapid, and requires less than one mL of sample volume. The new technique was applied to the analysis of several surface, ground, and bottled waters. In waters previously thought to have no perchlorate contamination, concentrations were discovered at 100 to more than 300 ng/L. Of 15 commercially available bottled waters tested, over 30% contained detectable levels of perchlorate at concentrations ranging from 120 to 170 ng/L.

Trace Level Determination of Perchlorate in Water Matrices and Human Urine Using ESI-FAIMS-MS
Ells, Barbara; David A. Barnett; Randy W. Purves; Roger Guevremont Journal of Environmental Monitoring, Vol 2 No 5, p 393-397, Oct 2000

Abstract not available.

Trace Level Perchlorate Analysis by Ion Chromatography-Mass Spectrometry
Mathew, J. (U.S. EPA, Houston, TX); J. Gandhi (Metrohm-Peak, Houston, TX); J. Hedrick (Agilent Technologies, Wilmington, DE).
Journal of Chromatography A, Vol 1085 No 1, p 54-59, 26 Aug 2005

Ion chromatography with conductivity detection can be used to measure perchlorate levels in drinking water and wastewaters as per U.S. EPA method 314, but at lower levels and in complex matrices there could be false positive and/or false negative results. This paper presents a study undertaken to demonstrate the detection of perchlorate with lower detection limit with high ionic matrix by ion chromatography-mass spectrometry.

Tracing the Origin of Perchlorate
Erickson, Britt E. Analytical Chemistry, p 388A-389A, 1 Nov 2004

This article discusses the analytical techniques that researchers are employing to trace the ubiquitous occurrence of perchlorate in the environment and to answer the question: How much of it is man-made and under what circumstances might it occur naturally? Perchlorate has been detected in locales unlikely to have been affected by the modern manufacture or use of materials that contain it. For example, nitrate salt deposits from the Atacama Desert in Chile are known to contain trace levels of naturally occurring perchlorate. Researchers are still trying to determine how the perchlorate got there.
More Info: http://www.geol.lsu.edu/DeptNews/FacNewsItems/2004BaoPerchlorate.pdf

The Use of Anthropogenic Tracers to Determine Groundwater Age and Resolve Contaminate Sources
Reimer, Janet J. and Henry Bokuniewicz, Stony Brook Univ., Stony Brook, NY. Eleventh Conference on Geology of Long Island and Metropolitan New York, 17 April 2004, Stony Brook University.

The determination of groundwater age can be used to ascertain the rate of degradation of contaminants, to verify mathematical models of groundwater flow that predict travel time of source water to wells, and to determine the probable sources of contaminants whose initial applications occurred during a specific time period. The main objective of the research described in this paper is to determine the age of groundwater at two particular well fields in which perchlorate and nitrate have been detected at levels of concern. Three dating methods using carbon 14, the ratio of Freon 11(CFC 11) to Freon 12 (CFC 12) (chlorofluorocarbons), and the ratio of tritium (3H) to helium (He), will be applied to determine the age of the groundwater collected from wells which deliver water from Long Island=s sole source aquifer. The age of a parcel of water implies the length of time since the water was last in contact with the atmosphere. The age of the groundwater, SWAP data, and the known hydraulic conductivities of the sole source aquifer will then be used to determine if the sources of contamination can be traced to recent events, or if unknown sources of contamination exist that would warrant further investigation. Thus far, it appears there is another unknown source of perchlorate contamination at this public supply well field other than the application of Chilean Saltpeter in the late 1950s.
More Info: http://pbisotopes.ess.sunysb.edu/lig/Conferences/abstracts 04/reimer.htm

Use of Temperature Programming to Improve Resolution of Inorganic Anions, Haloacetic Acids and Oxyhalides in Drinking Water by Suppressed Ion Chromatography
Barron, L., P.N. Nesterenko, and B. Paull, Dublin City Univ., Dublin, Ireland.
Journal of Chromatography A, Vol 1072 No 2, p 207-215, 29 Apr 2005

Selectivity in the suppressed ion chromatographic (IC) separation of inorganic anions, haloacetic acids, and oxyhalides in drinking water samples was improved using temperature programming with NaOH gradient elution to exploit varying responses of the inorganic anions to changes in temperature. Heats of adsorption for 17 anionic species were calculated from van't Hoff plots. For haloacetic acids, both the degree of substitution and log P (log of n-octanol-water partition coefficient) values correlated well with the magnitude of the temperature effect, with monochloro- and monobromoacetic acids showing the largest effect, dichloro- and dibromoacetic acids showing a reduced effect, and trichloro-, bromodichloro- and chlorodibromoacetic acids showing the least effect. The effect of temperature on the oxyhalides perchlorate and iodate was also calculated. The effectiveness of two commercial column ovens was investigated for the application of temperature gradients during chromatographic runs, with the best system applied to improve the resolution of closely retained species at the start, middle, and end of the separation obtained using a previously optimized hydroxide gradient in a real drinking water sample matrix.

USEPA Method 314.0 Enhancements for the Routine Analysis of Perchlorate at the Low and Sub Part Per Billion Level in Environmental Water Samples
Eaton, Andrew and Ali Haghani, MWH Labs.
PITTCON 2004, 7-12 March 2004, Chicago, Illinois.

EPA method 314 was originally validated with a reporting limit of 4 ppb. This paper discusses various options that have been evaluated to enhance the sensitivity of the method, i.e., evaluation of various trapping techniques with several different columns, off-line preconcentration, opportunities to use larger sample sizes, different suppressors, and variations in modes of operation. Several of these approaches show promise for precise (±25%) and accurate measurements below 1 ppb, without going to more expensive techniques, such as IC-MS. Using a combination of the Dionex Ultra-ASRS or an AMMS-III with smoothing techniques yields baseline noise of <0.3 nS, which is more than adequate to get a 10:1 signal to noise ratio at 1 ppb. Use of trapping columns, such as combined Cryptand/AS16, allows an even greater signal-to-noise ratio and also has the advantage of providing an alternative confirmation method because the separation characteristics are different from classic 314 analyses. These approaches were verified through analysis of potable water and groundwater monitoring-well samples on an ongoing basis. Interlaboratory comparison of blind real-world samples by two labs using different suppressors in the sub-ppb range showed excellent agreement, thus demonstrating the viability of method 314 for measurements at this level.

Using Ion Chromatography to Detect Perchlorate
Okamoto, Howard S.; Dharmendra K. Rishi,Frank J. Baumann, S. Kusum Perera, William R. Steeber
California Dept. of Health Services, Berkeley, CA Journal AWWA, Vol 91 No 10, p 73?84, Oct 1999

Preliminary studies by the U.S. EPA established 4?18 µg/L as a "safe" concentration for perchlorate in drinking water; however, until recently no available method could detect this toxic substance at such low concentrations. Researchers at the California Department of Health Services initiated a study to develop and validate a new method to analyze trace amounts of perchlorate in water. The "California DHS Method" relies on ion chromatography with suppressed conductivity. It was found to provide reliable and reproducible results in detecting perchlorate at concentrations >4 µg/L in ground water and surface water. It has also been successfully used to test California drinking water wells considered vulnerable to perchlorate contamination. The method can provide quality results that should be acceptable to regulatory and health agencies.

Validation of a U.S. EPA Method for the Ion Chromatographic Determination of Perchlorate in Fertilizers Using a Polyvinyl Alcohol Gel Resin
De Borba, Brian M. (Metrohm-Peak, Inc., Houston, TX); Edward Todd Urbansky (U.S. EPA, Cincinnati, OH). American Laboratory News, p 14-16, Jul 2002

This article describes the results of a study that demonstrated the suitability of a polyvinyl alcohol gel column for separating and quantitating perchlorate using a modified eluent of 4-cyanophenoxide salt as an additive to NaOH. Despite the high ionic strength present in many fertilizer products, a satisfactory separation of perchlorate from other anions found in fertilizers was obtained, allowing analyte detection and quantitation by suppressed conductivity. The column is robust in these matrixes, allowing them to be used to validate U.S. EPA Method 600/R-01/026 for screening fertilizers for perchlorate. The performance on fortifications, quality control standards, and precision are comparable to columns used in EPA's previous investigation.
More Info: http://www.iscpubs.com/articles/entirealn.html

Viability of Applying Curie Point Pyrolysis/Gas Chromatography Techniques for Characterization of Ammonium Perchlorate Based Propellants
Barnett, J.L. (Sandia National Labs., Albuquerque, NM); B.M. Montoya (Sandia National Labs., Livermore, CA).
SAND2002-1922, July 2002

Curie Point pyrolysis-gas chromatography was investigated for use as a tool for characterization of aged ammonium perchlorate-based composite propellants. Propellant samples were prepared by separating the propellant into reacted (oxidated) and unreacted zones. The experimental design included the determination of system reliability, followed by reproducibility, sample preparation, and analysis of pyrolysis products. Polystyrene was used to verify the reliability of the system and showed good reproducibility. Application of the technique showed high variation in the data. Modifications to sample preparation did not enhance the reproducibility. It was determined that the high concentration of ammonium perchlorate in the propellant matrix was compromising the repeatability of the analysis.
http://www.prod.sandia.gov/cgi-bin/techlib/access-control.pl/2002/021922.pdf

The World of Separation Science: IICS '99?A Solid Year of Progress in Ion Analysis [editorial]
Stevenson, Robert. American Laboratory News, Apr 2000

Ion chromatography (IC) is not on every radar screen, but a small group of researchers are making consistent progress in improving ease of use and detection limits. Economic impact is huge, since IC is employed to monitor water used in the production of semiconductors, electrical power generation, drinking water disinfection, and numerous environmental sites. In the area of column selection in IC, Jeff Rohrer of Dionex compared several columns for the analysis of polarizable anions with a special emphasis on perchlorate. Perchlorate is cropping up in many unexpected places, primarily as a result of propellants in space and military activities. Perchlorate is suspected of affecting thyroid function as well as causing Reye's syndrome. Last year, Mr. Rohrer described the use of the AS-16 column with the EG 40 eluent generator. This provided better peak shape than the AS-11. However, there was a need to determine traces of perchlorate in groundwater with high chloride or sulfate. Although there are sample preparation techniques that can reduce the background, such as chloride precipitation with silver ion, these techniques are extra steps and may also occlude part of the sample. Thus, the Dionex column developers devised a high-capacity version called the AS-16 HC. The column, combined with the eluent generator, provides an LOD of less than 0.2 ppb with a linear range extending up to 10 ppb in the presence of high ppm levels of sulfate or chloride. A study for thiosulfate showed similar results.

PERFLUOROOCTANE SULFONATE (PFOS) AND PERFLUOROOCTANOIC ACID (PFOA)

Analysis of Perfluorinated Acids at Parts-per-Quadrillion Levels in Seawater Using Liquid Chromatography-Tandem Mass Spectrometry
Yamashita, N., K. Kannan, S. Taniyasu, Y. Horii, T. Okazawa, G. Petrick, and T. Gamo, National Inst. of Advanced Industrial Science and Technology, Tsukuba, Ibaraki, Japan.
Environmental Science & Technology, Vol 38 No 21, p 5522-5528, 1 Nov 2004

Determination of sub-parts-per-trillion or parts-per-quadrillion concentrations of perfluorinated acids (PFAs) in aqueous media has been hindered by relatively high background levels arising from procedural or instrumental blanks. Methods to determine ultratrace levels of these compounds in seawater are needed to understand the role of the oceans in the transport and fate of PFAs. This paper discusses work to identify and eliminate sources of procedural and instrumental blank contamination by PFAs, reduce background levels in blanks, and thereby improve limits of quantitation. The developed method is capable of detecting perfluorooctanesulfonate (PFOS), perfluorohexanesulfonate (PFHS), perfluorobutanesulfonate (PFBS), perfluorooctanoate (PFOA), perfluorononanoate (PFNA), and perfluorooctanesulfonamide (PFOSA) at low pg/L levels in oceanic waters.

Application of LC-MS/MS Methodology to Determination of Telomer B Alcohols, Perfluorinated Acids, and Fluorosurfactants in Environmental Matrices
Szostek, B., V. Capka, K.B. Prickett, and S.M. Kennedy (DuPont Haskell Laboratory, Newark, DE); R.C. Buck (DuPont Chemical Solutions, Wilmington).
SETAC Europe Conference, 18-22 April 2004, Prague, Czech Republic. Poster presentation MOPO15/017, 2004

Though LC-MS/MS methodology is predominantly utilized for determination of perfluorinated acids, and GC-MS methodology has been traditionally utilized for determination of telomer B alcohols, the authors sought to develop a means to measure both of these types of analytes by a single technique--by LC-MS/MS. This presentation discusses sample preparation, cleanup procedures, sample storage conditions, method validation data, achievable limit of detection, and analyte-specific recommendations, as well as the challenges of analyzing complex mixtures of fluorosurfactants and applicable analytical methodology.

Attenuated Total Reflectance Fourier Transform Infrared Sensor for ppb Aqueous Anions of Environmental Concern
Hebert, Gretchen N. and Matthew A. Odom.
PITTCON 2002, 17-22 March, Pittsburgh, Pennsylvania. Abstract 1141.

Commercially available silicon and diamond ATR crystals have been surface modified with highly selective thin films that enhance the sensitivity of the sensor for aqueous anions by 3 to 5 orders of magnitude. Aqueous detection limits after 10 minutes in contact with the sensor are 15, 13, and 50 ug/L for perchlorate, cyanide, and perfluorooctylsulfonate (PFOS) respectively. Each anion is positively identified by its unique IR absorption bands. Aqueous solutions containing perchlorate, cyanide, and PFOS are detectable at only mg/L concentrations using conventional ATR-FTIR spectroscopy with no extractant film. The thin films, typically less than 0.1 um, consist of highly selective organometallic ion-exchange compounds and have been characterized by XPS and ellipsometry to determine composition and thickness. These organometallic extractants can be rapidly and efficiently regenerated to enable the reuse of the films for multiple studies. The high selectivity of the extractants allows the targeted anion to be detected even in the presence of a large excess of a competing anion or a more complex matrix, such as a simulant for seawater. Perchlorate has been quantified at ug/L concentrations from complex matrices, including three nitrate fertilizer solutions, using the method of standard additions.

Attenuated Total Reflectance Fourier Transform Quantification of ppb Aqueous Anions
Hebert, Gretchen N. and Steven H. Strauss, Strauss Research Group, Ft. Collins, CO.
PITTCON 2002, 17-22 March, Pittsburgh, Pennsylvania. Abstract 1972P.

The sensitivity of a commercially available ATR-FTIR spectrometer is enhanced more than 4000-fold by coating silicon and diamond ATR crystals with thin films (75 to 100 nm) of highly selective organometallic ion-exchange compounds. Tetraalkylated ferricenium, for example 1,1',3,3'-tetrakis(2-methyl-2-nonyl)ferricenium cations ion-paired with nitrate or chloride were used to extract and detect many contaminant anions of concern, while a nickel compound, dichloro(1,3-bisdiphenylphosphinopropane)nickel(II), was used to extract and detect cyanide. Aqueous detection limits after 10 minutes of aqueous solution contact with the sensor are 15, 13, and 50 ug/L for perchlorate, cyanide, and perfluorooctylsulfonate (PFOS), respectively. Pinacoyl methylphosphonate (PMPA), a breakdown product of the nerve agent Soman, can be detected at 1.8 mg/L after 30 minutes of aqueous contact. Positive identification of the anions extracted into the highly selective films is possible by observing their unique IR spectra. The major peaks used to quantify the anions in the extractant films were 1096/cm for perchlorate, 2104/cm for cyanide, 1266/cm for PFOS, and 1061/cm for PMPA. Quantification was readily achieved through the use of calibration curves, which are based on the linear relationship between the initial rate of absorbance change with time, dA/dt, and the concentration of the anion in aqueous solution. Calibration curves were prepared for perchlorate with a range from 3 to 1000 ug/L, cyanide with a linear range from 2.6 to 260 ug/L, PFOS with a linear range from 25 to 500 ug/L, and PMPA with a range from 1.8 to 1800 mg/L. The method of standard additions was used for detection and quantification of perchlorate in high-nitrate fertilizers. This ATR-FTIR method gave the percent weight of perchlorate in the fertilizer samples to within the error limits of two other analytical methods, ion chromatography and electrospray ionization mass spectrometry.

Attenuated Total Reflectance FTIR Detection and Quantification of Low Concentrations of Aqueous Polyatomic Anions
Hebert, G.N., M.A. Odom, S.C. Bowman, and S.H. Strauss, Colorado State Univ., Fort Collins.
Analytical Chemistry, Vol 76 No 3, p 781-787, 1 Feb 2004

In the development of a new quantitative method for determining low concentrations of aqueous polyatomic anions using attenuated total reflectance (ATR) FTIR spectroscopy, evaporated thin-film coatings of anion-selective tetraalkylated ferrocenium salts were applied to the surface of ATR crystals. This application enabled anion detection limits to be lowered up to 23,000-fold below those achieved using the commercially available spectrometer with identical uncoated ATR crystals.

Linear calibration curves were established in the 0.04 to 30 uM range. The method was applied to detection of perchlorate, chlorate, trifluoromethanesulfonate, perfluoro-n-butanesulfonate, perfluoro-n-octanesulfonate, tetrafluoroborate, hexafluorophosphate, and pinacolylmethylphosphonate in aqueous solution, obtaining limits of detection (10-min analyses) of 0.03, 0.2, 0.05, 0.07, 0.06, 0.06, 0.6, and 0.7 uM, respectively, using the thin-film coatings. This simple detection/quantification method afforded good reproducibility with relatively fast detection times.

Collection of Airborne Fluorinated Organics and Analysis by Gas Chromatography/Chemical Ionization Mass Spectrometry

Martin, J.W., D.C. Muir, C.A. Moody, D.A. Ellis, W.C. Kwan, K.R. Solomon, and S.A. Mabury, University of Guelph, ON, Canada.
Analytical Chemistry, Vol 74 No 3, p 584-590, 1 Feb 2002

A suite of potential perfluorooctane sulfonate (PFOS) precursors (sulfonamides) and fluorotelomer alcohols (FTOHs) were separated by gas chromatography and detected by chemical ionization mass spectrometry (GC/CI-MS). Full-scan spectra were collected in both positive and negative chemical ionization (PCI and NCI, respectively) mode to determine retention time windows and fragmentation patterns. PCI mode was preferred for routine analysis because of the simple mass spectra produced, typified by the presence of a major molecular ion. High-volume air samplers collected gaseous and particle-bound fluoroorganics on composite media of XAD-2, polyurethane foam (PUF), and quartz-fiber filters. Application of the method to the analysis of ambient air from urban and rural sites confirmed the presence of six novel fluorinated atmospheric contaminants at picogram per cubic meter concentrations. Low concentrations of fluoroorganics were consistently detected in blanks but did not prevent confirmation or quantification of environmental concentrations. The combined collection efficiency for individual analytes was 87 to 136% in breakthrough experiments.

Comparison of Pressurized Solvent and Reflux Extraction Methods for the Determination of Perfluorooctanoic Acid in Polytetrafluoroethylene Polymers Using LC-MS-MS

Larsen, B.S., M.A. Kaiser, M. Botelho, G.R. Wooler, and L.W. Buxton, DuPont Corporate Center for Analytical Sciences, Wilmington, DE.
Analyst, Vol 130 No 1, p 59-62, Jan 2005

Both pressurized solvent extraction (PSE) and reflux extraction in various solvents were used to select the most efficient system for the determination of the quantity of perfluorooctanoic acid (PFOA) present in polytetrafluoroethylene polymers. After evaporating the solvent, PFOA was determined using liquid chromatography tandem mass spectrometry. Ethanol, water, and methanol were shown to be good solvents for this extraction with comparable results. PSE proved to be the more efficient extraction method.

Decomposition of Environmentally Persistent Perfluorooctanoic Acid in Water by Photochemical Approaches

Hori, H., E. Hayakawa, H. Einaga, S. Kutsuna, K. Koike, T. Ibusuki, H. Kiatagawa, and R. Arakawa, National Inst. of Advanced Industrial Science and Technology, Onogawa, Tsukuba, Japan.
Environmental Science & Technology, Vol 38 No 22, p 6118-6124, 15 Nov 2004

The decomposition of persistent and bioaccumulative perfluorooctanoic acid (PFOA) in water was examined using three different techniques: UV-visible light irradiation, H_20_2 with UV-visible light irradiation, and a tungstic heteropolyacid photocatalyst. Of the three approaches, the heteropolyacid photocatalyst led to efficient PFOA decomposition and the production of F- ions and CO_2 and suppressed the accumulation of short-chain perfluorocarboxylic acids in the reaction solution. PFOA in the concentrations of 0.34-3.35 mM was completely decomposed by the catalyst within 24 h of irradiation from a 200-W xenon-mercury lamp, with no accompanying catalyst degradation, permitting the catalyst to be reused in consecutive runs. When the (initial PFOA)/(initial catalyst) molar ratio was 10: 1, the turnover number for PFOA decomposition reached 4.33 over 24 h of irradiation. Further study of the tungstic heteropolyacid photocatalyst approach may lead to the development of a technique to counteract stationary sources of PFOA.

Degradation of Fluorotelomer Alcohols: A Likely Atmospheric Source of Perfluorinated Carboxylic Acids
Ellis, D.A., J.W. Martin, A.O. De Silva, S.A. Mabury, M.D. Hurley, M.P. Sulbaek Andersen, and T.J. Wallington, Univ. of Toronto, Toronto, ON, Canada.
Environmental Science & Technology, Vol 38 No 12, p 3316-3321, 15 June 2004

Smog chamber studies indicate fluorotelomer alcohols (FTOHs) can degrade in the atmosphere to yield a homologous series of perfluorinated carboxylic acids (PFCAs), which suggests that atmospheric degradation of FTOHs is likely to contribute to the widespread dissemination of PFCAs. The significance of the gas-phase peroxy radical cross reactions that produce PFCAs has not been recognized previously. Such reactions are expected to occur during the atmospheric degradation of all polyfluorinated materials, necessitating a reexamination of the environmental fate and impact of this class of industrial chemicals. [Commented upon in ES&T 38(12):215A-216A, 15 June 2004]

Detection of Perfluorooctane Surfactants in Great Lakes Water
Boulanger, B., J. Vargo, J.L. Schnoor, and K.C. Hornbuckle, Univ. of Iowa, Iowa City.
Environmental Science & Technology, Vol 38 No 15, p 4064-4070, 1 Aug 2004

Eight perfluorooctane surfactants in 16 Great Lakes water samples were quantitatively determined using single quadrupole HPLC/MS and qualitatively confirmed using ion trap MS/MS. PFOS was quantitatively confirmed using triple quadrupole LC/MS/MS. This paper describes the concentrations of PFOS, PFOA, and PFOS precursors (N-EtFOSAA, FOSA, and PFOSulfinate) found in two of the lakes. Other PFOS precursors--N-EtFOSE, PFOSAA, and N-EtFOSA--were not observed at any of the sampling locations. These are the first reported concentrations of perfluorooctane surfactants in Great Lakes water and the first report of PFOS precursors in any water body.

Determination of Extractable Perfluorooctanoic Acid (PFOA) in Water, Sweat Simulant, Saliva Simulant, and Methanol from Textile and Carpet Samples by LC/MS/MS
Mawn, M.P., R.G. McKay, T.W. Ryan, B. Szostek, C.R. Powley, R.C. Buck, DuPont Haskell Laboratory for Health and Environmental Sciences, Newark, DE.
Analyst, Vol 130 No 5, p 670-678, May 2005

This paper describes methods developed to quantify the amount of perfluorooctanoic acid (PFOA) extracted from textile and carpet samples through contact with water, methanol, and sweat and saliva simulants using LC/MS/MS. The limit of quantitation (LOQ) for samples extracted in water and sweat simulant is 1 ppb (ng PFOA/g sample) while the limits of quantitation for samples extracted in saliva simulant and methanol were 3 ppb and 2.5 ppb, respectively. For routine application of these methods to a large number of sample sets differing in chemical and physical compositions, a complete validation for each sample type is not practical or possible since control samples for fortifications are often not available. The authors instead describe suitable analytical methods and acceptance criteria that ensure accurate PFOA quantitation in each of the solvent extract types.

