Mass Spectrometry in Environmental Sciences

Susan D. Richardson

National Exposure Research Laboratory, U.S. Environmental Protection Agency, Athens, Georgia 30605

Received April 4, 2000

Contents

I. Introduction 211
II. Historical Perspective 211
III. General Reviews 213
IV. Regulatory Methods 214
V. Air Analyses 215
A. Aerosols/Particulate Matter: Organics 215
B. Aerosols/Particulate Matter: Inorganics 217
C. Industrial Air Emissions/Flue Gas 217
D. Biogenic Air Emissions 217
VI. Drinking Water, Surface Waters, Wastewater, and Soil 217
A. Organic Analyses 218
1. General Organic Analyses 218
2. Pesticides 219
3. PAHs and PCBs 221
4. Dioxin 222
5. VOCs 223
6. Textile Dyes 223
7. Surfactants 223
8. Disinfection Byproducts 224
9. Taste and Odor Compounds 226
10. Algal and Bacterial Toxins 226
11. Other Organic Pollutants 227
B. Inorganic Analyses 229
1. Disinfection Byproducts 229
2. Perchlorate and Dissolved Gases 230
3. Multiple Elements 230
4. Arsenic and Selenium 231
5. Lithium, Boron, Nitrogen, Sulfur, and Halogens 232
6. Group IIIA Elements 232
7. Group IVB and VB Elements 232
8. Group IIA