Determination of Fluorinated Surfactants and Their Metabolites in Sewage Sludge Samples by Liquid Chromatography with Mass Spectrometry and Tandem Mass Spectrometry after Pressurised Liquid Extraction and Separation on Fluorine-Modified Reversed-Phase Sorbents
Schroder, H.F., Aachen University, Aachen, Germany.
Journal of Chromatography A, Vol 1020 No 1, p 131-151, 5 Dec 2003

An analytical method developed for simultaneous extraction and determination of fluorinated anionic and non-ionic surfactants in sewage sludge involves the use of liquid chromatography-mass spectrometry (LC-MS) after Soxhlet extraction, hot steam extraction, and pressurized liquid extraction (PLE) using spiked sludge samples. A multiple-step PLE procedure consisting of sequential use of ethyl acetate-dimethylformamide and methanol-phosphoric acid resulted in the most efficient extraction. Quantitative analyses of the fluorinated anionic perfluorooctanesulfonate (PFOS) and the partly fluorinated non-ionic alkylpolyglycol ether (FAEO) surfactants were performed by selected ion monitoring LC-MS. Electrospray ionization or atmospheric pressure chemical ionization in negative or positive mode was performed. Recoveries between 105 and 120% could be reached. Lab-scale biological wastewater treatment under aerobic or anaerobic conditions led to the elimination of fluorinated surfactants by biodegradation.

Determination of Perfluorinated Carboxylates and Sulfonates from Aqueous Samples by HPLC-ESI-MS-MS and Their Occurrence in Surface Waters in Germany
Lange, F.T., C.K. Schmidt, M. Metzinger, M. Wenz, and H.-J. Brauch, DVGW-Technologiezentrum Wasser, Karlsruhe, Germany.
SETAC Europe Conference, 18-22 April 2004, Prague, Czech Republic. Poster presentation MOPO15/006, 2004

The authors present a sensitive analytical method for the determination of perfluorinated carboxylates and sulfonates from aqueous samples, utilizing solid-phase extraction followed up by high-performance liquid chromatography coupled to electrospray tandem mass spectrometry in the negative ion mode. The method was validated and limits of quantitation are in the low ng/L range. This method is capable of determining perfluorinated carboxylates and sulfonates with alkyl chain length of 6 to 12 carbon atoms. The presentation includes a report of measurements of surface water samples, providing the first scientific basis of aquatic pollution by perfluorinated compounds, such as perfluorooctanoate (PFOA) and perfluorooctane sulfonate (PFOS), in Germany.

Determination of Perfluorinated Carboxylic Acids in Biological Samples by High-Performance Liquid Chromatography
Ohya, T., N. Kudo, E. Suzuki, and Y. Kawashima, Josai Univ., Sakado, Saitama, Japan.
Journal of Chromatography B, Vol 720 No 1-2, p 1-7, 11 Dec 1998

This paper describes a method for the quantitative determination of perfluorinated carboxylic acids (PFCAs), perfluorohexanoic acid, perfluoroheptanoic acid, perfluorooctanoic acid, perfluorononanoic acid, and perfluorodecanoic acid in biological samples. PFCA in liver homogenates was extracted as an ion pair with tetrabutylammonium ion into organic solvent, then the PFCA was derivatized with 3-bromoacetyl-7-methoxycoumarin and quantified by HPLC with fluorescence detection.

Determination of Perfluorooctane Sulfonate and Perfluorooctanoic Acid in Human Plasma by Large Volume Injection Capillary Column Switching Liquid Chromatography Coupled to Electrospray Ionization Mass Spectrometry
Holm, A., S.R. Wilson, P. Molander, E. Lundanes, T. Greibrokk, Univ. of Oslo, Blindern, Norway.
Journal of Separation Science, Vol 27 No 13, p 1071-1079, Sep 2004

This paper describes a rapid, selective, and sensitive methodology for the quantification of perfluorooctanoic acid (PFOA) and perfluorooctane sulfonate (PFOS) in human plasma using packed capillary liquid chromatography coupled to electrospray ionization ion-trap mass spectrometry. Plasma proteins were precipitated using acetonitrile and the resulting supernatant was diluted 1/1 with water containing 10 mM ammonium acetate prior to injection. Perfluoroheptanoic acid (PFHA) was used as an internal standard to improve the robustness and performance of the method. Separation and detection of PFOA, PFHA, and PFOS were achieved within 10 minutes.

Determination of Perfluorooctane Sulfonate in River Water by Liquid Chromatography/Atmospheric Pressure Photoionization Mass Spectrometry by Automated On-Line Extraction Using Turbulent Flow Chromatography
Takino, M., S. Daishima, and T. Nakahara, Yokogawa Analytical Systems Inc., Yodogawa, Osaka, Japan.
Rapid Communications in Mass Spectrometry, Vol 17 No 5, p 383-390, 2003

A simple, fast, and sensitive technique was developed for the determination of perfluorooctane sulfonate (PFOS) in river water using liquid chromatography/atmospheric pressure photoionization mass spectrometry (LC/APPI-MS) method, with automated on-line extraction using turbulent flow chromatography (TFC). Following an on-line extraction by injection onto a column under TFC conditions, PFOS is back-flushed onto a reversed-phase column via on-line column switching and resolved chromatographically at a laminar flow rate of 1 ml/min. Using this tandem LC-LC/APPI-MS system, the extraction, separation, and selective detection of PFOS in river water could be achieved in a total analysis time of 18.75 min.

Determination of Perfluorooctane Sulfonate, Perfluorooctanoate and Perfluorooctane Sulfonylamide in Human Plasma by Column-Switching Liquid Chromatography-Electrospray Mass Spectrometry Coupled with Solid-Phase Extraction
Inoue, K., F. Okada, R. Ito, M. Kawaguchi, N. Okanouchi, H. Nakazawa, Hoshi University, Shinagawa-ku, Tokyo, Japan.
Journal of Chromatography B, Vol 810 No 1, p 49-56, 14 Oct 2004

The described method for determining fluorinated organic compounds (e.g., perfluorooctane sulfonate, perfluorooctanoate, and perfluorooctanesulfonylamide) in human blood samples involves column-switching liquid chromatography-electrospray mass spectrometry. The sample preparation prior to solid phase extraction (Waters Oasis HLB extraction column) calls for simply mixing the plasma sample with the internal standard followed by centrifugation and extraction. The compounds were separated by reversed-phase chromatography with a C(8) column, and detected by mass spectrometry using selected ion monitoring in the negative mode.

Determination of Perfluorooctanoic Acid (PFOA) Extractable from the Surface of Commercial Cookware under Simulated Cooking Conditions by LC/MS/MS
Powley, C.R., M.J. Michalczyk, M.A. Kaiser, L.W. Buxton,
Analyst, Vol 130 No 9, p 1299-1302, Sep 2005

A method was developed to determine if pentadecafluorooctanoic acid (PFOA) might be present in and extracted from the surface of commercial frying pans coated with a DuPont fluoropolymer under simulated cooking conditions. After extraction with water and ethanol/water mixtures at 100 and 125 degrees C, the resulting extracts were analyzed by liquid chromatography tandem mass spectrometry (LC/MS/MS). Detection and quantification limits as low as 100 pg/square cm were demonstrated. None of the fluoropolymer treated cookware samples analyzed showed detectable levels of PFOA when extracted under simulated cooking conditions.

Development and Characterization of a Solvent Extraction-Gas Chromatographic/Mass Spectrometric Method for the Analysis of Perfluorooctanesulfonamide Compounds in Solid Matrices
Tittlemier, S.A., K. Pepper, L. Edwards, G. Tomy, Health Canada, Ottawa, ON, Canada.
Journal of Chromatography A, Vol 1066 Nos 1-2, p 189-195, 25 Feb 2005

Perfluorooctanesulfonamide, N-ethyl perfluorooctanesulfonamide, and N,N-diethyl perfluorooctanesulfonamide are suspected metabolic precursors of perfluorooctane sulfonate. A method utilizing solvent extraction and analysis by gas chromatography-positive chemical ionization mass spectrometry (SE-GC-PCIMS) was developed for the analysis of these three neutral hydrophobic perfluorooctanesulfonamide compounds in fast food, fish, and Arctic marine mammal liver samples. The SE-GC-PCI-MS method produced relatively higher recoveries of the analytes, with lower coefficients of variation and less susceptibility to matrix effects, than ion pair extraction/liquid chromatography/tandem mass spectrometric methods.

Development of a Solid-Phase Extraction-HPLC/Single Quadrupole MS Method for Quantification of Perfluorochemicals in Whole Blood
Karrman, A., B. van Bavel, U. Jarnberg, L. Hardell, and G. Lindstrom, Orebro Univ., Orebro, Sweden.
Analytical Chemistry, Vol 77 No 3, p 864-870, 1 Feb 2005

A method for the determination of perfluorooctanesulfonate and perfluorooctanoic acid simultaneously with 10 closely related perfluorochemicals (PFCs) in human whole blood was developed and validated. The method developed involves solid-phase extraction (SPE) and HPLC negative electrospray single quadrupole mass spectrometry (HPLC/ES-MS). A whole blood aliquot was treated with formic acid and extracted on a octadecyl (C18) SPE column. The PFCs were isolated with methanol, and quantification was performed using single quadrupole mass spectrometry and perfluoroheptanoic acid as internal standard. Validation was performed in the range 0.3 to 194 ng/ml with recovery between 64 and 112% and limit of detection in the 0.1 to 0.5 ng/m range for 11 of the 12 PFCs studied.

Efficient Decomposition of Environmentally Persistent Perfluorocarboxylic Acids by Use of Persulfate as a Photochemical Oxidant
Hori, H., A. Yamamoto, E. Hayakawa, S. Taniyasu, N. Yamashita, S. Kutsuna, H. Kiatagawa, R. Arakawa, National Inst. of Advanced Industrial Science and Technology, Tsukuba, Japan.
Environmental Science & Technology, Vol 39 No 7, p 2383-2388, 1 Apr 2005

Photochemical decomposition (photolysis) of persulfate ion produced highly oxidative sulfate radical anions that efficiently decomposed perfluorooctanoic acid (PFOA) and other perfluorocarboxylic acids bearing C4 to C8 perfluoroalkyl groups. PFOA at a concentration of 1.35 mM was completely decomposed by a photochemical system with 50 mM persulfate ion and 4 h of irradiation from a 200-W xenon-mercury lamp. The use of the lamp resulted in an initial PFOA decomposition rate 11 times higher than with photolysis alone. All sulfur-containing species in the reaction solution were eventually transformed to sulfate ions by this method. This method was successfully applied to the decomposition of perfluorononanoic acid contained in a floor wax solution. The major products were F- and CO_2, and small amounts of PFCAs with shorter than initial chain lengths were also detected in the reaction solution.

Environmental Analytical Techniques and Fate of Perfluorooctane Surfactants
Boulanger, Bryan O'Neil, Ph.D. dissertation, University of Iowa.
University Microfilm, Pub No AAT 3157956, ISBN: 0-496-90832-4, 124 pp, 2004

Standardized analytical techniques and reliable extraction procedures have been developed to elucidate the concentrations and sources of perfluorooctane surfactants in the environment. Sixteen Great Lakes water samples and nine Great Lakes air samples were analyzed for eight perfluorooctane surfactants: PFOA, PFOS, and six PFOS precursors. PFOA, PFOS, and two PFOS precursors (N-EtFOSAA and FOSA) were detected in all Lake Erie and Ontario water samples above their limit of quantification. PFOSulfinate, another PFOS precursor, was identified in 75% of the samples. N-EtFOSA and N-EtFOSE were detected in gaseous phase air samples. PFOS was detected in particulate phase air samples. A mass budget of perfluorooctane surfactants for Lake Ontario was created using Lake Ontario hydrologic flow data, Great Lakes air and water concentration data, and wastewater treatment plant (WWTP) effluent concentration data reported by 3M. The budget was used to identify the lake's primary sources of perfluorooctane surfactants and to estimate steady-state concentrations of the perfluorooctane compounds in the water. Findings from this effort indicate WWTP effluent discharge as the primary source of the compounds to the Great Lakes. To evaluate the contribution of WWTP systems on the environmental release of perfluorooctane surfactants, influent, effluent, and river water at the point of effluent discharge were sampled at a local treatment plant. Aerobic and anaerobic sludge systems from the sampled plant were also evaluated for their ability to transform N-EtFOSE, the most highly substituted perfluorooctane sulfonamide, to lesser substituted metabolites. This work presents the first reports of concentrations of perfluorooctane surfactants in Great Lakes water, concentrations of PFOS precursors in any water body, over-water gaseous phase air concentrations for this compound class, concentrations of PFOS in particulate phase air samples, concentrations of these compounds in WWTP influent, and a mass budget model for these compounds in a natural system.

Fluorotelomer Alcohol Biodegradation Yields Poly- and Perfluorinated Acids
Dinglasan, M.J., Y. Ye, E.A. Edwards, and S.A. Mabury, Univ. of Toronto, Toronto, ON, Canada.
Environmental Science & Technology, Vol 38 No 10, p 2857-2864, 15 May 2004

It has been suggested that fluorinated telomer alcohols (FTOHs) are probable precursor compounds to perfluorinated acids (PFCAs), such as perfluorooctanoic acid (PFOA) and its longer chained homologs. The FTOHs may undergo transformation reactions in the environment leading to the formation of the potentially toxic and bioaccumulative PFCAs. The authors examined the aerobic biodegradation of the 8:2 telomer alcohol using a mixed microbial system. The degradation of the telomer alcohol was monitored using a gas chromatograph equipped with an electron capture detector (GC/ECD). Volatile metabolites were identified using gas chromatography/mass spectrometry

(GC/MS), and nonvolatile metabolites were identified and quantified using liquid chromatography/ tandem mass spectrometry (LC/MS/MS). Telomer acids and PFOA were identified as metabolites during the degradation, the unsaturated telomer acid being the predominant metabolite measured. The overall mechanism involves the oxidation of the 8:2 FTOH to the telomer acid via the transient telomer aldehyde. The telomer acid via a beta-oxidation mechanism was further transformed, leading to the unsaturated acid and ultimately producing the highly stable PFOA. Telomer alcohols were shown to be potential sources of PFCAs as a consequence of biotic degradation.

A Gas Chromatograph/Resonant Electron Capture-TOF Mass Spectrometer for Four Dimensions of Negative Ion Analytical Information
Voinov, V.G., Y.V. Vasil'ev, H. Ji, B. Figard, J. Morre, T.F. Egan, D.F. Barofsky, and M.L. Deinzer, Oregon State Univ., Corvallis.
Analytical Chemistry, Vol 76 No 10, p 2951-2957, 15 May 2004

A prototype gas chromatograph (GC) electron monochromator reflectron time-of-flight mass spectrometer has been constructed and demonstrated to simultaneously record 4-D resonant electron capture mass spectra of electron-capturing compounds in real time. Complete resonant electron capture mass spectra of all of the components in a mixture of perfluorocarboxylic acids and in a sample of pentafluorobenzyl alcohol were recorded in the GC mode. For each compound, the data enable different electronic states of the molecular ion and different possible decomposition pathways for each state to be distinguished. This instrument can be used to obtain analytical information unrecognizable by any other mass spectrometric technique from the isomeric species of a variety of electron-capturing structures.

Gas-Phase NMR Technique for Studying the Thermolysis of Materials: Thermal Decomposition of Ammonium Perfluorooctanoate
Krusic, P.J. and D.C. Roe, E.I. Du Pont de Nemours & Company, Wilmington, DE.
Analytical Chemistry, Vol 76 No 13, p 3800-3803, 1 July 2004

The kinetics of the thermal decomposition of ammonium perfluorooctanoate (APFO) have been studied by high-temperature gas-phase nuclear magnetic resonance spectroscopy over the temperature range 196 to 234 degrees C. APFO is shown to cleanly decompose by first-order kinetics to give the hydrofluorocarbon 1-H-perfluoroheptane and to decompose completely (>99%) in a matter of minutes at the upper limit of this temperature range. The activation parameters provided may be used to calculate the rate of APFO decomposition at the elevated temperatures (350 to 400 degrees C) at which fluoropolymers are processed; for example, at 350 degrees C the half-life for APFO is estimated to be less than 0.2 s. These studies provide the fundamental parameters involved in the decomposition of the ammonium salt of perfluorooctanoic acid and indicate the utility of gas-phase NMR for thermolysis studies of a variety of materials.

General Fugacity-Based Model to Predict the Environmental Fate of Multiple Chemical Species
Cahill, T.M., I. Cousins, and D. Mackay, Trent Univ., Peterborough, ON, Canada.
Environmental Toxicology and Chemistry, Vol 22 No 3, p 483-493, Mar 2003

Multispecies chemical assessments are warranted when a degradation product of a released chemical is either more toxic or more persistent than the parent chemical or where there is cycling between species, as occurs with association, disassociation, or ionization. This paper presents a general multimedia environmental fate model capable of simulating the fate of up to four interconverting chemical species. To illustrate the use of this tool for assessing the environmental fate and behavior of a group of chemicals, the model is applied to chlorpyrifos, pentachlorophenol, and perfluorooctane sulfonate.

High Performance Liquid Chromatography-Mass Spectrometry of Perfluoroalkylated Substances in Sediment and Water
De Voogt, P., P. DeVoogt, A. Van der Horst, and P. Slot, (Univ. of Amsterdam, Amsterdam); J. Pijnenburg and M. Schrap (RIZA, Lelystad, Nederlands).
SETAC Europe Conference, 18-22 April 2004, Prague, Czech Republic. Poster presentation MOPO15/009, 2004

For the analysis of perfluorooctanoic acid (PFOA), perfluorooctyl sulfonate (PFOS), perfluorononanoic acid (PFNA), and perfluorododecanoic acid (PFDoA) in sediment and coastal or freshwater in the Netherlands, scientists used a high-performance liquid chromatographic (HPLC) separation hyphenated with electro-spray ionization mass spectrometry detection (ESI-MS). Sample treatment was performed using an ultrasound method for sediments and solid-phase extraction (SPE) for surface water. This presentation reports on the optimization of sample treatment and the LC-ESI-MS conditions. Detection limits, sensitivity, linearity, and recoveries of some PFAS are compared. The methods were applied to field samples (n=40) collected in the Netherlands. PFOS concentrations in freshwater sediments ranged from less than 0.4 to 50 ng/g, and in marine sediments from less than 0.4 to 9 ng/g. PFOA was detected only occasionally (11 out of 33 sediment samples) above the LOD of 0.4 ng/g. Freshwater and sediments adjacent to a site where a recent fire had been extinguished contained relatively high concentrations of PFOS.

Identification of the Isomer Composition in Technical Perfluorooctane Sulfonate Solution by LC-ESI(-)-IT-MS/MS
Langlois, Ingrid and Michael Oehme, Univ. Basel.
Dioxin 2004: 24th International Symposium on Halogenated Environmental Organic Pollutants and POPs, 6-10 September 2004, Germany.
Organohalogen Compounds, Vol 66, 4023-4028, 2004

Reversed-phase HPLC combined with triple quadrupole mass spectrometry is the method of choice for the quantification of perfluorooctanesulfonate (PFOS). PFOS contains several isomers, which are usually not completely separated and are reported as an additional signal 'shoulder.' PFOS is produced mainly by an electrochemical process that forms a main PFOS isomer with a linear chain and many branched isomers. Hundreds of structural PFOS isomers are theoretically possible. This paper describes work to characterize the isomer composition of commercial PFOS solutions and to separate as many isomers as possible. The fragmentation behavior of PFOS isomers was also investigated using ion-trap mass spectrometry with electrospray ionization in negative mode for structure elucidation.
http://dioxin2004.abstract-management.de/pdf/p148.pdf

Indoor and Outdoor Air Concentrations and Phase Partitioning of Perfluoroalkyl Sulfonamides and Polybrominated Diphenyl Ethers
Shoeib, M., T. Harner, M. Ikonomou, K. Kannan, Environment Canada, Toronto, ON, Canada
Environmental Science & Technology, Vol 38 No 5, p 1313-1320, 1 Mar 2004

Researchers are envisioning connections between indoor sources of perfluoroalkyls (PFAs) and polybrominated diphenyl ethers (PBDEs) and the potential and mode for their transport in air. Three potential precursors of the PFA perfluorooctane sulfonate (PFOS) were investigated: N-methyl perfluorooctane sulfonamidoethanol, N-ethyl perfluorooctane sulfonamidoethanol, and N-methyl perfluorooctane sulfonamidethylacrylate. High-volume samples were collected for indoor and outdoor air to investigate the source signature and strength. The gas and particle phases were collected separately to investigate the partitioning characteristics of these chemicals. Measured particulate percentages were compared to predicted values determined using models based on the octanol-air partition coefficient (K_{OA}) and supercooled liquid vapor pressure (pL(o)). Both the pL(o)-based model and the K_{OA} model worked well for the PBDEs but were not valid for the PFASs, greatly underpredicting particulate percentages. [Commented upon in ES&T 38(5):80A, 1 Mar 2004]

Method for the Determination of Perfluorooctanoic Acid in Air Samples Using Liquid Chromatography with Mass Spectrometry
Kaiser, M.A., B.S. Larsen, B.J. Dawson, K. Kurtz, R. Lieckfield Jr., J.R. Miller, and J. Flaherty, E.I. DuPont de Nemours, Inc., Wilmington, DE.
Journal of Occupational & Environmental Hygiene, Vol 2 No 6, p 307-313, June 2005

This paper reports on the development and validation of a method for the determination of perfluorooctanoic acid (PFOA) in air samples. This method uses the Occupational Safety and Health Administration (OSHA) Versatile Sampler (OVS) with a nominal 0.3 micro m filter and polystyrene resin sorbent (XAD-2 or XAD-4), followed by determination of the perfluorooctanoate anion by liquid chromatography mass spectrometry. The method was validated in the range of 0.474 to 47.4 ug/cubic m for a 480-L sample. Breakthrough studies showed samples could be collected at 1 L/min for 24 hours or at 15 L/min up to 8 hours without breakthrough. Extract storage stability tests showed that sample extracts in methanol remain stable in glass autosampler vials for up to 13 days following initial injection. PFOA stability on OVS tubes was unaffected at both refrigerated and ambient temperatures. The overall average retention efficiency was 92.1%.

Method for the Determination of Sub-ppm Concentrations of Perfluoroalkylsulfonate Anions in Water
Hebert, G.N., M.A. Odom, P.S. Craig, and S.H. Strauss, Univ. of Colorado,
Journal of Environmental Monitoring, Vol 4 No 1, p 90-95, 2002
The determination of sub-ppm concentrations of aqueous perfluoroalkylsulfonate anions, including perfluorooctylsulfonate (PFOS), has been accomplished with a relatively simple mass spectrometric procedure that does not require extraction of the analytes into an organic solvent or a chromatographic separation prior to injection into the negative-ion electrospray ionization mass spectrometer. Sample pretreatment was minimized and consisted of dilution of the aqueous samples of groundwater, surface water, tap water, and distilled water with acetonitrile, addition of dodecylsulfate as an internal standard, and, in some cases, addition of known amounts of perfluorobutylsulfonate or PFOS for standard-addition experiments. The detection limit and quantification limit for PFOS in these standards are 5.0 ug/L and 25.0 ug/L, respectively.

Monitoring Perfluorinated Surfactants in Biota and Surface Water Samples Following an Accidental Release of Fire-Fighting Foam into Etobicoke Creek
Moody, C.A., J.W. Martin, W.C. Kwan, D.C. Muir, and S.A. Mabury, Univ. of Toronto, ON, Canada.
Environmental Science & Technology, Vol 36 N 4, p 545-551, 15 Feb 2002

In June 2000, an accidental release of 22,000 L of fire-retardant foam containing perfluorinated surfactants at L.B. Pearson International Airport, Toronto, ON, entered Etobicoke Creek, a tributary to Lake Ontario. Fish and surface water samples were subsequently collected and analyzed using a suite of analytical tools that included liquid chromatography/tandem mass spectrometry (LC/MS/MS) and

19F NMR. This paper details the findings. The residence time of perfluorooctanesulfonate in Etobicoke Creek and the high contaminant bioaccumulation in fish liver suggests that perfluorinated surfactants will persist and bioaccumulate following release into the aquatic environment.

Nuclear Magnetic Resonance and LC/MS Characterization of Native and New Mass-labeled Fluorinated Telomer Alcohols, Acids and Unsaturated Acids
Arsenault, G. and B. Chittim (Wellington Laboratories Inc., Guelph), D. Ellis, T. Halldorson, S. Mabury, A. McAlees, R. McCrindle, N. Stock, G. Tomy, B. Yeo.
Dioxin 2004: 24th International Symposium on Halogenated Environmental Organic Pollutants and POPs, 6-10 September 2004, Germany.
Organohalogen Compounds, Vol 66, 4015-4022, 2004

Research has shown that telomer alcohols, such as 2-perfluorooctylethanol, can be metabolized by living organisms or biodegrade under environmental conditions to sequentially give the saturated fluorinated telomer acid (2- perfluorooctylethanoic acid), then the unsaturated telomer acid (2H-Perfluorooct-2-enoic acid), and eventually perfluorooctanoic acid (PFOA). The analysis for fluorinated compounds in environmental samples is performed primarily using LC/MS techniques, though these analyses have been hindered by the lack of any commercially available mass-labeled fluorinated compounds for use as surrogates. The authors have synthesized the mass-labeled perfluoroalkyl telomer alcohols and the corresponding acids and unsaturated acids, and the results are reported in this study of 1 H-, 2 H-, 19 F- and 13 C-NMR characterizations, along with GC/MS and LC/MS data and evaluation of their use as surrogate standards.
http://dioxin2004.abstract-management.de/pdf/p142.pdf

Occurrence and Persistence of Perfluorooctanesulfonate and Other Perfluorinated Surfactants in Groundwater at a Fire-Training Area at Wurtsmith Air Force Base, Michigan, USA
Moody, C.A., G.N. Hebert, S.H. Strauss, J.A. Field, Oregon State Univ., Corvallis.
Journal of Environmental Monitoring, Vol 5 No 2, p 341-345, Apr 2003

Various formulations of fire-extinguishing materials, including aqueous film-forming foams (AFFFs), were used as part of fire-training exercises conducted at Wurtsmith Air Force Base from the 1950s until the base was decommissioned in 1993. As a result, AFFF-laden wastewater containing fuels, solvents, and other materials have affected the groundwater beneath the facility. Groundwater was analyzed for perfluoroalkanesulfonates and perfluorocarboxylates, which are key components in some AFFF formulations. Perfluoroalkanesulfonates were directly detected using negative-ion electrospray ionization mass spectrometry. Derivatized perfluorocarboxylates were detected using electron impact gas chromatography-mass spectrometry. Groundwater from wells around fire-training area FTA-02 at Wurtsmith contained four perfluorinated surfactants ranging in concentration from 3 to 120 ug/L: perfluorooctanesulfonate (PFOS), perfluorohexanesulfonate, perfluorooctanoate, and perfluorohexanoate. This work shows that PFOS is still present in groundwater in measurable quantities five or more years after its last known use.

Perfluorooctane Sulfonate--a Quite Mobile Anionic Anthropogenic Surfactant, Ubiquitously Found in the Environment
Meesters, R.J. and H.F. Schroder, Aachen Univ., Aachen, Germany.
Water Science Technology, Vol 50 No 5, p 235-242, 2004

The biochemical degradation of perfluorooctanesulfonate (PFOS) and perfluorooctanoic acid (PFOA) under aerobic and anaerobic conditions in closed-loop systems was monitored in the laboratory using liquid chromatography/mass spectrometry under negative electrospray conditions for determination. Elimination of PFOS was seen under anaerobic conditions; aerobic treatment was not effective. Adsorptive effects of PFOS and PFOA to glass and polypropylene were also examined.

Perfluorooctane Sulfonate Concentrations in Surface Water in Japan
Saito, N., K. Sasaki, K. Nakatome, K. Harada, T. Yoshinaga, A. Koizumi,
Research Inst. for Environmental Sciences and Public Health of Iwate Prefecture, Morioka Iwate, Japan.
Archives of Environmental Contamination & Toxicology, Vol 45 No 2, p 149-158, Aug 2003

Several analytical methods have been developed for determination of perfluorooctane sulfonate (PFOS) in environmental samples and biological matrices; however, these methods employ liquid chromatography/tandem mass spectrometry (LC/MS/MS), which has limited accessibility because it is expensive to use and maintain. This paper presents the development of a robust analytical method using liquid chromatography/mass spectrometry (LC/MS) in combination with solid phase extraction. The high yield and concentration of this method enabled quantification of PFOS as low as 0.1 ng/L. The results of the application of the method to the determination of PFOS in 142 surface water samples collected from various geographic locations around Japan are described.

Perfluorooctanoate and Perfluorooctane Sulfonate Concentrations in Surface Water in Japan
Saito, N., K. Harada, K. Inoue, K. Sasaki, T. Yoshinaga, A. Koizumi, Research Inst. for Environmental Sciences and Public Health of Iwate Prefecture, Japan.
Journal of Occupational Health, Vol 46 No 1, p 49-59, Jan 2004

Researchers analyzed the concentrations of perfluorooctanoate (PFOA) and perfluorooctane sulfonate (PFOS) in surface water samples collected from all over Japan by LC/MS with a solid phase extraction method. The lowest limits of detection (LOD) (ng/L) were 0.06 for PFOA and 0.04 for PFOS. The lowest limits of quantification (LOQ) (ng/L) were 0.1 for both analytes. Systematic searches of the Yodo and Kanzaki Rivers revealed two highly contaminated sites: PFOA at a public-water disposal site and PFOS at an airport.
http://joh.med.uoeh-u.ac.jp/pdf/E46/E46_1_06.pdf

Perfluorooctanoic Acid and Perfluorooctane Sulfonate in Michigan and New York Waters
Sinclair, E. (Wadsworth Center, Albany); S. Taniyasu and N. Yamashita (National Inst. of Advanced Industrial Science and Technology, Tsukuba); K. Kannan (Wadsworth Center, Albany).
Dioxin 2004: 24th International Symposium on Halogenated Environmental Organic Pollutants and POPs, 6-10 September 2004, Germany.
Organohalogen Compounds, Vol 66, p 4069-4073, 2004

Water analysis of perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA) has been carried out with several methods. The most commonly used methods involve solid phase extraction (SPE) followed by HPLC-MS-MS. Method detection limits for PFOS and PFOA varied between 5 and 17 ng/L and 9 and 25 ng/L, respectively. Generally, PFOS and PFOA concentrations in

ambient waters, with no point source of pollution, are less than 5 ng/L. The authors have developed a method using the Oasis HLB solid phase cartridge to achieve the required method detection limits. The current ion-pairing, liquid/liquid extraction method has been used for measuring concentrations of PFOS and PFOA at the micrograms-per-liter level in surface waters collected from Michigan and New York and in the livers of fish from these waters. The data for fish and water concentrations have been compared and bioaccumulation factors calculated.
http://dioxin2004.abstract-management.de/pdf/p437.pdf

Predicting the Biodegradation Products of Perfluorinated Chemicals Using CATABOL
Dimitrov, S., V. Kamenska, J.D. Walker, W. Windle, R. Purdy, M. Lewis, and O. Mekenyan, Univ. Prof As. Zlatarov, Bourgas, Bulgaria.
SAR QSAR in Environmental Research, Vol 15 No 1, p 69-82, Feb 2004

To evaluate the fate of perfluorinated chemicals in the environment, a set of principal transformations was developed and implemented in the simulator of microbial degradation using the catabolite software engine (CATABOL). The simulator was used to generate metabolic pathways for 171 perfluorinated substances. Investigators found that although the extent of biodegradation of parent compounds could reach 60%, persistent metabolites could be formed in significant quantities. During microbial degradation, a trend was observed in which perfluorinated chemicals were transformed to more bioaccumulative and more toxic products. Perfluorooctanoic acid (PFOA) and perfluorooctanesulfonate (PFOS) were predicted to be the persistent biodegradation products of 17 and 27% of the perfluorinated sulphonic acid- and carboxylic acid-containing compounds, respectively.

Quantitative Characterization of Trace Levels of PFOS and PFOA in the Tennessee River
Hansen, K.J., H.O. Johnson, J.S. Eldridge, J.L. Butenhoff, L.A. Dick, 3M Environmental Laboratory and 3M Medical Department, St. Paul, MN.
Environmental Science & Technology, Vol 36 No 8, p 1681-1685, 15 Apr 2002

A solid-phase extraction method coupled with HPLC-negative-ion electrospray tandem mass spectrometry was developed to quantitatively measure trace levels of organic fluorochemicals in drinking water and surface water. Certain fluorochemicals can be quantitatively measured in water samples down to 25 ppt with this method, a level well below calculated drinking water advisory levels. Forty water samples were collected on an 80-mile stretch of the Tennessee River near a fluorochemical manufacturing site in Decatur, AL. Low levels (ppt) of perfluorooctane sulfonate were determined throughout the stretch of river sampled. Concentrations of the measured fluorochemicals increased downstream of the fluorochemical manufacturing facility, indicating that effluent from manufacturing is one likely source of organic fluorochemicals in the river.

Quantitative Determination of Perfluorochemicals in Sediments and Domestic Sludge
Higgins, C.P., J.A. Field, C.S. Criddle, and R.G. Luthy, Stanford Univ., Stanford, CA.
Environmental Science & Technology, Vol 39 No 11, p 3946-3956, 1 June 2005

A quantitative analytical method was developed for perfluorochemicals (PFCs) that consists of liquid solvent extraction of the analytes from sediments and sludge, cleanup via solid-phase extraction, and injection of the extracts with internal standards into a high-performance liquid chromatography (HPLC) system coupled to a tandem mass spectrometer (LC/MS/MS). The limits of detections of the method were analyte and matrix dependent, but ranged from 0.7 to 2.2 ng/g and 0.041 to 0.246 ng/g (dry weight) for sludge and sediment, respectively. This paper describes a demonstration of the method during a limited survey of domestic sludge and sediments that found widespread occurrence of PFCs in sediments at the low ng/g to sub-ng/g level, including substances that may be transformed to perfluorooctane sulfonate (PFOS), such as 2-(N-ethylperfluorooctanesulfonamido) acetic acid and 2-(N-methylperfluorooctanesulfonamido) acetic acid.

Quantitative Determination of Perfluorooctanoic Acid in Serum and Plasma by Liquid Chromatography Tandem Mass Spectrometry
Flaherty, J.M., P.D. Connolly, E.R. Decker, S.M. Kennedy, M.E. Ellefson, W.K. Reagen, and B. Szostek, Exygen Research, Inc., State College, PA
Journal of Chromatography B, Vol 819 No 2, p 329-338, 25 May 2005

A selective and sensitive method for analysis of perfluorooctanoic acid (PFOA) in human serum and plasma, utilizing liquid chromatography tandem mass spectrometry (LC-MS/MS), has been developed and thoroughly validated to satisfy FDA guidelines for bioanalytical methods. A simple, automated sample preparation procedure, involving extraction of the target analyte with acetonitrile on protein precipitation media in a 96-well plate format was developed, allowing efficient handling of large numbers of samples. The proposed method uses the calibration standards prepared in a surrogate matrix (rabbit serum or plasma) and (13)C-labeled PFOA as the internal standard to account for matrix effects, instrument drift, and extraction efficiency. Precision and accuracy of the method were demonstrated by analysis of rabbit serum and plasma control samples.

Sonochemical Decomposition of Perfluorooctane Sulfonate and Perfluorooctanoic Acid
Moriwaki, H., Y. Takagi, M. Tanaka, K. Tsuruho, K. Okitsu, and Y. Maeda, Osaka City Inst. of Public Health & Environmental Sciences, Tennoji-ku, Osaka, Japan.
Environmental Science & Technology, Vol 39 No 9, p 3388-3392, 1 May 2005

Though the toxicities of perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA) have been widely studied and reported, the means to cleanse them from the environment has not been developed. In observations of the sonochemical degradation of PFOS and PFOA to daughter products through the fission of the perfluorocarbon chains, the half-lives of PFOS and PFOA degradation under an argon atmosphere were determined to be 43 and 22 min, respectively. The shortening of perfluorocarbon chain of PFOS and PFOA lowers the toxicity due to decreased persistence. These observations may lead to the development of a technique for the remediation of environmental pollution by these compounds.

A Survey of Perfluoroalkyl Sulfonamides in Indoor and Outdoor Air Using Passive Air Samplers
Shoeib, M. and T. Harner, B. Wilford and K. Jones, Jiping Zhu
Dioxin 2004: 24th International Symposium on Halogenated Environmental Organic Pollutants and POPs, 6-10 September 2004, Germany.
Organohalogen Compounds, Vol 66, p 3999-4003, 2004

Because perfluorooctane sulfonate (PFOS) is not particularly volatile, it is hypothesized that its occurrence in remote regions is the result of atmospheric transport of more volatile precursor compounds, such as the perfluoroalkyl sulfonamides (PFASs). In a recent pilot study employing high volume air samples, indoor air concentrations of PFASs were approximately 100 times greater than outdoor levels. A current study involves the use of passive air samplers composed of polyurethane foam (PUF) disks. These quiet, non-intrusive samplers operate without the aid of a pump or electricity. Air

movement delivers chemical to the sampler, which has a high retention capacity for persistent organic pollutants. The results of indoor air from 58 randomly selected residential homes show that some PFASs exhibit very high indoor air concentrations. Because people spend the majority of their time indoors, inhalation exposure to these chemicals should be considered in human exposure assessments. The researchers conclude that indoor air may be a key source of PFASs to the outdoor environment. The study has demonstrated the versatility of PUF disks passive samplers for surveying environmental contaminants, such as PFASs, in indoor and outdoor air.
http://dioxin2004.abstract-management.de/pdf/p94.pdf

Validation of a Screening Method Based on Liquid Chromatography Coupled to High-Resolution Mass Spectrometry for Analysis of Perfluoroalkylated Substances in Biota
Berger, U. and M. Haukas, Norwegian Inst. for Air Research (NILU), Tromso, Norway.
Journal of Chromatography A, Vol 1081 No 2, p 210-217, 22 July 2005

A screening method for analysis of perfluoroalkylated substances (PFASs) in biota samples is based on extraction of target compounds from homogenized samples into the solvent mixture used as the mobile phase in high-performance liquid chromatography (HPLC), i.e. methanol/water (50:50; 2 mM ammonium acetate). The extract was filtered and directly injected into a HPLC/time-of-flight mass spectrometry (TOF-MS) system. The method is very time and cost efficient. Except for long-chain compounds and perfluorooctane sulfonamide (which cannot be covered by this method), recoveries were between 60 and 115%, and method detection limits were in the range 0.04 to 1.3 ng/g wet weight. Blank values could be neglected, with the exception of perfluorooctane sulfonate, perfluorohexanoic acid, and perfluorooctanoic acid. One of the major challenges in PFAS analysis is ionization disturbance by co-eluting matrix in the ion source of the mass spectrometer.

POLYBROMINATED BIPHENYL (PBB)
AND POLYBROMINATED DIPHENYL ETHER (PBDE)

Abiotic Transformation of Polybrominated Diphenylethers (PBDEs): Photolytic Debromination of Decabromo Diphenyl Ether
Tysklind, M., U. Sellstrom, G. Soderstrom, and C. de Wit.
BFR 2001: The Second International Workshop on Brominated Flame Retardants, Stockholm, Sweden. Book of Abstracts, p 42-45, 2001

The authors investigated the debromination process of DeBDE on different matrices (both dissolved in toluene and on natural matrices such as sand, soil and, sediment) and exposed to sunlight or artificial ultraviolet (UV) light. These studies were conducted to characterize and identify the degradation products and thereby increase the understanding of the possible transformation and fate of PBDEs in the environment.
http://www.bfr2004.com/BFR2001_del2.pdf

Accelerated Solvent Extraction (ASE) as Sample Preparation Technique for PolyBrominated Diphenyl Ethers (PDBE) in Biosolids and Waste Samples
Henderson, S., R.E. Carlson, E. Francis, J. Peterson, and B.E. Richter, Dionex Corp.
PITTCON 2004, 7-12 March 2004, Chicago, Illinois.

This presentation discusses the extraction and analysis of samples that contain various congeners of polybrominated diphenyl ether (PBDE). The samples are spiked with known quantities of

PBDEs. Implementation of accelerated solvent extraction (ASE), a sample preparation tool, can reduce the amount of solvent required for an extraction and increase the actual speed of the sample preparation step. Precision and accuracy data are presented on the recoveries of target PDBE congeners using ASE as a sample preparation technique.

Air-Surface Exchange of Polybrominated Diphenyl Ethers and Polychlorinated Biphenyls
Gouin, T., G.O. Thomas, I. Cousins, J. Barber, D. Mackay, and K.C. Jones, Canadian Environmental Modelling Centre, Trent Univ., Peterborough, Ontario.
Environmental Science & Technology, Vol 36 No 7, p 1426-1434, 1 Apr 2002

Air and leaf-litter samples were collected over a 3-day period from a rural site in southern Ontario under meteorologically stable conditions in the early spring, prior to bud burst, to measure the simultaneous diurnal variations in polybrominated diphenyl ethers (PBDEs) and polychlorinated biphenyls (PCBs). The data indicate that both PCBs and PBDEs were experiencing active air-surface exchange. Total PBDE concentrations in the daily air samples were dominated by the lighter congeners, PBDE 17, 28, and 47. The authors hypothesize that the high PBDE concentrations observed at the beginning of the sampling period are the result of an "early spring pulse" in which PBDEs deposited in the snowpack over the winter are released with snowmelt, resulting in elevated concentrations in the surface and air. Following bud burst, PBDE concentrations in air fell, possibly due to the high sorption capacity of the freshly emerging foliage compartment.
Commented on in ES&T 36(9):188A-192A, 2002.

Analysis of Brominated Flame Retardants: Methodological Issues
de Boer, J. and P. Korytar, Netherlands Inst. for Fisheries Research.
BFR 2001: The Second International Workshop on Brominated Flame Retardants, Stockholm, Sweden. Book of Abstracts, p 37-41, 2001

Various GC/MS methods for a congener-specific analysis of PBDEs and PBBs are now available, and methods for HBCD, TBBP-A, and decaBDE are being developed. The use of large volume injection and multi-dimensional GC techniques may help to enhance the sensitivity and selectivity of the methods.

Analysis of Brominated Flame Retardants and Brominated Dibenzodioxins and Biphenyls for Ah Receptor Activation Using the CALUX(R) Bioassay
Brown, D.J. (Xenobiotic Detection Systems, Inc., Durham, NC); I. Van Overmeire and L. Goeyens (Scientific Inst. of Public Health, Brussels, Belgium); M.S. Denison (Univ. of California, Davis); G.C. Clark.
Organohalogen Compounds, Vol 54, p 12-15, 2001 [Dioxins 2001, 9-14 September]

Brominated flame retardants (BFRs) such as polybrominated diphenylethers (PBDE) and polybrominated biphenyls (PBB) can be contaminated with brominated dioxins and polybrominated biphenyls (PBB), or these compounds may be produced upon incineration. The aim of this study was to investigate whether commonly used BFRs and associated compounds elicit dioxin-like toxicity in the cell-based CALUX(R) reporter gene bioassay. In the CALUX(R) bioassay, compounds like dioxins that activate the Ah receptor cause firefly luciferase to be expressed. The amount of light produced by the luciferase reporter is directly proportional to the degree of Ah receptor activation. Several types of compounds were analyzed for dioxin-like activity: pure compounds used as flame retardants; pure

compounds such as brominated dioxins and biphenyls, which are potential contaminants of flame retardants; and commercial mixtures of BFRs.
http://www.dioxins.com/pdfdocs/Brominated%20Flame%20Retardants%202001.pdf

Analyses of Known and New Types of Polyhalogenated Aromatic Substances in Oven Ash from Recycled Aluminium Production
Sinkkonen, S., M. Lahtipera, A. Vattulainen, V.V. Takhistov, I.V. Viktorovskii, V.A. Utsal, J. Paasivirta, Univ. of Jyvaskyla, Jyvaskyla, Finland.
Chemosphere, Vol 52 No 4, p 761-775, July 2003

Persistent aromatic bromine, chlorine and mixed chlorine-bromine compounds were analysed from recycled aluminium smelter (ALS) ashes to explore the impact of brominated flame retardants (BFR) on their formation. Polybrominated diphenyl ethers (PBDE) were the most abundant original BFRs found. Induction furnace ash contained tetra- to deca-BDEs. The highest PCB level measured was that of deca-CB (450ng/g) in the induction furnace ash. In this fraction, bromo compounds were non-detectable. A fraction of the most polar compounds contained PCDDs, PCDFs and polychlorinated dibenzothiophenes (PCDTs) in similar amounts and congener profiles as earlier investigated ALS ash samples. Bromine-containing dioxin and furan congeners were not detected. Twelve novel brominated and chlorinated compounds were found as abundant (8-441ng/g in the induction furnace ash) contaminants from the fraction. Four of them were bisphenol derivatives, five biphenylols, octachlorofluorenone, and octachlorobiphenylene. Their structures or structure types were deduced from total low-resolution EI mass spectra by theoretical isotope cluster simulation (ICLU) and through known fragmentation rules.

Analysis of Polybrominated Diphenyl Ethers by GC/MS with Large Volume Injection
Grindstaff, Jeff, Jerry Peterson, and Mary Thompson, Columbia Analytical Services, Inc., Kelso, WA.
The 15th Annual AEHS Meeting and West Coast Conference on Soils, Sediments and Water, 14-17 March 2005, San Diego, California.
Association for Environmental Health and Sciences (AEHS), 2005

Abstract not available.

Analytical Methods for the Determination of Alkylphenolic Surfactants and Polybrominated Diphenyl Ethers in Wastewaters and Sewage Sludges: II. Method Development
Langford, K.H., M.D. Scrimshaw, and J.N. Lester, Imperial College London, London.
Environmental Technology, Vol 25 No 9, p 975-985, Sep 2004

Analytical methods developed for the determination of two groups of compounds—the non-polar alkyl phenols along with their more polar ethoxylates and the hydrophobic polybrominated flame retardants in wastewater samples—allow for determination of the analytes in both the aqueous and solid phases, separated by centrifugation and filtration. Extraction from the aqueous phase involved the use of SPE for the surfactants; however, liquid-liquid extraction was found to be more efficient for the PBDE. Alkyl phenols and their ethoxylates were extracted from the solid phase by shaking with solvent, and soxhlet was used for extraction of PBDE. Sample cleanup was based on alumina columns for the PBDE and surfactants when extracted from solids. Surfactants were quantified using LC-MS with ESI in both positive and negative ionization mode, and GC-MS (NCI) was used to determine the PBDE (with the exception of the deca congener), where a 10 m column installed on GC-ECD resulted in short run times and reduced thermal decomposition.

Analytical Strategies for Successful Enantioselective Separation of Atropisomeric Polybrominated Biphenyls 132 and 149 in Environmental Samples
Gotsch, A., E. Mariussen, R. von der Recke, D. Herzke, U. Berger, and W. Vetter, Univ. of Hohenheim, Stuttgart, Germany.
Journal of Chromatography A, Vol 1063 Nos 1-2, p 193-199, 21 Jan 2005

Analytical methods were developed that allow determining the enantiomer fraction (EF) of axially chiral (atropisomeric) polybrominated biphenyls (PBBs) in environmental samples. Egg extract (white-tailed sea eagle) was purified and further fractionated by normal phase (NP) high-performance liquid chromatography (HPLC), yielding enriched fractions of axially chiral PBB 132 and PBB 149. Gas chromatographic (GC) enantioseparation of the atropisomers of PBB 149 was achieved on one of nine tested modified cyclodextrin phases. Due to coelution with an unknown brominated compound, conventional GC/ECNI-MS, which is based on the detection of the bromide ion, did not allow for the establishment of the EF; however, an EF of 0.42-0.43 could be verified by GC/EI-MS-MS. This is the first proof of non-racemic proportions of a chiral PBB in environmental samples. Despite the testing of nine different chiral stationary phases, GC enantioseparation of PBB 132 or other atropisomeric PBB congeners failed, which led to the development of an enantioselective reversed-phase HPLC method. With this powerful tool for the separation of PBB atropisomers, a standard of the di-ortho substituted PBB 153 could be partially separated into atropisomers at 0 degrees C. For establishing the EF of PBB 132 in the bird egg sample, a combination of enantioselective HPLC followed by non-chiral gas chromatography was employed.

Analytical Strategy for the Multi-Residue Analysis of TBBP-A and PBDEs in Various Biological Matrices from Unique Reduced Size Sample
Cariou, R. and J.-P. Antignac (LABERCA, Nantes, France), L. Debrauwer and D. Zalko (UMR 1089 Xenobiotiques, INRA, Toulouse, France), B. Le Bizec, and F. Andre.
BFR 2004: Third International Workshop on Brominated Flame Retardants, 6-9 June 2004, University of Toronto, Toronto, Ontario, Canada. p 333-336, 2004

Many studies related to the detection of tetrabromobisphenol A (TBBP-A) and polybrominated diphenylethers (PBDEs) have been developed over the last few years, mainly based on GC-ECD, GC-NCI-MS, or GC-EI-HRMS, and recently GC-EI-MS/MS. The sample treatment is usually derived from the analytical methods used for dioxins, but some authors have proposed the utilization of solid phase extraction (SPE) cartridges. A new analytical strategy is presented for the multi-residue analysis of TBBP-A and PBDEs from a unique reduced size sample. The main objective of this analytical development is to assess background exposure of French population groups to brominated flame retardants. A second objective is to provide an efficient analytical tool to study the transfer of these contaminants through the environment to living organisms, including degradation reactions and metabolic biotransformations.

Assessing the Environmental Fate of Chemicals of Emerging Concern: a Case Study of the Polybrominated Diphenyl Ethers
Palm, A. (Umea Univ., Sweden), I.T. Cousins, D. Mackay, M. Tysklind, C. Metcalfe, and M. Alaee.
Environmental Pollution, Vol 117 No 2, p 195-213, 2002

Assessments of chemicals of emerging concern can be rationally structured around a multistage process in which fate and risk are evaluated with increasing accuracy as new data become available. This approach was demonstrated for the polybrominated diphenyl ethers (PBDEs), about which class of contaminants comprehensive data on properties, sources, fate, and effects are lacking. Twenty PBDE congeners were investigated using the suggested approach, and research needs are identified.

Atmospheric Emissions of Polybrominated Diphenyl Ethers and Other Persistent Organic Pollutants During a Major Anthropogenic Combustion Event
Farrar, N.J., K.E. Smith, R.G. Lee, G.O. Thomas, A.J. Sweetman, and K.C. Jones, Lancaster Univ., Lancaster, UK.
Environmental Science & Technology, Vol 38 No 6, p 1681-1685, 15 Mar 2004

Air samples were taken for the analysis of persistent organic pollutants before, during, and after the national UK "Bonfire Festival" in November 2000. Ambient levels of polynuclear aromatic hydrocarbons (PAHs) increased sharply in response to the widespread diffusive combustion processes that occurred at the time. Polybrominated diphenyl ethers (PBDEs) also increased at the suburban sampling location, to a greater extent than the PAHs. The rise and fall in PBDE concentrations was rapid, coinciding closely with the PAH "combustion markers." These data provide evidence for a novel mechanism responsible for dissipation of PBDEs into the environment. The mixture of PBDEs in the air during the Bonfire Festival was enriched in higher brominated congeners (e.g., BDE-99, -153, and -154) compared to that in background air. The authors estimate the masses of compound classes that may have been emitted to the atmosphere during the festival.

Automated Rotary Valve Injection for Polybrominated Diphenyl Ethers in Gas Chromatography
Bjorklund, J., P. Tollback, E. Dyremark, and C. Ostman.
Journal of Separation Science, Vol 26, p 594-600, 2003

A simple, automated rotary valve injector for gas chromatography was constructed and evaluated for injection of polybrominated diphenyl ethers (PBDEs) with molecular weights ranging from 485 to 949 Dalton. These congeners, particularly those with nine and ten bromine substituents, constitute a severe problem when a split/splitless vaporizing injector was used for gas chromatographic determination of PBDEs. Volumes up to 50 L were injected without the need for a solvent vapor exit. Discrimination of the high molecular weight BDE congeners with seven to ten bromine substituents was strongly reduced. The injector exhibited both high reproducibility and low carry-over effects. Average relative standard deviation of the absolute peak area was less than 3.5% and for the carryover it was less than 0.4%. The electron capture detector response factors remained constant independent of injection volume, allowing large volume injection to decrease sample concentration detection limits, which is an important feature in determination of high molecular weight PBDEs. A further advantage is that the rotary valve large volume injector facilitates on-line coupling of various cleanup systems to the gas chromatograph.

BFR 2004: The Third International Workshop on Brominated Flame Retardants, 6-9 June 2004, University of Toronto, Toronto, Ontario, Canada. Book of Abstracts

BFR 2004 is the third in a series of international workshops on brominated flame retardants. There has been a tremendous increase in the number of publications on BFRs in the environment since BFR 2001, indicating that the interest in BFRs as global environmental pollutants continues to grow. More information on the levels and trends of polybrominated diphenyl ethers (PBDEs, a sub-class of BFRs) in the environment is becoming available. The workshop includes presentations on all different brominated flame-retardants, addressing levels in the environment and the workplace, spatial and temporal trends, sources, transport mechanisms and pathways, toxicology, ecotoxicology, environmental fate and modeling, and human and environmental exposure.
http://www.bfr2004.com/

BFR 2001: The Second International Workshop on Brominated Flame Retardants: Book of Abstracts
University of Stockholm, Sweden, 2001

BFR 2001 is the second in a series of international workshops on brominated flame retardants. The workshop drew over 200 participants. The book of abstracts contains presentations on all different brominated flame-retardants, addressing levels in the environment and the workplace, spatial and temporal trends, sources, transport mechanisms and pathways, toxicology, ecotoxicology, environmental fate and modeling, and human and environmental exposure.
http://www.bfr2004.com/bfr2001.html

Bio/Chemical Analysis of Dioxin-Like Compounds in Sediment Samples from Osaka Bay, Japan
Takigami, H. (National Inst. for Environmental Studies, Tsukuba, Ibaraki, Japan), S. Sakai, and A. Brouwer.
Environmental Technology, Vol 26 No 4, p 459-469, Apr 2005

The biochemical investigation of sediments (six surface samples and one core sample) from Osaka Bay, Japan, was conducted to clarify the horizontal and vertical distribution profiles of persistent organic pollutants in the sediments. Concentrations of polychlorinated dibenzo-p-dioxins and dibenzofurans, polychlorinated biphenyls, polybrominated dibenzo-p-dioxins and dibenzofurans, and polybrominated diphenylethers were determined by chemical analysis and compared to bioassay results using H4IIE-luc/Dioxin Responsive-Chemical Activated LUciferase eXpression (DR-CALUX).

Brominated Flame Retardants: Commercially Available Analytical Standards
Priest, B., Cambridge Isotope Laboratories, Andover, MA.
BFR 2001: The second international workshop on brominated flame retardants, Stockholm, Sweden. Book of Abstracts, p 120-121, 2001

Cambridge Isotope Laboratories has produced a series of analytical standards for bromated dioxins and furans, mixed bromo/chloro dioxins and furans, and cocktails of these compounds, both C-13-labeled and unlabeled. This presentation describes the development of these resources.
http://bfr2004.com/BFR2001_del2.pdf

Challenges of Gas Chromatography-High-Resolution Time-of-Flight Mass Spectrometry for Simultaneous Analysis of Polybrominated Diphenyl Ethers and Other Halogenated Persistent Organic Pollutants in Environmental Samples
Cajka, T., J. Hajslova, R. Kazda, and J. Poustka, Inst. of Chemical Technology, Prague, Czech Republic.
Journal of Separation Science, Vol 28 No 7, p 601-611, May 2005

The potential of a gas chromatographic method employing high-resolution time-of-flight (TOF) mass spectrometry was evaluated for detection of polybrominated diphenyl ethers (PBDEs) in the environmental matrices represented by fish and river sediment. Two ionization techniques were used: electron ionization (EI) and negative ion chemical ionization (NICI), the latter with methane as a reagent gas. While the lowest calibration levels obtained in El ranged from 1 to 5 pg, their values ranged between 10 to 250 fg in NICI mode. This enhancement in detectability of target analytes enabled identification/quantification of even minor PBDE congeners and supported improved characterization of particular sample contamination patterns. The method also allowed estimation of the PCB levels in examined samples. CB 153 was used as a contamination marker.

Characterization of Five Technical Mixtures of Brominated Flame Retardants
Huber, S. and K. Ballschmiter.
Fresenius' Journal of Analytical Chemistry, Vol 371 No 6, p 882-890, 2001

The main components of five technical mixtures of brominated flame retardants were identified by mass spectroscopy, H-NMR, IR spectroscopy, elementary analysis, and HRGC-MS, respectively. Gas chromatographic retention data of the various constituents were measured on standard GC columns. The data indicate that some of the brominated compounds interfere with PCBs and other halogenated pesticides in HRGC using the electron capture detector.

Characterizing the Origin and Long-Range Transport Behavior of Persistent Organic Pollutants in the North American Atmospheric Environment Using Passive Samplers
Shen, Li, Ph,D. dissertation, University of Toronto (Canada).
University Microfilm, Pub No AAT NQ94263, ISBN: 0-612-94263-5, 235 pp, 2004

To investigate the origin and long-range transport behavior of persistent organic pollutants (POPs) in air, a novel passive air sampler (PAS) based on the polystyrene/divinylbenzene co-polymeric resin XAD was developed. The PAS was characterized by sorption measurements of chlorobenzenes onto XAD at various temperatures, wind tunnel experiments and computer simulations of the uptake kinetics, and field calibration experiments under Arctic and temperate conditions. The performance of this PAS was evaluated by comparing PAS-derived concentrations with those measured by conventional HiVol samplers. These studies demonstrated the usefulness of XAD-based PAS for atmospheric POP monitoring. A PAS network was established across North America, consisting of 40 stations covering 72 degrees of latitude (10 to 82 degrees N) from the Arctic to Costa Rica and 72 degrees of longitude (53 to 125 degrees W) from Newfoundland to Vancouver Island. Annually averaged air concentrations of organochlorine pesticides (OCPs), polychlorinated biphenyls (PCBs), and polybrominated diphenyl ethers (PBDEs) were determined in 2000/2001 at these stations, as was the enantiomeric composition of chiral OCPs.

Chromatographic and Ionization Properties of Polybrominated Diphenyl Ethers Using GC/High-Resolution MS with Metastable Atom Bombardment and Electron Impact Ionization
Ikonomou, M.G. and S. Rayne, Fisheries and Oceans Canada, Sidney, British Columbia.
Analytical Chemistry, Vol 74 No 20, p 5263-5272, 15 Oct 2002

The chromatographic and ionization properties of 35 polybrominated diphenyl ether (PBDE) congeners were investigated using GC/HRMS with metastable atom bombardment (MAB) and electron impact (EI) ionization. A multiple linear regression model based on bromine substitution patterns and MOPAC calculated physical properties was developed to predict relative GC retention times of individual PBDE congeners. Although five different sources of metastable rare gas atoms (He, N_2, Ar, Xe, and Kr) were investigated with MAB ionization, only MAB-N_2 provided adequate ionization efficiency and predictability. Because of reduced background noise to the MS detector, MAB-N_2 had a lower limit of detection for tetra- and penta-BDEs than EI, despite having a lower sensitivity. Multiple linear regression models representing the molecular ion response of PBDE congeners analyzed by GC/HRMS with MAB-N_2 and EI ionization were developed using the number and type of Br substituents and ionization potentials, showing a significantly higher level of predictability for the MAB-N_2 response model than for EI.

Chromatographic Enrichment and Enantiomer Separation of Axially Chiral Polybrominated Biphenyls in a Technical Mixture
Berger, U., W. Vetter, A. Gotsch, and K. Kallenborn, Norwegian Institute for Air Research, Tromso.
Journal of Chromatography A, Vol 973 Nos 1-2, p 123-133, 11 Oct 2002

In a study of the separation properties of different chromatographic methods regarding the enantioselective separation of axially chiral (atropisomeric) polybrominated biphenyls (PBB), the technical hexabromobiphenyl product Firemaster BP-6 was characterized by gas chromatography coupled to electron capture detection (GC/ECD) and electron-capture negative ion mass spectrometry (GC/ECNI-MS), as well as by liquid chromatographic fractionating on active carbon and celite. Twelve individual PBBs including potential atropisomeric PBBs were isolated from Firemaster BP-6 by reversed-phase high-performance liquid chromatography (HPLC) on three serially coupled octadecylsilane columns. Six of the 12 isolated PBBs were separated into atropisomers on a HPLC column containing permethylated beta-cyclodextrin on silica. Gas chromatographic enantiomer separation of PBBs is a very demanding task due to high elution temperatures; however, the use of a column coated with randomly modified heptakis(6-O-tert.-butyldimethylsilyl-2,3-di-O-methyl)-beta-cyclodextrin in OV 1701 allowed the atropisomers of one tri-ortho substituted PBB congener (PBB 149) to be resolved.

Comparing Electron Ionization High-Resolution and Electron Capture Low-Resolution Mass Spectrometric Determination of Polybrominated Diphenyl Ethers in Plasma, Serum, and Milk
Thomsen, C., L.S. Haug, H. Leknes, E. Lundanes, G. Becher, and G. Lindstrom, National Inst. of Public Health, Oslo, Norway.
Chemosphere, Vol 46 No 5, p 641-648, Feb 2002

Gas chromatography coupled to low-resolution mass spectrometry with electron capture negative ionization as detection mode (GC-LRMS (ECNI)) has been compared to gas chromatography coupled to high-resolution mass spectrometry using electron ionization as detection mode (GC-HRMS (EI)) for determination of polybrominated diphenyl ethers (PBDEs) in biological samples. When extracts of 5.0 g plasma, serum, and milk samples were analyzed using both methods, the systems were found to be equally well suited for determination of PBDEs in the biological samples, as well as in standard solutions, with respect to response, detection limits, and repeatability at the pg level.

Determination of 39 Polybrominated Diphenyl Ether Congeners in Sediment Samples Using Fast Selective Pressurized Liquid Extraction and Purification
de la Cal, A., E. Eljarrat, and D. Barcelo, IIQAB, CSIC, Barcelona, Spain.
Journal of Chromatography A, Vol 1021 No 1-2, p 165-173, 22 Dec 2003

A new pressurized liquid extraction (PLE) method that automatically and rapidly achieves quantitative and selective extraction of 39 polybrominated diphenyl ether (PBDE) congeners in sediment samples has been optimized. It consists of on-line cleanup by inclusion of sorbents in the extraction cell. Using sediment samples, the new method was compared with a conventional method based on Soxhlet extraction followed by solid-phase extraction (SPE) with cartridges. The instrumental determination was performed by GC-MS, using negative chemical ionization in the selected-ion monitoring mode. The detection limits obtained with the new developed method were between 1 and 46 pg/g dry weight. The reduction in the sample preparation (extraction + cleanup) time (from days to 30 min) with an efficiency similar to that afforded by the conventional Soxhlet extraction-SPE cleanup technique indicates the suitability of this method.

Determination of Brominated Flame Retardants in Environmental Matrices
Alaee, M., D. Sergeant, J. Luross, and C. Cannon.
48th American Society for Mass Spectrometry Conference on Mass Spectrometry and Allied Topics, 11-15 June 2000, Long Beach, CA. Poster presentation TPH 263.

Brominated flame retardants were determined in freshwater and marine organisms and in wildlife by GC/MS with a high-resolution instrument. Whole fish were homogenized with sodium sulfate spiked with (13)C-labeled mixture of tetra- to octachlorodiphenyl ethers (PBDEs) and extracted. with dichloromethane. Extracts were delipidated by GPC and fractionated on deactivated silica gel. The fragmentation patterns were similar to those of PCBs. Relative response parameters within the same homologous group are similar, so the use of an ave. response factor gives a reasonable estimate. To minimize variations in the relative response factors, fragmentation patterns under FI conditions were investigated: PBDEs do not fragment and produce M+ exclusively. The levels and congeners found in wildlife and aquatic organisms are discussed.

Determination of Brominated Flame Retardants in Environmental Samples
Hyotylainen, T. and K. Hartonen, Univ. of Helsinki, Helsinki, Finland
TrAC Trends in Analytical Chemistry, Vol 21 No 1, p 13-30, Jan 2002

This article provides a brief overview of the analytical methodology used for the determination of brominated flame retardants (BFRs) in environmental samples and the levels of BFRs found in the samples.

Determination of Brominated Flame Retardants in Household Dust using GC/ECNI-MS
Stapleton, Heather M., National Inst. of Standards and Technology.
The 11th Annual Sigma Xi Postdoctoral Poster Presentation, 19 February 2004, National Institute of Standards and Technology.

Brominated flame retardants (BFRs) are chemical additives that are applied to many types of electronic equipment, such as TVs, computers, and circuit boards, as well as to many textiles and furniture products. These compounds are flame retardants: at high temperatures, bromide ions are liberated that quench and slow down the oxidative combustion reactions in fire. Polybrominated diphenyl ethers (PBDEs) are a specific class of BFRs. Three different mixtures of PBDEs are used commercially that vary by their degree of bromination. The European Union and the state of California have banned the use of two of the three commercial mixtures (pentaBDE and octaBDE) due to their persistent and bioaccumulative nature; however, the third commercial mixture, decaBDE, is still being used quite heavily. Recent studies have shown that 2,2',3,3',4,4',5,5',6,6'-decabromodiphenyl ether (BDE 209), the dominant compound in the decaBDE commercial mixture, can debrominate both biotically and abiotically. Debromination of this highly brominated congener can lead to the formation of numerous less brominated diphenyl ether isomers, an important point given recent observations of increased bioaccumulation with decreasing degree of bromination. BDE 209, the fully brominated diphenyl ether, can be difficult to measure accurately in environmental samples due to its instability at high temperatures. A method has been developed to quantify BDE 209 using GC/ECNI-MS with on-column injection. The method provides a more accurate and precise means for quantifying BDE 209 than more common methods employing split/splitless injections onto a GC capillary column. This method has been used to quantify PBDEs in candidate Standard Reference Material (SRM) 2585 (household dust) to examine the levels and distribution of BDE congeners. The results showed significant levels of PBDEs that are common components of both the pentaBDE and the decaBDE commercial mixtures. The BDE 209 concentration in this material was 3145 plus/minus 233 ug/kg dry mass, which is higher than levels reported in dust collected immediately following the collapse of the world trade center. Other BDE congeners that are not found in the commercial mixtures were detected in this material, which may indicate that debromination of PBDEs is occurring in households.

Determination of Brominated Flame Retardants, with Emphasis on Polybrominated Diphenyl Ethers (PBDEs) in Environmental and Human Samples: a Review
Covaci, A. (Univ. of Antwerp, Antwerpen Wilrijk, Belgium); S. Voorspoels and J. de Boer (Netherlands Inst. for Fisheries Research, IJmuiden, The Netherlands).
Environment International, Vol 29 No 6, p 735-756, Sep 2003

The authors review analytical methods for the determination of brominated flame retardants (BFRs), with a special emphasis on polybrominated diphenyl ethers (PBDEs). Descriptions and recommendations are provided of procedures that can be applied to the analysis of PBDEs and polybrominated biphenyls, and in some cases, hexabromocyclododecane (HBCD), in environmental and human samples. Several BFRs, such as tetrabromobisphenol-A (TBBP-A), BDE 209, and to some extent HBCD, may require a different approach, and specific advice on their analysis is given separately.

Determination of Decabromodiphenyl Ether in Sediments Using Selective Pressurized Liquid Extraction Followed by GC-NCI-MS
Eljarrat, E., A. de la Cal, and D. Barcelo, IIQAB, CSIC, Jordi Girona 18-26, 08034 Barcelona, Spain.
Analytical and Bioanalytical Chemistry, Vol 378 No 3, p 610-614, Feb 2004

A method based on selective pressurized liquid extraction (SPLE) followed by gas chromatography-negative ion chemical ionization-mass spectrometry (GC-NICI-MS) has been evaluated for analysis of decabromodiphenyl ether (PBDE-209) in sediment samples. Instrument operating conditions, such as source temperature and system pressure, were optimized in the NICI-MS system, giving an instrumental detection limit of 2 pg. The limit of determination of the entire SPLE-GC-NICI-MS procedure was around 50 pg/g dry weight, with repeatability of replicates between 4 and 21% relative standard deviation. This paper describes application of the method to 13 different river and marine sediment samples collected in Spain, with results.

Determination of High Molecular Weight PBDE by Isotopic Dilution in ECNI-MS
Bjorklund, J., P. Tollback, and C. Ostman, Stockholm Univ., Sweden.
Organohalogen Compounds, Vol 61, p 163-166, 2003 [Dioxins 2003]

The separation and detection of polybrominated diphenyl ethers (PBDEs) is most commonly performed using gas chromatography (GC) with mass spectrometric detection (MS). High resolution MS (HRMS) operated in electron ionization (EI) mode offers a good sensitivity and the possibility to use (13)C-labeled standards for an accurate and precise determination of the BDE congeners utilizing isotopic dilution. For low resolution MS (LRMS), the most sensitive operational mode is electron capture negative ion (ECNI) monitoring the [79Br] and [81Br] fragments, but this mode generally provides little structural information about the compounds compared to EI. The authors propose (13)C-labeled BDE-209 as an internal surrogate standard and its application for quantification by isotopic dilution in LRMS ECNI.

Determination of Polybrominated Diphenyl Ethers and PBDD/Fs During the Recycling of High Impact Polystyrene Containing Decabromodiphenyl Ether and Antimony Oxide
Hamm, Stephan, Matthias Strikkeling, Paul F. Ranken, Klaus P. Rothenbacher.
Chemosphere, V 44(6), p 1353-60, 2001

During the recycling processing of a high-impact polystyrene plastic flame-retarded with decabromodiphenyl ether (DecaBDE) and antimony trioxide (Sb_2O_3), the amount of debromination of the flame retardant and possible formation of PBDD/F was monitored. No indications of debromination were found. The concentrations of relevant PBDD/F congeners were at least one order of magnitude below the regulated limit values for PBDD/F (in Germany, 1 ppb for the sum of four congeners, 5 ppb for the sum of all eight regulated congeners).
http://www.bsef-site.com/newsmanager/uploads/article.pdf

Determination of Polybrominated Diphenyl Ethers in Marine Biological Tissues Using Microwave-Assisted Extraction
Bayen, S. (National Univ. of Singapore), H.K. Lee, and J.P. Obbard.
Journal of Chromatography A, Vol 1035 No 2, p 291-294, 7 May 2004

The authors present the first validated method for the quantification of major PBDE congeners (47, 99, and 100) in marine biological tissues using microwave-assisted extraction (MAE). MAE was compared to Soxhlet extraction efficiency for PBDEs in the standard reference materials SRM2978 and SRM1588a and gave comparable results (<15% variation). Analytical accuracy, precision, limits of detection, and cleanup efficiency were evaluated for PBDE congeners, and empirical data justifies the use of MAE for the extraction and analysis of PBDEs in biological matrices. The recovery of polychlorinated biphenyls and various organochlorine pesticides has also been ascertained.

Determination of Polybrominated Diphenyl Ethers in Soil and Sediment from an Electronic Waste Recycling Facility
Wang, D. and Z. Cai (Hong Kong Baptist Univ., Hong Kong SAR, China); G. Jiang; A. Leung; M.H. Wong; W.K. Wong.
Chemosphere, Vol 60 No 6, p 810-816, Aug 2005

Soil and sediment collected in the vicinity of an open electronic waste disposal and recycling facility located in Guiyu, Guangdong, China, were analyzed for the levels of common polybrominated diphenyl ethers (PBDEs) using Soxhlet extraction and gas chromatography/mass spectrometry. The PBDEs were detected in the soil and sediment samples at levels of 0.26 to 824 ng/g (dry weight).

Determination of Polybrominated Diphenylethers (PBDE) in Sewage Sludge Originating from SEA Monitoring Network
Swiss Agency for the Environment, Forests and Landscape, 89 pp, 2004

The described study focuses on polybrominated diphenylethers (PBDE), gammahexabromocyclododecane (gHBCD), tetrabromobisphenol A (TBBPA), and dimethylated TBBPA (mTBBPA) in sewage sludge originating from municipal waste water treatment plants of the SEA monitoring network. An analytical method was developed and improved for the analysis of PBDE in sewage sludge. It includes a Soxhlet extraction using an acetone/hexane mixture and several cleanup steps (sulphuric acid treatment, gel permeation chromatography, copper assisted silicagel chromatography). The final determination was performed by (MD)GC/ECD using different columns

to avoid interferences with PCB or pesticides. The recovery rates of this method was 58 % for TBBPA and ranged between 79 and 112% for all PBDEs. Accuracy was satisfactory with highest standard deviations found for BDE154 (90.3% +/- 11.0). Further adaptations of the method are needed for the analysis of BDE209, mTBBPA, TBBPA, and gHBCD. An interlaboratory test for analysis of PBDE using a sediment and sewage sludge sample showed good agreement with the results of the partner laboratories, except for BDE209.
http://cecotox.epfl.ch/sea/inhalt/sites/projekte/pdf/B_PBDE_2004.pdf

Determination of Potential Sources of PCBs and PBDEs in Sediments of the Niagara River
Samara, F., C.W. Tsai, and D.S. Aga, State Univ. of New York, Buffalo.
Environmental Pollution, in press 2005

Sediments from Niagara River were analyzed for 14 congeners of polychlorinated biphenyls (PCBs) and 9 congeners of polybrominated diphenyl ethers (PBDEs) using accelerated solvent extraction and gas chromatography/mass spectrometry. All sites but one showed PBDE in sediments with total concentrations as high as 148ng/g, suggesting that PBDE is becoming an important class of persistent organic pollutant. A land-use and coverage map was used to trace potential localized sources of PCB and PBDE contamination. The highest levels of PCBs and PBDEs were found in sediments collected from areas closest to the discharge locations of municipal wastewater treatment plants (WWTP) and local industries. This study indicates the importance of WWTP discharges as a potential source of PBDE contamination in the Great Lakes.

Development and Application of a Method for the Analysis of Brominated Flame Retardants by Fast Gas Chromatography with Inductively Coupled Plasma Mass Spectrometric Detection
Vonderheide, Anne P., Maria Montes-Bayon, and Joseph A. Caruso.
Journal of Analytical Atomic Spectrometry, Vol 17 No 11 p 1480-1485, 2002

Inductively coupled plasma mass spectrometry (ICP-MS) coupled to gas chromatography (GC) in the form of fast gas chromatography has been explored as an option to shorten analysis times for polybrominated diphenyl ethers (PBDEs). A run time of 10 min was ultimately established. A new, commercially available interface has been achieved that requires heating the entire device at 325 degrees C to maintain the resolution between the species previously separated. The introduction of helium as an optional gas provides an increase in sensitivity; instrument detection limits within the low ppb level are demonstrated for all species examined. Rigorous control of the interface temperature seems to be required for analyzing the species with more than six bromine atoms per molecule. The method was applied to the analysis of sewage sludge samples, which revealed the presence of three of the most abundant PBDEs (BDE-47, BDE-99 and BDE-100).

Development of a Matrix Solid-Phase Dispersion Method for the Screening of Polybrominated Diphenyl Ethers and Polychlorinated Biphenyls in Biota Samples Using Gas Chromatography with Electron-Capture Detection
Martinez, A., M. Ramil, R. Montes, D. Hernanz, E. Rubi, I. Rodriguez, and R. Cela Torrijos, Univ. de Santiago de Compostela, Santiago de Compostela, Spain.
Journal of Chromatography A, Vol 1072 No 1, p 83-91, 22 Apr 2005

This paper presents a low-cost method for the screening of six polybrominated diphenyl ethers (PBDEs) and seven polychlorinated biphenyls (PCBs) in biological samples containing up to 100% fat.

Compounds are extracted from the sample and isolated from lipids using a matrix solid-phase dispersion (MSPD) cartridge and 20 ml of n-hexane as elution solvent. PBDEs and PCBs are fractionated on a second cartridge containing 2 g of a normal phase sorbent. The potential of neutral silica, Florisil, and basic alumina to separate PBDEs and PCBs in two independent fractions was evaluated, with the best results obtained using silica. The applicability of the method for the screening of PBDEs and PCBs in samples containing both groups of compounds has been demonstrated using spiked, certified, and real polluted samples from different biota materials.

Development of a Semi-Automated Comprehensive Extraction and Multiple Fractionation (S-ACEMF) Method. Part I: Evaluation of Different Solid Phase Sorbets and Optimization of Overall Recovery
Sjodin, A., C.D. Sandau, M.D. Davis, A.L. Waterman, W. Roman, and D.G. Patterson, Centers for Disease Control and Prevention, Atlanta, GA.
PITTCON 2002, 17-22 March, Pittsburgh, Pennsylvania. Abstract 967.

A semi-automated extraction method developed to increase sample throughput employs solid-phase extraction with automation on the RapidTrace(R) (Zymark Corporation). The methodology has been evaluated for polychlorinated biphenyls (PCBs), hydroxylated PCB metabolites, methylsulphonyl PCB metabolites, persistent pesticides, polychlorinated naphthalenes and polybrominated diphenyl ethers (PBDEs). Nine different sorbents from several manufacturers were evaluated: C18(R) (Varian Inc.), ENV(R) (Varian Inc.), NEXUS(R) (Varian Inc.), OASIS(R) (Waters Corporation), and Chromabond(R) (Macherey-Nagel). Cartridges of all sorbents were packed in-house to correspond to bed heights of 4, 12, 22 and 30mm, respectively, in 3ml cartridges. The weight of the sorbents used to obtain a certain bed height varied due to different densities of the sorbents. Duplicate samples were extracted for each bed height, using the RapidTrace(R), employing the same extraction procedure. The procedure included conditioning, application of sample, drying of cartridge, and elution of compounds of interest. All serum samples (2ml) were pretreated using the same methodology employing formic acid (2ml), sonication, and subsequent dilution with water (2ml). Sorbent heights were plotted against absolute recoveries for each sorbent and analyte. Recoveries for highly lipophilic compounds, such as decachlorobiphenyl (CB-209), were lower than recoveries for less chlorinated and less lipophilic compounds, such as 2,2,3,3',4,4'-hexachlorobiphenyl (CB- 153); however, recoveries increased for CB-209, to approximately 80% using a bed height of 30mm for most sorbents, illustrating the importance of these experiments for determining the amount of sorbent needed for efficient extraction.

Development of a Semi-Automated Comprehensive Extraction and Multiple Fractionation (S-ACEMF) Method. Part II: Isolation and Purification of PBDEs, Persistent Pesticides, PCBs and PCB Metabolites from Serum
Sandau, C.D., A. Sjodin, M.D. Davis, A.L. Waterman, W. Roman, and D.G. Patterson, Centers for Disease Control and Prevention, Atlanta, GA.
PITTCON 2002, 17-22 March, Pittsburgh, Pennsylvania. Abstract 968.

A new, comprehensive extraction method was coupled with a multiple fractionation method to allow the separation and quantitation of polybrominated diphenyl ethers (PBDEs), polychlorinated biphenyls (PCBs), persistent pesticides, halogenated phenolic compounds (including hydroxylated PCBs), and methylsulphonyl-PCBs (MSF-PCBs). Each of the fractions was isolated using specific interactions with different commercially available sorbents and semi-automated using the Zymark RapidTrace(R) system (Zymark Corporation). The serum extract from the polymeric extraction sorbent was reduced in volume and separated into two fractions on activated (100%) silica gel: non-polar compounds (F1) and polar compounds, which includes phenolic compounds, MSF-PCBs, and polar pesticides (F2). Phenolic compounds in F2 were then derivatized to their methyl ethers and cleaned up further on silica/sulfuric acid columns to remove residual biogenics prior to mass spectral analysis. The non-polar fraction (F1) can be fractionated further on a carbon column to separate PCBs/persistent pesticides (F1a) from planar compounds, such as polychlorinated naphthalenes, dioxins, and furans (F1b). Both fractions were purified when necessary prior to gas chromatography-mass spectral analysis. The final semi-automated method is described, along with the application of the method to human serum and plasma. The Zymark RapidTrace(R) allowed semi-automation of a complex method that significantly increased throughput of samples and also increased the number of analytes monitored due to the fractionation techniques described above. The potential of this method to replace the current vacuum manifold methods and to expand to other classes of compounds, such as dioxins, furans, and polychlorinated naphthalenes, is also discussed.

Development of Analytical Method for PBDEs and PBDDs/DFs in Environmental Matrices and Some Chemical Formulations
Hanari, N. and T. Okazawa, K. Guruge, J. Falandysz, and N. Yamashita DIOXIN 2004: 24th International Symposium on Halogenated Environmental Organic Pollutants and Persistent Organic Pollutants (POPs), 6-10 September 2004, Berlin, Germany.
Organohalogen Compounds, Vol 66, p 207-212, 2004

Some PDBE congeners are liable for debromination and photodegradation during chemical laboratory analysis. Co-occurrence of PBDDs/DFs and PBDEs also can cause interferences during quantitative analysis of PBDFs with high resolution GC/high resolution MS (HRGC/HRMS). This paper describes work toward a method of perfect separation of PBDDs/DFs from PBDEs and their congener-specific determination using HRGC/HRMS, as well as efforts to optimize quantification of BDE 209 in environmental samples.
http://dioxin2004.abstract-management.de/pdf/p244.pdf

Direct Measurement of Octanol/Water Partition Coefficients of Some Environmentally Relevant Brominated Diphenyl Ether Congeners
Braekevelt, E. (Dept. of Fisheries and Oceans, Freshwater Inst., Winnipeg, Manitoba, Canada); S.A. Tittlemier (Health Canada, Ottawa, ON); G.T. Tomy (Dept. of Fisheries and Oceans, Freshwater Inst., Winnipeg, Manitoba, Canada).
Chemosphere, Vol 51 No 7, p 563-567, May 2002

Octanol-water partition coefficients (K_{OW}) of nine brominated diphenyl ether (BDE) congeners present in two technical mixtures were directly measured using a slow-stir technique. The directly determined K_{OW} values were generally lower than those calculated using fragment constant methods, particularly at higher levels of bromine substitution. The quasi-experimental approach of using fragment constants to modify a "backbone" compound of known K_{OW} was much more successful than using the fragment constants to "build" the entire molecule.

Evaluation of Four Capillary Columns for the Analysis of Organochlorine Pesticides, Polychlorinated Biphenyls, and Polybrominated Diphenyl Ethers in Human Serum for Epidemiologic Studies
Rogers, E., M. Petreas, J.S. Park, G. Zhao, and M.J. Charles, Univ. of California, Davis.
Journal of Chromatography B, Vol 813 Nos 1-2, p 269-285, 25 Dec 2004

The separation of organochlorine pesticides (OCPs), polychlorinated biphenyls (PCBs), and polybrominated diphenyl ether (PBDE) congeners was evaluated on four capillary columns. Based on performance, capacity, and cost, the RTX-5MS and the DB-XLB were selected for the analysis of human serum extracts by gas chromatography/electron-capture detection. In contrast to previous studies, the oven temperature program allows the separation of congeners not separated using other combinations of capillary columns, particularly PBDE-47 and PCB 180. The method enables determination of OCPs, PCBs, and PBDEs prevalent in a single extract of serum, which can save time in the analysis of large number of samples collected for epidemiologic studies.

Evaluation of the Gas Chromatographic Column System for the Determination of Polybrominated Diphenyl Ethers
Bjorklund, J., P. Tollback, and C. Ostman, Stockholm Univ., Sweden.
Organohalogen Compounds, Vol 61, p 239-242, 2003

The fully brominated diphenyl ether, BDE-209 is one of the most commonly used PBDEs today due to pending regulations in the European Union regarding the technical PBDE mixtures with a lower degree of bromination. The physical and chemical properties of the BDE-209 put great demands on the analytical method, including sampling, extraction and cleanup, as well as the final chromatographic separation. The gas chromatographic separation of PBDE is often performed on two separate systems, one for the low molecular weight BDE congeners using a 30-60 m long column, while the analysis of the high molecular weight BDE-209 is performed on a shorter column (ca 10m). The authors evaluate a number of columns with different dimensions from different manufacturers with respect to the yield of the PBDE congeners with particular attention to the high molecular weight BDE congeners.

Evaluation of Gas Chromatographic Injection Techniques for PBDE
Tollback, P., J. Bjorklund, and C. Ostman.
Organohalogen compounds, Vol 61, p 49-52, 2003 [Dioxins 2003, Boston, MA]

Gas chromatography is presently the method of choice for the separation of polybrominated diphenyl ether (PBDE) due to high resolution and low detection limits using either the electron capture detector (ECD) or mass spectrometry (MS). Splitless is the most commonly used injection technique for GC separation of PBDE, though both the septum-equipped temperature-programmable injector (SPI) and the programmable temperature-vaporizing (PTV) injector, as well as on-column, have been used successfully. Large volume injections (LVI) using either the PTV in solvent elimination mode or the loop type interface have also been used. The injection of PBDE into the GC system is a critical and important part of the chromatographic analysis, hence careful selection and optimization the injection techniques must be performed to reduce the discrimination of these compounds. This paper contains evaluations and suggested optimizations of the most commonly used injection techniques for PBDE.

Gas Chromatography and Mass Spectrometry of Polybrominated Diphenyl Ethers
Bjorklund, Jonas, Ph.D. thesis, Stockholm University, Sweden. ISBN 91-7265-563-1. 180 pp, 2003

The principal goal of the thesis work was to develop accurate and sensitive analytical methods for the determination of polybrominated diphenyl ethers (PBDEs). Initial lab studies indicated that specific problems associated with gas chromatographic analysis of these compounds needed to be addressed. A special emphasis has been placed on key stages of the gas chromatographic analysis of PBDEs, including the injection techniques, the chromatographic separation per se, and the modes of detection that can be used. A further objective has been to develop methods for the measurement of PBDEs in indoor air using personal exposure monitoring equipment. This work involved the exploration of large volume injection techniques and optimization of the sampling and sample cleanup procedures for indoor air samples. This thesis is intended to provide an overview of the procedures used

in the analysis of PBDEs on gas chromatographic separation systems with the aim to improve the accuracy and reliability of determinations of PBDEs in the future by highlighting key aspects of the gas chromatographic analysis, including the high molecular weight congeners such as the decabrominated congener BDE-209.
http://www.anchem.su.se/downloads/ diss_pdf/j_bjorklund_diss2003.pdf

A Gas Chromatography/High-Resolution Mass Spectrometry (GC/HRMS) Method for Determination of Polybrominated Diphenyl Ethers in Fish
Alaee, M., D.B. Sergeant, M.G. Ikonomou, and J.M. Luross, Environment Canada, Burlington, ON.
Chemosphere, Vol 44 No 6, p 1489-1495, Sep 2001

The mass spectroscopic (MS) evaluation of 23 brominated diphenyl ethers under electron ionization and electron capture negative ion conditions using magnetic sector and quadrupole mass spectrometers showed that high-resolution mass spectrometry (HRMS) under electron ionization conditions was the most reliable technique, with high selectivity and adequate sensitivity. The effectiveness of the method was evaluated by analyzing the occurrence of PBDEs in commercially available CRMs comprising Lake Ontario lake trout, Pacific herring, and sockeye salmon. Results indicate that the described method is reliable for determining PBDE concentrations in biological tissues.

Gas Chromatography/Ion Trap Mass Spectrometry Applied for the Determination of Polybrominated Diphenyl Ethers in Soil
Wang, D., Z. Cai, G. Jiang, M.H. Wong, and W.K. Wong, Hong Kong Baptist Univ., Hong Kong SAR, China.
Rapid Communications in Mass Spectrometry, Vol 19 No 2, p 83-89, 2005

A gas chromatography/ion trap mass spectrometry (GC/ITMS) method was developed for the determination of polybrominated diphenyl ethers (PBDEs). ITMS parameters were optimized to achieve the best sensitivity for the PBDE analysis. Tandem mass spectrometry, along with an isotope dilution internal standard method, was used for the quantitation. Chromatographic windows were developed for mono- to hepta-BDEs, depending on the retention times when using a 30-m GC column. A 15-m column was used to analyze deca-BDE. Environmental soil samples collected from an electronic waste recycling site were prepared by using Soxhlet extraction and column chromatographic cleanup. Average recoveries of 61-118% were obtained for the (13)C-labeled PBDE internal standards spiked in the samples prior to sample preparation. Method detection limits ranged from 0.013 to 0.25 ng/g for the PBDEs in soil.

GCxGC-TOFMS and GCxGC-ECD OF PBDEs
Cochran, Jack (LECO Corporation, Las Vegas, NV); F.L. Dorman (Restek Corporation, Bellefonte, PA); E. Reiner, T. Kolic, and K. MacPherson (Ministry of the Environment, Toronto, ON).
BFR 2004: Third International Workshop on Brominated Flame Retardants, 6-9 June 2004, University of Toronto, Toronto, Ontario, Canada. p 291-300, 2004

The polybrominated diphenyl ethers (PBDEs) used as flame-retardants are produced commercially as mixtures containing relatively few major congeners, and these are the ones often monitored in analytical schemes. Decabromodiphenyl ether (BDE 209) is the most widely used PBDE flame-retardant in the world; however, the high molecular weight, lack of volatility, and tendency to thermally degrade of this congener complicates the gas chromatography-mass spectrometry (GC-MS) analysis of PBDEs. In some labs, the analysis of BDE 209 is accomplished separately (using a shorter

GC column) from the other commonly analyzed tri- to heptabromo- BDEs. Vacuum-outlet GC with a 0.53mm column and TOFMS has recently been applied to the analysis of seventeen PBDEs in biosolids, including BDE 209, though the limit of detection for 209 was relatively high. A relatively new way to solve separation problems is to use comprehensive 2-D GC (GCxGC). GCxGC is a way to increase peak capacity by applying two independent separations to a sample in one analysis. Typically, GCxGC involves a serial column configuration (differing phases) separated by a thermal modulator. A separation is performed on the first column, and then effluent from the first column is continually (and quickly) focused and 'injected' onto the second column. By keeping the second column short, a series of high-speed chromatograms is generated, and the first column separation can be maintained. Separation results can be plotted as a retention plane, also known as a contour plot. Due to modulation, most GCxGC peaks are on the order of 100 to 500 ms wide, requiring a fast detector. When MS is used, only time-of-flight (TOF) has the necessary acquisition rates (hundreds of spectra/sec). The ability of the thermal modulator to narrow peaks (thereby increasing their height) prior to their detection also affords the ability to increase TOFMS sensitivity for all PBDEs, but especially the difficult 209 congener, without using a secondary column. In this case, only the first dimension column and the TOFMS provide selectivity from sample matrix components. A study was conducted to evaluate GCxGC-TOFMS for the analysis of PBDEs. Also investigated was the effect of thermal focusing on and reinjection to an uncoated, deactivated transfer line to the TOFMS to improve sensitivity for BDE 209. A new GCxGC-electron capture detector system was finally tested for PBDE analysis.
http://www.bfr2004.com/Table%20of%20Contents.pdf

Group Separation of Organohalogenated Compounds by Means of Comprehensive Two-Dimensional Gas Chromatography
Korytar, P., P.E. Leonards, J. de Boer, and U.A. Brinkman, Netherlands Inst. for Fisheries Research, AB IJmuiden, The Netherlands.
Journal of Chromatography A, Vol 1086 Nos 1-2, p 29-44, 9 Sep 2005

Scientists evaluated separations of 12 compound classes by comprehensive 2-D gas chromatography. Polychlorinated biphenyls (PCBs), diphenyl ethers (PCDEs), naphthalenes (PCNs), dibenzothiophenes (PCDTs), dibenzo-p-dioxins (PCDDs), dibenzofurans (PCDFs), terphenyls (PCTs) and alkanes (PCAs), toxaphene, organohalogenated pesticides (OCPs), and polybrominated biphenyls (PBBs) and diphenyl ethers (PBDEs) were evaluated. Five column combinations were used to study, primarily, group-type separations, but attention was devoted also to within-class separation, especially for those classes not previously addressed in much detail (i.e., the PCNs, OCPs, PBBs and PCTs). The performance of each column is described. The DB-1 x VF-23ms column yielded excellent within-class separations, especially of non-aromatic compounds, viz. OCPs, toxaphene and PCAs. No group separation was observed here. The applicability of the approach was demonstrated for a sediment extract and a dust extract. In the sediment extract, PCDDs, PCDFs, PCAs, and PCNs were identified and their efficient separation was achieved. In the dust sample, separation of PCAs and PBDEs was achieved, and several new PBDE congeners were identified.

Influence of the Injection Technique and the Column System on Gas Chromatographic Determination of Polybrominated Diphenyl Ethers
Bjorklund, J., P. Tollback, C. Hiarne1, E. Dyremark, and C. Ostman, Stockholm Univ., Stockholm, Sweden.
Journal of Chromatography A, Vol 1041 Nos 1-2, p 201-210, 2 July 2004

Capillary columns, retention gaps, press-fit connectors, and different injection techniques were evaluated with respect to yield and repeatability in a gas chromatographic separation system used to determine polybrominated diphenyl ethers (PBDEs). The split/splitless injection was optimized and compared to on-column injection, the septum-equipped temperature-programmable injector, and the programmable temperature-vaporizing (PTV) injector. The results show large variations in the yield of PBDEs depending on the column and the injection systems, especially the high molecular weight BDE congeners, which can be subject to severe discrimination. Unfavorable conditions can lead to a complete loss of nona- and deca-substituted BDE congeners.

An Intercalibration Study on Organobromine Compounds in Japan: First Report on PBDEs, PBDDs/DFs and PXDDs/DFs
Takahashi, Shin and Shin-ichi Sakai (National Inst. for Environmental Studies, Tsukuba, Ibaraki, Japan); Isao Watanabe (Osaka Prefectural Inst. of Public Health, Higashinari-ku, Osaka, Japan).
BFR 2004: Third International Workshop on Brominated Flame Retardants, 6-9 June 2004, University of Toronto, Toronto, Ontario, Canada. p 309-312, 2004

The Ministry of the Environment in Japan is working to promote studies on brominated dioxins and has conducted a pilot survey of occurrence in the environment. PBDDs/DFs and monobromo-polychloro dibenzo-p-dioxins and dibenzofurans (MoBPCDDs/DFs) were found in various environmental media with BFRs. Because commercially available standards for these compounds are still limited, 10 laboratories in Japan are participating in an intercalibration study to evaluate accuracy and reliability in the analysis of organobromine compounds. The study was initiated in April 2003. This presentation discusses the results of PBDEs, PBDD/DFs, and MoBPCDDs/DFs in 'Mixed Standard Solutions' and 'Air-Dried Sediment.'
http://www.bfr2004.com/Table%20of%20Contents.pdf

Is House Dust the Missing Exposure Pathway for PBDEs? An Analysis of the Urban Fate and Human Exposure to PBDEs
Jones-Otazo, H.A., J.P. Clarke, M.L. Diamond, J.A. Archbold, G. Ferguson, T. Harner, G.M. Richardson, J.J. Ryan, and B. Wilford, Univ. of Toronto, Toronto, ON, Canada.
Environmental Science & Technology, Vol 39 No 14, p 5121-5130, 15 July 2005

Polybrominated diphenyl ether (PBDE) body burdens in North America are 20 times higher than those of Europeans. Investigators estimated emissions and fate of sigma PBDEs (minus BDE-209) in a 470 square km area of Toronto, Canada, using the Multi-media Urban Model (MUM-Fate). A combination of measured and modeled concentrations was used to estimate exposure to indoor and outdoor air, soil, dust, and food. Fate calculations indicate that 57 to 85% of PBDE emissions to the outdoor environment originate from within the city and that the dominant removal process is advection by air to downwind locations. Inadvertent ingestion of house dust is the largest contributor to exposure of toddlers through to adults and is thus the main exposure pathway for all life stages other than the infant. Infant consumption of human milk is the largest contributor to lifetime exposure. Inadvertent ingestion of dust is the main exposure pathway for a scenario of occupational exposure in a computer recycling facility and a fish eater. Ingestion of dust can lead to almost 100-fold higher exposure than "average" for a toddler with a high dust intake rate living in a home in which PBDE concentrations are elevated.

Investigation of Photodegradation Products Generated after UV-Irradiation of Five Polybrominated Diphenyl Ethers Using Photo Solid-phase Microextraction
Sanchez-Prado, L., M. Llompart, M. Lores, C. Garcia-Jares, and R. Cela.
Journal of Chromatography A, Vol 1071 Nos 1-2, p 85-92, 15 Apr 2005

The photoinduced degradation of five polybrominated diphenyl ethers (PBDEs)—BDE-47, BDE-100, BDE-99, BDE-154 and BDE-153—was studied using solid-phase microextraction polydimethylsiloxane fibers as photolytic support. The PBDEs were extracted from aqueous solutions on SPME fibers that subsequently were exposed to UV irradiation for times ranging from 2 to 60 min. Photodegradation kinetics of the five PBDEs, tentative identification, photochemical behavior of the generated photoproducts, and photodegradation pathways were examined via on-fiber approach technique (photo-SPME) followed by gas chromatography/mass spectrometry analysis. Aqueous photodegradation studies also were performed and compared with photo-SPME. All the photoproducts detected in the aqueous experiments were previously found in the photo-SPME experiments. Reductive debromination by successive losses of bromine atoms was confirmed as the main photodegradation pathway of PBDEs. A large number of PBDEs were obtained as photoproducts of the five target analytes. This study shows the potential of photo-SPME to evaluate the photo-transformation of organic pollutants.

Large Volume Injection and Hyphenated Techniques for Gas Chromatographic Determination of PBDEs and Carbazoles in Air
Tollback, Petter, Ph.D. thesis, Stockholm University. ISBN: 91-7155-014-3, Paper V, 92 pp, 2005

This thesis is based on studies in which the suitability of various gas chromatography (GC) injection techniques was examined for the determination of polybrominated diphenyl ethers (PBDEs) and carbazoles, two groups of compounds that are thermally labile and/or have high boiling-points. For such substances, it is essential to introduce the samples into the GC system in an appropriate way to avoid degradation and other potential problems. In addition, different types of gas chromatographic column systems and mass spectrometric detectors were evaluated for the determination of PBDEs. Conventional injectors, such as splitless, on-column and programmed temperature vaporizing (PTV) injectors were evaluated and optimized for determination of PBDEs. The results show on-column injection to be the best option, providing low discrimination and high precision. The splitless injector is commonly used for 'dirty' samples; however, it is not suitable for determination of the high molecular weight congeners because it tends to discriminate against them and promote their degradation, leading to poor precision and accuracy. The PTV injector appears to be a more suitable alternative. The use of liners reduces problems associated with potential interferents such as polar compounds and lipids, and compared to the hot splitless injector, it provides gentler solvent evaporation, due to its temperature programming feature, leading to low discrimination and variance. Large-volume injections were utilized and optimized in the studies included in this thesis. With a loop-type injector/interface, large sample volumes can be injected on-column providing low risk of discrimination against compounds with low volatility. This injector was used for the determination of PBDEs in air and as an interface for the determination of carbazoles by LC-GC. The PTV can be used as a large volume injector, in so-called solvent vent mode. This technique was evaluated for the determination of PBDEs and as an interface for coupling dynamic sonication-assisted solvent extraction online to GC. The results show that careful optimization of the injection parameters is required, but also that the PTV is robust and yields reproducible results. A high molecular weight fragment at m/z 486/488 enables the use of (13)C-labeled BDE-209 as an internal surrogate standard.
http://www.diva-portal.org/diva/getDocument?urn_nbn_se_su_diva-367-1__fulltext.pdf

Large Volume Injection GC-MS in Electron Capture Negative Ion Mode Utilizing Isotopic Dilution for the Determination of Polybrominated Diphenyl Ethers in Air
Bjorklund, J., P. Tollback, and C. Ostman, Stockholm Univ., Sweden.
Journal of Separation Science, Vol 26, p 1104-1110, 2003

The authors present a large volume injection GC-MS method for the determination of polybrominated diphenyl ethers (PBDEs). A loop-type injection system with an early solvent vapor exit has been constructed and evaluated. Sample volumes up to 500 lL can be injected with high reproducibility and low carry-over. The peak distortion problem associated with this kind of injection system is discussed and solutions suggested. 13C-labeled BDE-209 is introduced as an internal surrogate standard for the determination of high molecular weight PBDEs in low-resolution mass spectrometry electron capture negative ionization mode. The complete method was applied to air samples from an electronic waste dismantling facility, collected with personal exposure measurement equipment. Nine BDE congeners were identified and quantified.

Large-Volume Programmed-Temperature Vaporiser Injection for Fast Gas Chromatography with Electron Capture and Mass Spectrometric Detection of Polybrominated Diphenyl Ethers
Tollback, P., J. Bjorklund, and C. Ostman, Stockholm Univ., Sweden.
Journal of Chromatography A 991, 241-253, 2003

A large volume injection fast-GC/MS method has been developed, optimized, and evaluated for the determination of polybrominated diphenyl ethers, including the decabrominated diphenyl ether (BDE-209). The programmed-temperature vaporizer injection parameters, temperature programming of the GC oven, and the physical dimensions of the narrow bore GC column were investigated to find the optimal operating conditions for the analysis. The yield of the PBDEs and particularly BDE-209 can vary significantly depending on parameter settings. Volumes up to 125 uL were successfully injected and a fast GC separation was performed, with retention times as short as 6.4 min for the last eluting compound, BDE-209. The technique is illustrated via analysis of an air sample collected at an electronics dismantling facility. Low-resolution mass spectrometry in electron capture negative ion mode was used for detection. Nine BDE congeners, including BDE-209, were identified and quantified.

Mass Spectrometric Characteristics of Decabromodiphenyl Ether and the Application of Isotopic Dilution in the Electron Capture Negative Ionization Mode for the Analysis of Polybrominated Diphenyl Ethers
Bjorklund, J., P. Tollback, and C. Ostman, Stockholm Univ., Sweden.
Journal of Mass Spectrometry, Vol 38 No 4, p 394-400, Apr 2003

This paper describes in detail the mass spectrometric properties of (12)C-and (13)C-labeled decabromodiphenyl ether (BDE-209) in the low-resolution mass spectrometry electron capture negative ionization mode (ECNI-MS). These properties are compared with those of polybrominated diphenyl ethers (PBDEs) with a lower degree of bromination. The mass spectrometric properties of BDE-209 make it possible to apply (13)C-labeled BDE-209 as an internal surrogate standard for the determination of BDE-209 by isotopic dilution. A combination of the [Br](-) and [C(6)Br(5)O](-) fragment ions is proposed for the detection with ECNI-MS in the selected ion monitoring mode to increase selectivity, sensitivity, and accuracy in the determination of BDE-209 together with other PBDEs. The authors also explain the importance of optimizing the instrument parameters to obtain optimal response from the mass spectrometer in the analysis of PBDEs.

Measurement of Henry's Law Constants of Seven Polybrominated Diphenyl Ether (PBDE) Congeners as a Function of Temperature
Cetin, Banu and Mustafa Odabasi, Dokuz Eylul Univ., Izmir, Turkey.
Atmospheric Environment, Vol 39 No 29, p 5273-5280, Sep 2005

The Henry's law constant is an important parameter in predicting the transport, behavior, and fate of semivolatile organic compounds in the environment, and it is required to model the chemical transfer between air and water. Henry's law constants for 7 polybrominated diphenyl ether (PBDE) congeners (BDE 28, 47, 99, 100, 153, 154, and 209) were experimentally determined between 5 and 40 degrees C using a gas-stripping technique. Dimensionless Henry's law constants of PBDEs increase with temperature more than 15 times (15.3 times for BDE 100 and 34.1 times for BDE 99) over the studied temperature range. The gas phase overall mass transfer coefficients (K_g) for 7 PBDE congeners calculated for a moderate wind speed (3 m/s) and a temperature of 25 degrees C ranged between 0.17 and 0.27 cm/s. Calculated resistances indicated that only the mass transfer of BDE 28 (which has a relatively higher Henry’s constant value) is controlled by both air- and water-side resistance. Mass transfer is controlled by air-side resistance for the remaining congeners.

Measurement of Selected Polybrominated Diphenyl Ethers, Polybrominated and Polychlorinated Biphenyls, and Organochlorine Pesticides in Human Serum and Milk Using Comprehensive Two-Dimensional Gas Chromatography Isotope Dilution Time-of-Flight Mass Spectrometry
Focant, J.F., A. Sjodin, W.E. Turner, and D.G. Patterson Jr., Centers for Disease Control and Prevention, Atlanta, GA.
Analytical Chemistry, Vol 76 No 21, p 6313-6320, 1 Nov 2004

This paper presents a new method using comprehensive 2-D gas chromatography and isotope dilution time-of-flight mass spectrometry (GCxGC-IDTOFMS) for the simultaneous measurement of selected polychlorinated biphenyls (PCBs), organochlorine pesticides, and brominated flame retardants. In contrast to the reference methods based on classical GC/MS, a single injection of the extract containing all compounds of interest results in accurate identification and quantification. Using GCxGC ensures the chromatographic separation of most compounds, and TOFMS allows mass spectral deconvolution of coeluting compounds as well as the use of (13)C-labeled internal standards for quantification. Isotope ratio measurements of the most intense ions for both native and labels ensure the required specificity. The use of this new method with an automated sample preparation procedure developed at the Centers for Disease Control and Prevention for the analysis of human serum and milk compared favorably to conventional isotope-dilution 1-D gas chromatography-high-resolution mass spectrometry (GC-IDHRMS) for the human serum and milk pools tested.

Measurements of Octanol-Air Partition Coefficients (K_{OA}) for Polybrominated Diphenyl Ethers (PBDEs): Predicting Partitioning in the Environment
Harner, T., Environment Canada, Toronto.
BFR 2001: The Second International Workshop on Brominated Flame Retardants, Stockholm, Sweden. Book of Abstracts, p 46-49, 2001

Octanol-air partition coefficients (K_{OA}) are reported for 13 polybrominated diphenyl ethers (PBDEs) over a range of temperatures. Examples are given of how K_{OA} can be used to describe the partitioning of PBDEs between air and environmental organic phases, such as aerosols and soil.
http://www.bfr2004.com/BFR2001_del2.pdf

Modelling the Environmental Fate of the Polybrominated Diphenyl Ethers
Gouin, T. and T. Harner, Trent Univ., Peterborough, ON, Canada.
Environment International, Vol 29 No 6, p 717-724, Sep 2003

Internally consistent physical-chemical property data are presented for five representative polybrominated diphenyl ether (PBDE) congeners--PBDE-15, -28, -47, -99, -153—and used in a multimedia modeling approach. Results of the Level II model indicate that PBDEs will largely partition to organic carbon in soil and sediment and that their persistence will be strongly influenced by degradation rates in these media. TaPL3 model estimates of their characteristic travel distance suggest limited long-range atmospheric transport potential. PBDEs are shown to be sensitive to seasonally and diurnally fluctuating temperatures. When vegetation is included in the model, 50% of the total mass of PBDE-47 deposited to vegetation returns to the atmosphere, suggesting that it may migrate through a series of deposition/volatilization hops. Future research needs include a better understanding of air-surface exchange (particularly to foliage) and measurements of degradation rates in soil, sediment, and vegetation.

Modified Clean-Up for PBDD, PBDF and PBDE with an Active Carbon Colum—Its Application to Sediments
Choi, J.W., J. Onodera, K. Kitamura, S. Hashimoto, H. Ito, N. Suzuki, S. Sakai, and M. Morita, National Inst. for Environmental Studies, Tsukuba-Shi, Ibaraki, Japan.
Chemosphere, Vol 53 No 6, p 637-643, Nov 2003

A cleanup method for polybrominated dibenzo-p-dioxins (PBDDs), dibenzofurans (PBDFs) and diphenyl ethers (PBDEs) was modified using combinations of multi-layered silica gel, Florisil and active carbon columns. By using active carbon column chromatography in the final procedure, PBDEs were well separated from PBDD/Fs in an elution test with reference standards. The method was applied to sediment samples taken from industrialized areas in Japan. The presence of PBDEs did not interfere with the quantification of PBDD/Fs.

Multi-Residue Screening of Chlorinated and Brominated Compounds from Aquaculture Samples Using Matrix Solid-Phase Dispersion/Gas Chromatography/Mass Spectrometry
Carro, A.M., R.A. Lorenzo, F. Fernandez, R. Rodil, and R. Cela, Univ. de Santiago de Compostela, Santiago de Compostela, Spain.
Journal of Chromatography A, Volume 1071, Issues 1-2, p 93-98, 15 April 2005

This paper describes an effective multiresidual method for the trace analysis of 15 compounds from a diverse group of pesticides, polybrominated diphenyl ethers (PBDEs), polychlorinated biphenyls (PCBs) and polybrominated biphenyls (PBBs) in aquaculture feed. The analytical procedure is based on the matrix solid-phase dispersion (MSPD) of feed sample and subsequent elution with hexane. The MSPD process was evaluated using an asymmetrical experimental design. The results suggest that the operational MSPD conditions are elution with pressure, 1 g of C18, basic alumina as adsorbent, and 30 ml of hexane. The overall method including MSPD procedure and GC coupled to mass spectrometry (MS/MS) has been applied to several samples of aquaculture feed and marine species. Application of the method to reference material from the International Atomic Energy Agency (IAEA-406) showed good agreement to the referenced values.

Non-Destructive Rapid Analysis of Brominated Flame Retardants in Electrical and Electronic Equipment Using Raman Spectroscopy
Kikuchi, Sonoko (Fujitsu Analysis Laboratory Ltd., Kawasaki, Japan); K. Kawauchi and S. Ooki; M. Kurosawa and H. Hisashi; T. Yagishita.
Analytical Sciences, Vol 20, p 1111-1112, Aug 2004

Investigators analyzed the brominated flame retardant, polybromodiphenyl ethers (PBDEs), using Raman spectroscopy without any preparation. The analysis detection limit was about 100 ppm, and the analysis took about 1 minute; the conventional method of solvent extraction using gas chromatography/mass spectroscopy takes 50 hours.
http://wwwsoc.nii.ac.jp/jsac/analsci/pdfs/a20_1111.pdf

Occurrence and Analysis of Polybrominated Diphenyl Ether in Sludge by Gas Chromatography Tandem Mass Spectrometry
Benanou, D. and V. Boireau, Anjou-Recherche Veolia Water.
PITTCON 2004, 7-12 March 2004, Chicago, Illinois.

There are no or few data concerning the presence of polybrominated diphenyl ethers (PBDEs) in sludges, particularly those used for agricultural landfilling The presented method describes the analysis of six PBDE congeners (47, 99, 100, 153, 154, and 183) in sludge by gas chromatography-tandem mass spectrometry. PBDEs are extracted from sludge with the SOXTEC technique. The extract is then purified on Florisil solid phase and spiked with labeled compounds just prior to analysis. Fragmentation of each congener is optimized to obtain the best sensitivity. The method was validated, obtaining a quantification limit of 5 ng/g for each compound, and used to investigate the occurrence of PBDE in over 25 French sludges.

Optimization of Congener-Specific Analysis of 40 Polybrominated Diphenyl Ethers by Gas Chromatography/Mass Spectrometry
Eljarrat, E., S. Lacorte, D. Barcelo, IIQAB, CSIC, Barcelona, Spain.
Journal of Mass Spectrometry, Vol 37 No 1, p 76-84, Jan 2002

Two different mass spectrometry approaches—negative chemical ionization (NCI-MS) and electron ionization (EI-MS)—were used in the analysis by gas chromatography of 40 different congeners of polybrominated diphenyl ethers (PBDEs) containing 1-7 bromine atoms. Operating parameters such as electron energy and source temperature were optimized to obtain the maximum sensitivity in the EI-MS study. The effects of the moderating gas (methane or ammonia), source temperature, and system pressure were studied for NCI-MS analyses. When the quality parameters of the two approaches tested were compared, NCI-MS gave detection limits between 30 fg and 1.72 pg, whereas EI-MS has detection limits between 0.53 and 32.09 pg. The main advantage of EI-MS is that it provides better structural information; it also allows the use of an isotope dilution method for quantification, making the analysis more reliable at trace levels.

Optimization of Quadrupole Ion Storage Mass Spectrometric Conditions for the Analysis of Selected Polybrominated Diphenyl Ethers: Comparative Approach with Negative Chemical Ionization and Electron Impact Mass Spectrometry
Larrazabal, D., M. Angeles Martinez, E. Eljarrat, D. Barcelo, and B. Fabrellas, CIEMAT, Madrid, Spain.
Journal of Mass Spectrometry, Vol 39 No 10, p 1168-1175, Oct 2004

Gas chromatography coupled to quadrupole ion storage mass spectrometry (QISTMS) operating in the non-resonant mode is presented as an innovative approach for the analysis of selected polybrominated diphenyl ethers (PBDEs). Although reductions in complexity and time needed for optimization are achieved in comparison with the resonant option, precise adjustment of the mass spectrometric conditions is required. The reliability of the method was confirmed using standard solutions. Detection limits ranged from 62 to 621 fg, providing sensitivity similar to that of negative chemical ionization (NCIMS) and greater than that of electron ionization mass spectrometry. The applicability of the QISTMS method to real samples and matrix effects was evaluated through the analysis of some PBDE congeners in a sewage sludge sample from a Spanish wastewater treatment plant. Comparable results were obtained using QISTMS and NCIMS. The authors conclude that QISTMS performed in the non-resonant mode may constitute a low-cost, rapid, and reliable alternative to high-resolution devices for the analysis of selected PBDEs in environmental samples.

Optimization of Solid-Phase Microextraction for the Gas Chromatography/Mass Spectrometry Analysis of Persistent Organic Pollutants
Gago-Martinez, A. (Univ. de Vigo, Vigo, Spain), M.J. Nogueiras, S. Rellan, J. Prado, M.F. Alpendurada, and W. Vetter.
Journal of AOAC International, Vol 87 No 4, p 1021-1027, July-Aug 2004

Solid-phase microextraction (SPME) has been applied as an alternative for the selective extraction of 3 polybrominated diphenyl ethers (PBDEs): 2,2',4,4'-tetrabromodiphenyl ether (PBDE-47); 2,2',4,4',5-pentabromodiphenyl ether (PBDE-99); and 2,2',4,4',6-pentabromodiphenyl ether (PBDE-100), as well as the alkylphenols 4-tert-OP and 4-NP, prior to their analysis by gas chromatography/mass spectrometry (GC/MS). The technique is simple, cost-effective, and time-saving, as well as being solvent-free. Different fiber coatings and the main parameters affecting the extraction procedure were evaluated to optimize the conditions for efficient extraction of the studied compounds. The results showed a good linearity in the range of concentrations investigated, and adequate relative standard deviation values were found according to the range accepted for SPME. Recovery values ranged from 78 to 108%, and good detection and quantitation limits at ppt levels were obtained for both methods, allowing the determination of the selected compounds in samples at trace levels.

An Optimized Method for the Analysis of Brominated Diphenyl Ethers (BDEs) by Dual Column GC/High Resolution Magnetic Sector Mass Spectrometry
Krumwiede, D., J. Griep-Raming, and H. Muenster, Thermo Electron Corp., Bremen, Germany.
BFR 2004: Third International Workshop on Brominated Flame Retardants, 6-9 June 2004, University of Toronto, Toronto, Ontario, Canada. p 345-350, 2004

The mass spectrometric analysis of brominated diphenyl ethers (BDEs) by high resolution magnetic sector mass spectrometry is complicated by a variety of factors. (1) A high mass range from m/z 248 (mono-BDE) to m/z 960 (deca-BDE) is required, therefore demanding a reference compound that provides sufficient intensity on high m/z ions. (2) Large electric jumps are necessary, which demands stable and rugged electric mass calibration. (3) Deca-BDE, being thermally labile, requires optimized chromatographic methods. The first and second complication can be overcome by the correct selection of instrument parameters and by proper selection of the reference compound. The most severe complication is the thermal lability of deca-BDE, which decomposes during GC analysis. Optimized chromatographic parameters (e.g., a very short GC column) are needed to achieve good sensitivity for deca-BDE. Unfortunately, such chromatographic parameters usually sacrifice separation efficiency for the other congeners. The authors present an optimized method for the analysis of BDEs that provides good separation for mono- to nona-BDE, as well as optimized sensitivity for deca-BDE.
http://www.bfr2004.com/Table%20of%20Contents.pdf

An Overview of Brominated Flame Retardants in the Environment
de Wit, C.A., Inst. of Applied Environmental Research (ITM), Stockholm Univ., Sweden.
Chemosphere, Vol 46 No 5, p 583-624, Feb 2002

The author reviews the current state of knowledge and recommends areas for further research to improve future monitoring and risk assessment efforts with regard to brominated flame retardant (BFR) chemicals, particularly polybrominated diphenyl ethers (PBDEs), tetrabromobisphenol A (TBBPA) and hexabromocyclododecane (HBCD).

Passive Air Sampling of PCBs, PBDEs, and Organochlorine Pesticides Across Europe
Jaward, F.M., N.J. Farrar, T. Harner, A.J. Sweetman, and K.C. Jones, Lancaster Univ., Lancaster, UK.
Environmental Science & Technology, Vol 38 No 1, p 34-41, 1 Jan 2004

Concurrently sampled ambient air data for a range of persistent organic pollutants at the continental scale were achieved using a passive air sampling system deploying polyurethane foam disks. The disks were prepared in one laboratory, sealed to prevent contamination, sent out by courier to volunteers participating in different countries, exposed for 6 weeks, collected, resealed, and returned to the laboratory for analysis. Samplers were deployed at remote/rural/urban locations in 22 European countries and analyzed for PCBs, a range of organochlorine pesticides (HCB, alpha-HCH, gamma-HCH, ppDDT, ppDDE), and PBDEs. Calculated air concentrations were in line with those obtained by conventional active air sampling techniques. The geographical pattern of all compounds reflected suspected regional emission patterns and highlighted localized hotspots. PCB and PBDE levels varied by over 2 orders of magnitude; the highest values were detected in areas of high usage and were linked to urbanized areas.

Passive Sampler Derived Air Concentrations of PBDEs Along an Urban Rural Transect: Spatial And Temporal Trends
Harner, T. and M. Shoeib (Environment Canada, Toronto, ON); M. Diamond and M. Ikonomou; G. Stern.
BFR 2004: Third International Workshop on Brominated Flame Retardants, 6-9 June 2004, University of Toronto, Toronto, Ontario, Canada, p 121-124, 2004

Passive air sampling campaigns can help to address questions regarding sources of persistent organic pollutants (POPs), their spatial pattern, and chemical signature. Passive samplers consisting of polyurethane foam (PUF) disks were deployed at seven sites along an urban-rural transect in Toronto to assess spatial and temporal trends of polybrominated diphenyl ethers. The levels and patterns of PBDEs along the transect will be compared to other classes of POPs to gain insight into their fate and transport. Results will also be compared to levels of PBDEs in indoor air, which is believed to be the key source to the outside.
http://www.bfr2004.com/Table%20of%20Contents.pdf

Passive Sampling Survey of Polybrominated Diphenyl Ether Flame Retardants in Indoor and Outdoor Air in Ottawa, Canada: Implications for Sources and Exposure
Wilford, B.H. (Environment Canada, Toronto, Ontario, Canada), T. Harner, J. Zhu, M. Shoeib, and K.C. Jones.
Environmental Science & Technology, Vol 38 No 20, p 5312-5318, 15 Oct 2004

In an investigation of general population exposure to polybrominated diphenyl ethers (PBDEs), air was sampled in 74 randomly selected homes in Ottawa, Canada, and at seven outdoor sites during the winter of 2002/2003, using polyurethane foam (PUF) disk passive air samplers. The passive sampling rate (2.5 cubic m/day) was determined in a pilot study employing active and passive samplers side-by-side at selected indoor locations. This paper describes the results.

Personal Air Sampling and Analysis of Polybrominated Diphenyl Ethers and Other Bromine Containing Compounds at an Electronic Recycling Facility in Sweden
Pettersson-Julander, A. (Orebro Univ., Orebro, Sweden), B. van Bavel, M. Engwall, and H. Westberg.
Journal of Environmental Monitoring, Vol 6 No 11, p 874-880, Nov 2004

To evaluate exposure to brominated flame retardants within an electronic recycling facility, personal air was monitored during a 2-year period. A total of 22 polybrominated diphenyl ethers (PBDEs) and 2 other bromine-containing organic compounds were analyzed and evaluated in 17 personal air samples. The most abundant congeners of PBDE were 209 and 183, indicating the use of the commercial octaBDE mixture, followed by PBDEs 99 and 47. The second most abundant peak in the chromatogram from all samples was identified as 1,2-bis(2,4,6-tribromophenyoxy)ethane (BTBPE) in the concentration range. The workers represented three different categories: dismantlers, other workers, and unexposed, with significant differences among the dismantlers and the unexposed categories for certain PBDE congeners. Air concentrations of PBDEs and BTBPE in the breathing zone were negatively correlated to the amount of recycled material. The exposure to brominated flame retardants varied within the electronic facility. Further research is needed to evaluate how the exposure differs with different products being dismantled as well as how the bioavailability of the different BFRs to humans is related to particle exposure. Commented upon in Journal of Environmental Monitoring, 2005 June;7(6):643; author reply p 644.

Photolytic Debromination of Decabromodiphenyl Ether (BDE 209)
Soderstrom, G., U. Sellstrom, C.A. de Wit, and M. Tysklind, Umea Univ., Umea, Sweden.
Environmental Science & Technology, Vol 38 No 1, p 127-132, 1 Jan 2004

The photolytic debromination of DecaBDE was investigated to study the formation of lower brominated diphenyl ethers. The time course of photolysis of DecaBDE was studied in toluene, on silica gel, sand, sediment, and soil using artificial sunlight and on the natural matrices (sediment, soil, sand) also using natural sunlight. DecaBDE was photolytically labile and formed debromination products in all matrices studied, forming nona- to tetraBDEs, as well as some PBDFs. The half-lives in toluene and on silica gel were less than 15 min, and half-lives on other matrices ranged between 40 and 200 h. No differences were seen in the debromination pattern of BDE congeners sequentially formed in the different matrices or under different light conditions, but the debromination rates were strongly dependent on the matrix, with longer half-lives on natural matrices than artificial ones.

Polybrominated Diphenyl Ether Congeners and Toxaphene in Selected Marine Standard Reference Materials
Kucklick, J.R. (National Inst. of Standards and Technology, Charleston, SC), K.J. Tuerk, S.S. Vander Pol, M.M. Schantz, and S.A. Wise.
Analytical and Bioanalytical Chemistry, Vol 378 No 5, p 1147-1151, Mar 2004

The National Institute of Standards and Technology has quantified polybrominated diphenyl ether (PBDE) congeners and toxaphene in several available Standard Reference Materials (SRMs) using methods of gas chromatography with electron impact mass spectrometry (GC-EI-MS) and GC negative chemical ionization (NCI) MS, respectively. This paper describes the determination of the values for PBDEs and toxaphene selected marine SRMs; while not certified, the results of these studies indicate that the SRMs will be suitable control materials for PBDE and toxaphene analyses.

Polybrominated Diphenyl Ether Residue Analysis Method for Fish Tissues from Remote, High Elevation Ecosystems
Ackerman, L.K., G.R. Wilson, and S.L. Simonich, Oregon State Univ., Corvallis.
BFR 2004: Third International Workshop on Brominated Flame Retardants, 6-9 June 2004, University of Toronto, Toronto, Ontario, Canada. p 341-344, 2004

This work discusses initial efforts to test whether polybrominated diphenyl ethers (PBDEs) are being atmospherically deposited in remote high elevation ecosystems, and if so whether or not they might pose a risk to these remote ecosystems. A 5-year, multi-agency program is underway in high elevation national park sites across the western continental United States and Alaska to sample fish, sediment, lake water, snow, and certain ecosystem characteristics from 15 isolated high altitude lake ecosystems to test for evidence of accumulation of airborne contaminants (including PBDEs) and any potential ecological threat. A new method has been developed for sensitive isotope dilution analysis of PBDEs in environmental extracts using less expensive, low-resolution GC-MS instruments, coupled with whole fish tissue sample preparation methods to achieve a single method for the analysis of 38 PBDE congeners and at least 40 other semivolatile organic compounds, including PCBs, PAHs, and pesticides. This paper describes the research plan, the methods developed to measure PBDEs in these ecosystems, and the initial results of such tests.
http://www.bfr2004.com/Table%20of%20Contents.pdf

Potential Chlorinated and Brominated Interferences on the Polybrominated Diphenyl Ether Determinations by Gas Chromatography-Mass Spectrometry
Eljarrat, E., A. de la Cal, and D. Barcelo, IIQAB, CSIC, Barcelona, Spain.
Journal of Chromatography A, Vol 1008 No 2, p 181-192, 8 Aug 2003

The analysis of polybrominated diphenyl ether (PBDE) congeners by GC-MS was studied in terms of potential interferences. The authors studied the presence of potential interferences in negative ion chemical ionization (NICI-MS) and electron ionization (EI-MS) instrument techniques, principally those corresponding to different chlorinated (PCBs, PCNs, etc.) and brominated compounds (PBBs, MeO-PBDEs, TBBPA, etc.). The two ionization modes are subject to different types of interferences. In general, EI-MS is affected by chlorinated interferences, especially PCBs. NICI-MS eliminated chlorinated interferences but presented different brominated interferences, well resolved with the EI-MS approach.

Predicting Gas Chromatographic Retention Times for the 209 Polybrominated Diphenyl Ether Congeners
Rayne, S. and M.G. Ikonomou, Univ. of Victoria, Victoria, BC.
Journal of Chromatography A, Vol 1016 No 2, p 235-248, 24 Oct 2003

A gas chromatographic relative retention time model was developed to predict retention times of the 209 individual polybrominated diphenyl ether (PBDE) congeners. Using the available 46 PBDE standards with mono- to deca-bromination, a multiple linear regression equation was implemented to predict the RRTs of the remaining 163 PBDE congeners. Molecular descriptors in the model included the number of ortho-, meta-, and para-bromine substituents, the semi-empirically calculated dipole moment, and the natural logarithm of molecular weight. A high level of predictability was obtained from the model.

Predicting Gas Chromatographic Retention Times of 209 Polybrominated Diphenyls (PBBs) [sic] for Different Temperature Programs
Zhao, H.X. (Chinese Acad. of Sciences, Dalian, P. R. China), Q. Zhang, X.Y. Xue, X.M. Liang, and A. Kettrup.
Analytical & Bioanalytical Chemistry, Vol 382 No 5, p 1304-1310, July 2005

A method has been developed to predict the retention times of the 209 individual polybrominated diphenyl congeners for different temperature programs. The retention equations of five PBBs in gas chromatography (GC) were used to evaluate the properties of the regression coefficients A and B. The quantitative relationships between the A and B values of PCBs and those of PBBs were found. The A, B values of any PBB can be predicted by using the A, B values of the PCB according to these relationships. Using these predicted A and B values, the retention times of all PBBs can be predicted.

Prediction of Vapour Pressures for Halogenated Diphenyl Ether Congeners from Molecular Descriptors
Oberg, T.G., T. Oberg Konsult AB, Lyckeby, Sweden.
Environmental Science and Pollution Research International, Vol 9 No 6, p 405-411, 2002

This paper describes an undertaking to characterize halogenated diphenyl ethers using computationally derived descriptors and develop calibration models for the vapor pressure from published experimental data. All congeners of polychlorinated diphenyl ethers (PCDEs) and polybrominated diphenyl ethers (PBDEs) were characterized by 795 molecular descriptors, and two principal components could account for about two thirds of the variance within each group. Bilinear calibration models were developed that could explain 99.4% of the variance in the external validation test sets. Vapor pressures were subsequently predicted for all congeners that were adequately described by these calibration models. The type and number of halogen atoms in the molecule were the main factors influencing the vapor pressures of halogen substituted diphenyl ethers, but variation in substitution pattern was also a significant factor. The work showed that molecular descriptor patterns of halogenated aromatic compounds such as diphenyl ethers can be described and interpreted using principal component analysis. The major sources of variation in the descriptor spaces for PCDEs and PBDEs are the same as those contributing to the differences in vapor pressure, similar to what has previously been reported for PCBs.

Pressurized Hot Water Extraction Coupled Online with Liquid Chromatography-Gas Chromatography for the Determination of Brominated Flame Retardants in Sediment Samples
Kuosmanen, K., T. Hyotylainen, K. Hartonen, and M.-L. Riekkola, Univ. of Helsinki, Finland.
Journal of Chromatography A, Vol 943 No 1, p 113-122, 11 Jan 2002

Pressurized hot water extraction (PHWE) was coupled online with liquid chromatography-gas chromatography (LC-GC) to determine brominated flame retardants in sediment samples. After extraction with pressurized hot water, the analytes were adsorbed in a solid-phase trap, then the trap was dried with nitrogen, and the analytes were eluted to the LC column, where the extract was cleaned, concentrated, and fractionated before transfer to the GC system. The fraction containing the brominated flame retardants was transferred to the GC system via an on-column interface.

Probing New Approaches Using Atmospheric Pressure Photo Ionization for the Analysis of Brominated Flame Retardants and Their Related Degradation Products by Liquid Chromatography-Mass Spectrometry
Debrauwer, L. (UMR 1089 Xenobiotiques, Toulouse, France), A. Riu, M. Jouahri, E. Rathahao, I. Jouanin, J.P. Antignac, R. Cariou, B. Le Bize, and D. Zalko.
Journal of Chromatography A, Vol 1082 No 1, p 98-109, 29 July 2005

Atmospheric pressure photo-ionization has been evaluated for the analysis of brominated flame retardants and their related degradation products by LC-MS. Degradation mixtures obtained from the photochemical degradation of tetrabromobisphenol A and decabromodiphenylether were used as model systems for the assessment of the developed methodology. The investigators found that the application of LC-MS by means of atmospheric pressure photo-ionization to the analysis of aromatic brominated flame retardants and their degradation products proved to be particularly useful for the characterization and structural identification of some compounds that are not amenable to GC-MS.

Qualitative Evaluation of Thermal Desorption-Programmable Temperature Vaporization-Comprehensive Two-Dimensional Gas Chromatography-Time-of-Flight Mass Spectrometry for the Analysis of Selected Halogenated Contaminants
Focant, J.F., A. Sjodin, and D.G. Patterson Jr., Centers for Disease Control and Prevention, Atlanta, GA.
Journal of Chromatography A, Vol 1019 No 1-2, p 143-156, 26 Nov 2003

Scientists have optimized the separation of 38 toxic and predominant polychlorinated biphenyl (PCB) congeners, 11 persistent halogenated pesticides, 1 brominated biphenyl (BB), and 8 polybrominated diphenyl ethers (PBDEs) using comprehensive 2-D gas chromatography coupled to time-of-flight mass spectrometry (GC x GC-TOFMS). A thermal desorption-programmable temperature vaporization (TD-PTV) step was used for the injection. Of the 58 compounds investigated, only one pair of PCBs was not resolved. All other analytes were either baseline separated into the chromatographic plane or were virtually separated using the deconvolution capability of the TOFMS.

Quantitative Analysis of 39 Polybrominated Diphenyl Ethers by Isotope Dilution GC/Low-Resolution MS
Ackerman, L.K., G.R. Wilson, and S.L. Simonich, Oregon State Univ., Corvallis.
Analytical Chemistry, Vol 77 No 7, p 1979-1987, 1 Apr 2005

In the development of a GC/low-resolution MS method for the quantitative isotope dilution analysis of 39 mono- to heptabrominated diphenyl ethers, the effects of two different ionization sources, electron impact (EI) and electron capture negative ionization (ECNI), were investigated, along with the effects of their parameters on production of high-mass fragment ions specific to PBDEs. Electron energy had the largest impact on PBDE high-mass fragment ion abundance for both the ECNI and EI sources. By monitoring high-mass fragment ions of PBDEs under optimized ECNI source conditions, quantitative isotope dilution analysis of 39 PBDEs was conducted using nine (13)C(12) labeled PBDEs on a low-resolution MS with low picogram to femtogram instrument detection limits.

Quantitative Structure-Property Relationships for Vapor Pressures of Polybrominated Diphenyl Ethers
Chen, J.W. (Dalian Univ. of Technology, Dalian, People's Republic of China), P. Yang, S. Chen, X. Quan, X. Yuan, K.W. Schramm, and A. Kettrup.
SAR & QSAR in Environmental Research, Vol 14 No 2, p 97-111, Apr 2003

The authors developed quantitative structure/property relationship models for subcooled liquid vapor pressures (LVP) of polybrominated diphenyl ether (PBDE) congeners by the use of partial least squares regression based on quantum chemical descriptors. The Q2cum value of the optimal model obtained is as high as 0.993, indicating good predictive ability and model robustness. Though disagreements were observed between the predicted log LVP values and the log LVP values of validation set, the model can nonetheless be used for estimating LVP of other PBDE congeners.

Radiocarbon Content of Synthetic and Natural Semi-Volatile Halogenated Organic Compounds
Reddy, C.M., L. Xu, T.I. Eglinton, J.P. Boon, and D.J. Faulkner, Woods Hole Oceanographic Inst., MA.
Environmental Pollution, Vol 120 No 2, p 163-168, 2002

Some halogenated organic compounds, such as PCBs, PCDDs, and PBDEs, have been suggested to have natural sources, but separating these compounds from their commercially synthesized counterparts is difficult. Most synthetic compounds are manufactured from petrochemicals (which are (14)C-free), and natural compounds should have "modern" or "contemporary" C-14 levels. Researchers undertook a baseline study to measure, for the first time, the C-14 abundance in commercial PCB and PBDE mixtures, various organochlorine pesticides, and one natural product, 2-(3',5'-dibromo-2'-methoxyphenoxy)-3,5-dibromoanisole, which is similar in structure to a PBDE. All of the synthetic compounds were (14)C-free except for the pesticide toxaphene, which had a modern C-14 abundance, as did the brominated natural compound. These results suggest that measuring the C-14 content of halogenated organic compounds may be useful in establishing whether organic compounds encountered in the environment have natural or synthetic origins (or both), provided that any synthetic counterparts derive from petrochemical feedstock.

Rapid Identification of RoHS-relevant Flame Retardants from Polymer Housings by Ultrasonic Extraction and RP-HPLC/UV
Pohlein, M., A.S. Llopis, M. Wolf, and R. van Eldik, Univ. of Erlangen-Nuremberg, Erlangen, Germany.
Journal of Chromatography A, Vol 1066 Nos 1-2, p 111-117, 25 Feb 2005

The Restriction of Hazardous Substances (RoHS) Directive is a complex piece of environmental legislation that encompasses huge volumes of equipment across 25 European Union member countries. RoHS will affect each and every electronics manufacturer directly or indirectly, regardless of geographical location or the equipment they produce. A rapid method has been developed for the extraction and identification of RoHS-relevant organic flame retardants in polymer material. Extraction is carried out using ultrasonic supported solvent extraction (USSE) and isopropanol. HPLC separation is achieved using a reversed-phase phenylhexyl-modified column and methanol, containing 2-aminoethanol-buffered alkaline water. The analytes are identified by scanning UV detection and comparison with a spectra reference library. The method was used to extract and identify polymer additives in TV and PC monitor housings, with an overall runtime of less than 10 minutes for extraction and chromatographic analysis. The limits of detection comply with the recommendations set by the German draft law.

Rapid, Sensitive Detection of Polybrominated Diphenyl Ethers by Gas Chromatography Coupled to ICP-MS
Wilbur, Steven M. and Emmett Soffey, Agilent Technologies Inc., Bellevue WA.
BFR 2004: Third International Workshop on Brominated Flame Retardants, 6-9 June 2004, University of Toronto, Toronto, Ontario, Canada. p 371-374, 2004

The authors examine suitability of GC-ICP-MS for the detection and quantification of PBDEs in standards and mixtures containing PCBs. Figures of merit include detection limits and response factors for various PBDE congeners, linear range, and chromatographic conditions and retention times.
http://www.bfr2004.com/Table%20of%20Contents.pdf

Recommendations for Monitoring of Polybrominated Diphenyl Ethers in the Canadian Environment
Alaee, M., National Water Research Inst., Burlington, ON, Canada.
Environmental Monitoring and Assessment, Vol 88 Nos 1-3, p 327-341, Oct-Nov 2003

Recent data on temporal trends strongly suggest that the concentrations of polybrominated diphenyl ethers (PBDEs) are on the rise in the Canadian environment. A key challenge currently facing Canada and other countries concerns how best to measure these chemicals in different matrices, such as air, surface waters, suspended sediments, soil, sediment, fish, marine mammals, and bird eggs. The author reviews several analytical methods cited in the scientific literature for determining PBDE concentrations in different abiotic and biological matrices. Critical criteria required for accurate determination of PBDEs in complex environmental matrices are discussed, including instrument sensitivity, reliability, potential interferences, and the need for specialized instrumentation for the determination of compounds up to 975 Daltons. While the review identifies no single analytical method that meets all the criteria, GC/HRMS-based methods amenable to isotope dilution techniques warrant further refinement, and may represent the best tools for future environmental monitoring programs.

Reconstructing Source Polybrominated Diphenyl Ether Congener Patterns from Semipermeable Membrane Devices in the Fraser River, British Columbia, Canada: Comparison to Commercial Mixtures
Rayne, S. and M.G. Ikonomou, Univ. of Victoria, British Columbia, Canada.
Environmental Toxicology and Chemistry, Vol 21 No 11, p 2292-2300, Nov 2002

Semipermeable membrane devices (SPMDs) were placed in the Fraser River near Vancouver, British Columbia, Canada, in late summer of 1996, and SPMD samples were subsequently analyzed for a suite of 36 polybrominated diphenyl ether (PBDE) congeners, plus all homologue groups from mono- through hexa-brominated. Observed congener patterns differed significantly from that of the commercial penta- and octa-BDE mixtures. A reconstruction approach was developed based on an aquatic transport model. It utilized published octanol-water partition coefficients, calculated SPMD uptake rates, and predicted water concentrations by using the EcoFate multimedia mass balance aquatic simulation model for the 13 major PBDE congeners. Composite technical mixtures were created by combining commercial penta-BDE mixtures with commercial octa-BDE mixtures in their relative 2000 North American production volumes. The reconstructed SPMD patterns more closely approximated the composite technical mixtures and suggest that PBDEs in such an industrial region arise primarily from penta- and octa-BDE source mixtures.

Relatively Rapid Detection of Polybrominated Diphenyl Ethers Using Element Selective GC Detection
Rice, Gary, Tom Chen, and Kara Paulus, College of William and Mary, Williamsburg, VA.
PITTCON 2002, 17-22 March, Pittsburgh, Pennsylvania. Abstract 1636P.

Polybrominated diphenyl ethers (PBDEs) are widely used as fire retardants in a variety of polymeric materials. Degradation of materials such as polyurethane foams used in the furniture industry has led to a rapid increase in the detection of PBDEs from the analysis of sediments, recycled sewage sludge, and fish tissues. Accurate quantitation using conventional GC detectors such as electron capture or coulometric detectors can be difficult due to the co-elution of polychlorinated biphenyls (PCBs) that are persistently present in environmental sampling. This work describes the utilization of an element selective helium discharge detector (HDD) for the detection and determination of PBDEs in the presence of PCBs and other species that are normally present in difficult sample matrices such as fish tissues, sediments, and recycled sewage sludges. Relatively few PBDE congeners are typically observed in environmental samples, thus significantly shorter GC columns (15m) with much thinner liquid phases (0.1 um) can be used. The 209-PBDE congeners can be eluted in less than twenty minutes with complete resolution of all other PBDE congeners in the mixtures. Relatively good baseline stability is maintained throughout the chromatograms even at the high temperatures required to elute the highly brominated congeners. This is in contrast to analysis times of over two hours that may be necessary using conventional detectors in order to physically separate the specific PCB and PBDE compounds. Quantification of the PBDEs can readily be accomplished using a single internal standard such as hexabromobenzene since the derived signal is only dependent on the amount of halogen present and not structure (extensive response factor calibrations are typically required for conventional halogen selective detectors). Peak to signal ratios obtained from the most abundant 47-PBDE congener via separations using conventional detectors can also be used to generate a response profile for the HDD as well. Absolute detection limits on the order of 50-100 ppb per congener are achievable. Preliminary results from the analysis of fish, sediments, and recycled sludge materials indicates that conventional GC detection methods result in some BDEs not being detected at all (due to overlap with PCBs), resulting in values being low by as much as 300% from values obtained using bromine selective detection.

Retention-Time Database of 126 Polybrominated Diphenyl Ether Congeners and Two Bromkal Technical Mixtures on Seven Capillary Gas Chromatographic Columns
Korytar, P., A. Covaci, J. de Boer, A. Gelbin, and U.A. Brinkman, Netherlands Inst. for Fisheries Research, Wageningen UR, The Netherlands.
Journal of Chromatography A, Vol 1065 No 2, p 239-249, 18 Feb 2005

The elution order of 126 polybrominated diphenyl ethers (PBDE) was determined for seven different gas chromatographic (GC) stationary phases. The resulting database facilitates selection of the most suitable GC columns for developing a quantitative, congener-specific PBDE analysis and the testing of retention prediction algorithms based on structure relationships of GC phases and congener substitution patterns. The researchers also investigated co-elutions of the principal PBDE congeners with other PBDEs and/or with other brominated flame retardants, as well as the composition of two Bromkal mixtures (70-5DE and 79-8DE).

Sample Preparation and Analysis of Brominated Flame Retardants (BFR) in Environmental Samples
Enge, Ellen Katrin, Martin Schlabach, and Espen Mariussen, Norwegian Inst. for Air Research.
Poster presentation 13, 2004

The BFRs have very different structures and characteristics. The most commonly used BFRs are the brominated diphenylethers, hexabromocyclododecane, and tetrabromobisphenol-A. This poster presents a method for separation and identification of several BFRs in different types of samples (biological samples, soils, sediments, sewage, and water) that is suitable for all levels of contamination and has proven useful for locating sources of contamination. The findings have shown various accumulative properties for different isomers.
http://www.nilu.no/data/inc/leverfil.cfm?id=8007&type=6

Screening of Halogenated Aromatic Compounds in Some Raw Material Lots for an Aluminium Recycling Plant
Sinkkonen, S., J. Paasivirta, M. Lahtipera, and A. Vattulainen, Univ. of Jyvaskyla, Jyvaskyla, Finland.
Environment International, Vol 30 No 3, p 363-366, May 2004

Four samples of scrap raw materials for an aluminium recycling plant were screened for the occurrence of persistent halogenated aromatic compounds. The samples contained waste from handling of electric and electronic plastics, filter dust from electronic crusher, cyclone dust from electronic crusher, and light fluff from a car shredder. Polybrominated diphenyl ethers (PBDE) were identified in all samples, primarily decabromo- and pentabromodiphenyl ethers. Concentrations of other halogenated organics (e.g., PCBs, polychlorinated naphthalenes, and nona- to undecachlorinated terphenyls) in some of the scrap samples were remarkably high.

Selective Extraction of Trace Levels of Polychlorinated and Polybrominated Contaminants by Supercritical Fluid-Solid-Phase Microextraction and Determination by Gas Chromatography/Mass Spectrometry: Application to Aquaculture Fish Feed and Cultured Marine Species
Rodil, R., A.M. Carro, R.A. Lorenzo, and R. Cela Torrijos.
Analytical Chemistry, Vol 77 No 7, p 2259-2265, 1 Apr 2005

A new analytical approach based on simultaneous supercritical fluid extraction-sample cleanup, followed by solid-phase microextraction-gas chromatography/mass spectrometry (SFE-SPME-GC/MS/MS) has been developed as a tool for the determination of 15 organohalogenated compounds in aquaculture feed at very low levels. The procedure provides an excellent linearity, detection, and quantification limits (below 10 pg/g) for most of the analytes investigated. The procedure was applied to the analysis of aquaculture feed and cultured marine species and tested for accuracy against IAEA 406 reference material.

Semiautomated High-Throughput Extraction and Cleanup Method for the Measurement of Polybrominated Diphenyl Ethers and Polybrominated and Polychlorinated Biphenyls in Breast Milk
Sjodin, A., E.E. McGahee III, J.F. Focant, R.S. Jones, C.R. Lapeza, Y. Zhang, D.G. Patterson Jr., Centers for Disease Control and Prevention, Atlanta, GA.
Analytical Chemistry, Vol 76 No 15, p 4508-14, 1 Aug 2004

A semiautomated extraction and cleanup method has been developed to measure eight polybrominated diphenyl ethers (PBDEs), 2,2',4,4',5,5'-hexabromobiphenyl (BB-153), and 2,2',4,4',5,5'-hexachlorobiphenyl (CB-153). The method employs solid-phase dispersion on diatomaceous earth in a solid-phase extraction cartridge followed by automated addition of internal standards ((13)C-labeled). Extraction is performed using an automated modular solid-phase extraction system. The extraction procedure includes drying the sample on diatomaceous earth by pressurized nitrogen and eluting target analytes and lipids with dichloromethane. Lipid content is determined gravimetrically. Final analytical determination of target analytes was performed by gas chromatography-isotope dilution high-resolution mass spectrometry.

Study of Kovats Retention Indices of Polybrominated Diphenyl Ethers
Kozloski, Richard P., Anke Gelbin, and Russ Cooper, AccuStandard, Inc., New Haven, CT.
BFR 2004: Third International Workshop on Brominated Flame Retardants, 6-9 June 2004, University of Toronto, Toronto, Ontario, Canada. p 359-362, 2004

This paper describes an effort to chromatograph and measure the retention time of over 130 different polybrominated diphenyl ethers (PBDEs) congeners to obtain their Kovats retention indices and thereby predict absolute and relative retention data for those PBDE congeners not yet commercially available to the scientific community.
http://www.bfr2004.com/Table%20of%20Contents.pdf

A Study of the Analysis of Polybrominated Diphenyl Ether Flame Retardants by GC-MSMS
Worrall, K. and A. Newton (Waters Corporation, Manchester, UK); B. Van Bavel, A. Pettersson, and G. Lindstrom (Orebro Univ., Örebro, Sweden); E. Reiner, K. MacPherson, and T. Kolic (Ontario Ministry of Environment, Toronto, ON, Canada); N. Ordsmith, S. Catterall, and K. Hall (Hall Analytical, Manchester, UK).
BFR 2004: Third International Workshop on Brominated Flame Retardants, 6-9 June 2004, University of Toronto, Toronto, Ontario, Canada. p 317-320, 2004

Current analytical techniques for polybrominated diphenyl ether (PBDE) flame retardants analysis generally involve the use of HRGC/HRMS, a costly technique requiring highly trained operators. Methods have recently been published using single quadrupole GC-MS, or GC-MS/MS (ion trap). This paper describes an investigation of the suitability of a GC-triple-quadrupole instrument for the analysis of PBDEs, monitoring compound-specific fragmentation patterns with the use of multiple reaction monitoring acquisitions.
http://www.bfr2004.com/Table%20of%20Contents.pdf

Synthesis of Fluorinated Polybrominated Diphenylethers (F-PBDEs) as Reference Standards for Environmental Analysis
Liu, H., A. Skalvoll, G.S. Reijerink, G. Luthe, and J.E. Johansen, Chiron AS, Trondheim, Norway.
BFR 2004: Third International Workshop on Brominated Flame Retardants, 6-9 June 2004, University of Toronto, Toronto, Ontario, Canada. p 321-324, 2004

Efficient PBDE analysis has been hampered by a lack of practical and cost-efficient standards. Chiron AS is working to develop efficient methods of large-scale PBDE synthesis for toxicological studies, as well as to search for better and more efficient internal standards for PBDE analysis. PBDE analysis is complicated due to the large number of bromine isomers, in particular for the higher brominated members. Previous work showed that mono-fluorination of PAH leads to small but detectable differences, which is extremely useful in analytical contexts. This paper describes an investigation of the mono- and di-fluoroPBDEs (F-PBDEs) as possible internal standards as an alternative to more traditional and costly alternatives, such as C-13 labeling.
http://www.bfr2004.com/Table%20of%20Contents.pdf

Toxicological Profile for Polybrominated Biphenyls and Polybrominated Diphenyl Ethers (PBBs and PBDEs), Chapter 9: Analytical Methods
Agency for Toxic Substances and Disease Registry, p 467-478, Sep 2004

Discusses analytical methods for biological materials and environmental samples.
http://www.atsdr.cdc.gov/toxprofiles/tp68.html

Tracking Polybrominated Diphenyl Ether Releases in a Wastewater Treatment Plant Effluent, Palo Alto, California
North, K.D., City of Palo Alto, Environmental Compliance Division, CA.
Environmental Science & Technology, Vol 38 No 17, p 4484-4488, 1 Sep 2004

Wastewater treatment plants are one source of polybrominated diphenyl ethers (PBDEs) to the environment through discharge of treated effluent and land application of sewage sludge. Effluent and sludge collected and analyzed for PBDEs at a wastewater treatment plant in California showed that the total concentration of PBDEs ranged from 4 to 29,000 pg/L in discharged effluent and from 61 to 1440 ug/kg dry wt in the sludge. The congeners with the highest abundance in sludge were BDE-47, BDE-99, and BDE-209, while in treated effluent BDE-47 and BDE-99 were the most abundant. The sum of the major congeners in the penta-formulation (BDE-47, 99, 100, 153, and 154) comprises 88% of the total PBDEs in the effluent, while BDE-209 is only 6%. The loading analysis indicates that the total PBDE concentration loaded to the San Francisco Estuary through effluent discharge from this wastewater treatment plant is 2 lb/year.

Two Approaches for Extraction and Analysis of Brominated Flame Retardants (BFR) and Their Degradation Products in Recycled Polymers and BFR Containing Water
Gallet, G., G. Perez, and S. Karlsson.
BFR 2001: The Second International Workshop on Brominated Flame Retardants, Stockholm, Sweden. Book of Abstracts, p 67-69, 2001

The authors were able to develop a fast method (microwave-assisted extraction combined with liquid chromatography) for identifying and quantifying TBBPA, oligomeric epoxy with TBBPA, DBDPE, DBB, and brominated trimethylphenyl Indan in recycled ABS and PS. In a second step the influence of water and pH on the degradation products of TBBPA, DBB, and DBDPE was followed by solid phase microextraction/gas chromatography-mass spectrometry. TBBPA was the most sensitive flame retardant toward aging. Five degradation products, including Bromophenol, 2,4 dibromophenol and 2,4,6 tribromophenol, were successfully identified.
http://bfr2004.com/BFR2001_del2.pdf

Vapor Pressures, Aqueous Solubilities, and Henry's Law Constants of Some Brominated Flame Retardants
Tittlemier, S.A., T. Halldorson, G.A. Stern, and G.T. Tomy.
Environmental Toxicology and Chemistry, Vol 21 No 9, p 1804-1810, 2002

The subcooled liquid vapor pressures and aqueous solubilities were determined and Henry's law constants were estimated for a number of brominated flame retardants (BFRs) at 25 degrees C. A simple four-compartment equilibrium distribution model suggested that the majority of BFRs being released into the environment would reside in soil and sediment and have localized distributions. The model also suggested that lower brominated congeners tend to be somewhat more mobile. Degradative debromination reactions that yield these congeners would mobilize them environmentally and ultimately affect the fate and distribution of BFRs.

Vapor Pressures of Six Brominated Diphenyl Ether Congeners
Tittlemier, S.A. and G.T. Tomy, Carleton Univ., Ottawa, ON, Canada.
Environmental Toxicology and Chemistry, Vol 20 No 1, p 146-148, Jan 2001

Subcooled liquid vapor pressures (PLo) of six polybrominated diphenyl ether (PBDE) congeners containing three to seven bromine atoms were determined using the gas chromatograph retention time technique. The first such data for individual PBDE congeners shows that PLo would vary four orders of magnitude over environmentally relevant temperatures.

Vapor Pressures of the Polybrominated Diphenyl Ethers
Wong, A. (Univ. of Toronto at Scarborough), Y.D. Lei, M. Alaee, and F. Wania.
Journal of Chemical Engineering Data, Vol 46 No 2, p 239-242, 2001

The supercooled liquid vapor pressures of 23 polybrominated diphenyl ether congeners were determined as a function of temperature with a gas chromatographic retention time technique. Using a Junge-Pankow approach, the fraction of chemical adsorbed to aerosols as a function of temperature was estimated for three congeners and used to speculate on the likely environmental behavior of these chemicals.
http://publish.uwo.ca/~awong37/pubs/jced2001.pdf

Variability of Concentrations of Polybrominated Diphenyl Ethers and Polychlorinated Biphenyls in Air: Implications for Monitoring, Modeling and Control
Gouin, T., T. Harner, G.L. Daly, F. Wania, D. Mackay, and K.C. Jones.
Atmospheric Environment, Vol 39 No 1, p 151-166, Jan 2005

Organic compounds with high octanol-air partition coefficients, such as polybrominated diphenyl ethers (PBDEs) and polychlorinated biphenyls (PCBs), exhibit seasonally variable air concentrations, especially during early spring, shortly after snow melt and before bud-burst when levels are elevated. This variability can complicate the interpretation of monitoring data designed to assess year-to-year changes. The authors suggest that relatively simple dynamic multimedia mass balance models can assist interpretation by factoring out variability attributable to temperature and other seasonal effects, as well as identifying likely contaminant sources. They illustrate this approach with a study of high-volume air samples collected from January to June, 2002 at a rural location in southern Ontario. The data were interpreted using simulation results from a fate model, including a seasonally variable forest canopy and snow pack, suggesting that the primary source is urban and that the "spring pulse" is the result of several interacting factors. The contaminants are believed to be efficiently deposited in winter, accumulate in the snow pack, and released to terrestrial surfaces upon snow melt in spring. Warmer temperatures cause volatilization and a rise in air concentrations until uptake in emerging foliage leads to a decline in late spring. Implications for monitoring are discussed.

1,2,3-TRICHLOROPROPANE (TCP)

1,2,3-Trichloropropane: Notification Level & Monitoring Results
California Department of Health Services, Aug 2005

The California DHS drinking water notification level for 1,2,3-TCP, first established in 1999, is 0.005 micrograms per liter. In 2001, to obtain information about the presence of 1,2,3-TCP in drinking water sources, DHS adopted a regulation that included it as an unregulated contaminant for which

monitoring is required. For this monitoring, DHS developed protocols for analytical methods for 1,2,3-TCP at levels comparable to the notification level of 0.005 ug/L.
http://www.dhs.ca.gov/ps/ddwem/chemicals/123tcp/notificationlevel.htm

Analysis of Volatile Organic Compounds, Using the Purge and Trap Injector Coupled to a Gas Chromatograph/Ion-Trap Mass Spectrometer: Review of the Results in Dutch Surface Water of the Rhine, Meuse, Northern Delta Area and Westerscheldt, over the Period 1992-1997
Miermans, C.J.H., L.E. van der Velde, and P.C.M. Frintrop.
Chemosphere, Vol 40 No 1, p 39-48, 2000

Liquid-liquid extraction and isolation with resins give poor recoveries for volatile organic compounds (VOCs). The authors developed a method to analyze VOCs with purge and trap injection (PTI) coupled to a chromatograph/ion trap mass spectrometer. Volatile compounds are purged from the sample by carrier gas flow and transported through a condenser to a cooled trap. The bulk of liquid matrix is condensed in the condenser, while volatile compounds are left unaffected. The compounds of interest (including 1,2,3-trichloropropane) are trapped at a low temperature by liquid nitrogen in the cooled trap of fused silica. Injection takes place by flash heating of the trap. The detection limits of the volatile compounds are in the range of 0.001-0.04 ug/L, in full spectrum mode. This paper reviews the results in Dutch surface water of the Rhine, Meuse, Northern Delta Area, and Westerscheldt over the period 1992-1997. This method is very useful for monitoring compounds over such a period of time.

Chemical Sampling Information: 1,2,3-Trichloropropane
U.S. Department of Labor, Occupational Safety & Health Administration, May 2000

This page identifies the OSHA primary and secondary sampling/analytical methods for TCP.
http://www.osha.gov/dts/chemicalsampling/data/CH_273200.html

Concise International Chemical Assessment Document 56: 1,2,3-Trichloropropane: 3. Analytical Methods
World Health Organization, Geneva, 2003

Analysis of 1,2,3-trichloropropane in air usually involves sorption of the chlorinated alkane onto a solid matrix, followed by thermal or solvent desorption prior to gas chromatography/flame ionization detection (GC/FID), gas chromatography/photoionization detection/electrolytic conductivity detection (GC/PID/ELCD), or gas chromatography/mass spectrometry (GC/MS). Yamamoto et al. (1998), using GC with ELCD, reported a detection limit of about 2 mg/cubic m. Peng & Batterman (2000) as well as Bonvalot et al. (2000), employing GC/MS, reported a method detection limit of 0.04 ug/cubic m. Pankow et al. (1998), also using GC/MS, reported a detection limit of about 30 ug/cubic m. Both Brock & Carroll (1985) and Bouhamra et al. (1997) analyzed air samples by similar techniques, but without specifying detection limits. For water, purge and trap techniques followed by gas chromatography/electron capture detection (GC/ECD) or GC/MS are generally employed. Bauer (1981a) reported a detection limit of 0.07 ug/L, Zebarth et al. (1998) determined a limit of quantification of 0.1 ug/L, and Miermans et al. (2000) obtained a limit of detection of 0.0004 ug/L. Yoshikawa et al. (1998) employed a similar system, although detection limits were not specified. Sediment was analyzed by GC/ECD after nitrogen blow-out, adsorption, and solvent elution, with a detection limit of 1 ug/kg (LWA, 1989). For the detection of 1,2,3-trichloropropane in sediments, Kawata et al. (1997) used GC/MS for head space analysis after thermal equilibration, obtaining a detection limit of 1 ng/g, while Zebarth et al. (1998) employed head space GC/ELCD, with a limit of detection of 0.2 ug/kg. Bauer (1981a) determined the presence of 1,2,3-trichloropropane in human tissue samples after blow-out and sorption techniques by GC/ECD, with a detection limit of 13 ug/kg.

Continuous Determination of Volatile Organic Compounds in the Atmosphere by an Automated Gas Chromatographic System
Yamamoto, N., H. Okayasu, T. Hiraiwa, S. Murayama, T. Maeda, M. Morita, and K. Suzuki.
Journal of Chromatography A, Vol 819 Nos 1-2, p 177-186, 1998

A fully automated gas chromatographic system has been developed for quick and continuous determination of trace levels of 54 selected volatile organic compounds (VOCs) in the atmosphere. The method is based on the preconcentration of an air sample using a multibed collection tube (Carbotrap B, Carboxen 1000, Carboxen 1001) at ambient temperature by thermal desorption, and analysis of the VOCs using a capillary gas chromatograph equipped with a photoionization detector and an electrolytic conductivity detector connected in series. The detection limit of 0.01 ppb for each compound (including 1,2,3-trichloropropane) was obtained using a 1-liter air sample.

Determination of 1,2,3-Trichloropropane in Drinking Water by Continuous Liquid-Liquid Extraction and Gas Chromatography/Mass Spectrometry
Okamoto, H.S., J. Dhoot, and S.K. Perera (eds.).
California Department of Health Services, 8 pp, Feb 2002

This method can be used to determine 1,2,3-trichloropropane (TCP), CAS No. 96-18-4, in water at concentrations below the quantifiable ranges of U.S. EPA methods 504.1, 551.1, and 524.2. A 1-liter sample is extracted for approximately 16 hours (overnight) with methylene chloride using a continuous liquid- liquid extractor. After extraction the methylene chloride extract is isolated, dried, then concentrated to 1 ml and analyzed by GC/MS. TCP is identified by matching the retention time and mass fragment ions from the sample with those of the reference standard. Quantitation is performed by the isotopic dilution procedure. 1,2,3-trichloropropane-D5 (TCP-D5) is used as the internal standard, which is added to the samples and standards, such that the final concentrations in the sample extracts and standards are the same. The California Drinking Water Action Level for 1,2,3-TCP is at
http://www.dhs.cahwnet.gov/ps/ddwem/chemicals/123tcp/actionlevel.htm
http://www.dhs.ca.gov/ps/ddwem/chemicals/unregulated/TCPbyLLE-GCMS.pdf

Determination of a Wide Range of Volatile Organic Compounds in Ambient Air Using Multisorbent Adsorption/Thermal Desorption and Gas Chromatography/Mass Spectrometry
Pankow, J.F., W. Luo, L.M. Isabelle, D.A. Bender, and R.J. Baker.
Analytical Chemistry, Vol 70 No 24, p 5213-5221, 1998

Adsorption/thermal desorption with multisorbent air-sampling cartridges was developed for the determination of 87 method analytes, including halogenated alkanes, halogenated alkenes, ethers, alcohols, nitriles, esters, ketones, aromatics, a disulfide, and a furan. The volatilities of the compounds ranged from that of dichlorofluoromethane to that of 1,2,3-trichlorobenzene. The eight most volatile compounds were determined using a 1.5-L air sample and a sample cartridge containing 50 mg of Carbotrap B and 280 mg of Carboxen 1000; the remaining 79 compounds were determined using a 5-L air sample and a cartridge containing 180 mg of Carbotrap B and 70 mg of Carboxen 1000. Analysis and detection were by gas chromatography/mass spectrometry. The minimum detectable level (MDL) concentration values ranged from 0.01 parts per billion by volume (ppbv) for chlorobenzene to 0.4 ppbv for bromomethane; most of the MDL values were in the range 0.02 to 0.06 ppbv. A detection limit of about 30 ug/cubic m was reported for 1,2,3-trichloropropane. No breakthrough was detected with the prescribed sample volumes. Analyte stability on the cartridges was very good. Excellent recoveries were obtained with independent check standards. This paper describes the method and results of its application to ambient atmospheric sampling conducted in New Jersey from April to December 1997.

Groundwater Contamination by Chlorinated Hydrocarbon Impurities Present in Soil Fumigant Formulations
Zebarth, B.J., S.Y. Szeto, B. Hii, H. Liebscher, and G. Grove.
Water Quality Research Journal of Canada, Vol 33 No 1, p 31-50, 1998

After the groundwater of the Abbotsford aquifer was found to be contaminated with 1,2-dichloropropane (1,2-DCP), investigators looked for other chlorinated hydrocarbon compounds present in fumigant formulations containing 1,2-DCP. Widespread contamination of 1,2,2-trichloropropane (1,2,2-TCP) was measured consistent with a non-point source. 1,2,2-TCP concentration generally decreased with depth, suggesting a surface source. The investigators quantified localized contamination by 1,2,3-trichloropropane, 2,3-dichloropropene and 1,3-dichloropropane and found it to be associated with higher concentrations of 1,2-DCP, suggesting contamination by these compounds may have been from the same fumigant sources. The lack of a decrease in the concentration of most of these compounds over time suggests that the measured contamination will persist for some time.

Method 504.1: 1,2-Dibromoethane (EDB), 1,2-Dibromo-3-Chloro-Propane (DBCP), and 1,2,3-Trichloropropane (123TCP) in Water by Microextraction and Gas Chromatography, Revision 1.1
Munch, J.W. (ed.).
U.S. EPA, National Exposure Research Laboratory, Cincinnati, OH. 20 pp, 1995

Thirty-five ml of sample are extracted with 2 ml of hexane. Two µl of the extract are then injected into a gas chromatograph equipped with a linearized electron capture detector for separation and detection. Analytes are quantitated using procedural standard calibration. The extraction and analysis time is 30 to 50 minutes per sample depending upon the analytical conditions chosen. Confirmatory evidence should be obtained for all positive results. These data may be obtained by using retention data from a dissimilar column, or when concentrations are sufficiently high by GC/MS. Purge and trap techniques using Methods 502.2 or 524.2 may also be used. Confirmation of all positive results of EDB are especially important, because of the potential for misidentification of dibromochloromethane (DBCM) as EDB.
http://www.accustandard.com/asi/pdfs/epa_methods/504_1.pdf?PHPSESSID=6604a8b07877d0ca824dd7349082e6cd

Method 1003: Hydrocarbons, Halogenated
NIOSH Manual of Analytical Methods, 7 pp, Mar 2003 (Issue 3)

This method can be used for simultaneous determination of two or more of the analytes of interest (i.e., benzyl chloride, bromoform, carbon tetrachloride, chlorobenzene, chlorobromomethane, chloroform, o-dichlorobenzene, p-dichlorobenzene, 1,1-dichloroethane, 1,2-dichloroethylene, ethylene dichloride, hexachloroethane, 1,1,1-trichloroethane, tetrachloroethene, 1,1,2-trichloroethane, and

1,2,3-trichloropropane) either by use of both of the capillary columns listed or by modifying the analytical parameters (i.e., temperature program) of the method. High humidity during sampling will decrease total breakthrough volume. Method improvements in this update include higher recoveries at lower sample recovery levels, lower LOD and LOQ values, incorporation of capillary column chromatography, and acceptable recoveries in a 30 day storage stability study.
http://www.cdc.gov/niosh/nmam/pdfs/1003.pdf

Performance Evaluation of a Sorbent Tube Sampling Method Using Short Path Thermal Desorption for Volatile Organic Compounds
Peng, C. and S. Batterman, Univ. of Michigan, Ann Arbor.
Journal of Environmental Monitoring, Vol 2 No 4, p 313-324, 2000

Air sampling using sorbents, thermal desorption, and gas chromatography is a versatile method for identifying and quantifying trace levels of volatile organic compounds (VOCs). Thermal desorption can provide high sensitivity; appropriate choices of sorbents and method parameters can accommodate a wide range of compounds and high humidity; and automated short-path systems can minimize artifacts, losses, and carry-over effects. This study evaluates the performance of a short-path thermal desorption method for 77 VOCs (including 1,2,3-trichloropropane) using laboratory and field tests and a dual sorbent system (Tenax GR, Carbosieve SIII). The laboratory results were confirmed in an analysis of replicate samples collected in two field studies that sampled ambient air along roadways and indoor air in a large office building. Replicates collected under field conditions demonstrated good agreement except for very low concentrations or large (> 4L volume) samples of high humidity air. Overall, the method provides excellent performance and satisfactory throughput for many applications.
http://pubs.rsc.org/ej/EM/2000/B003385P.pdf

Sampling Program for Residential Wood Combustion: Winter of 1998-99 Study Report
Bonvalot, Y., C. Gagnon, M. Benjamin, A. Germain, and T. Dann.
Public Works and Government Services Canada, Montreal. ISBN: 0-662-29797-0, 96 pp, 2000

A sampling program was undertaken in a Canadian city neighborhood during the winter of 1998-99 to assess the impact of residential wood burning. The work involved (a) determining concentrations of polycyclic aromatic hydrocarbons (PAH) and volatile organic compounds (VOCs), (b) determining concentrations of inhalable and respirable particulate matter with an aerodynamic diameter of less than 10 and 2.5 mm, respectively (PM10 and PM2.5), (c) gaining a better understanding of the relations between weather conditions and PAH, VOC, and fine particulate matter (PM10 and PM2.5) concentrations, and, if possible, (d) quantifying the impact of residential wood burning on air quality in the neighborhood studied (relative contributions of residential wood burning in relation to other potential sources). This report details the sampling and analysis methods used for the pollutants included in the sampling program, comprising PAHs, polar VOCs such as aldehydes and ketones, fine particulate matter, and nonpolar VOCs such as benzene, 1,2,3-trichloropropane, and toluene.
http://dsp-psd.pwgsc.gc.ca/Collection/En56-144-2000E.pdf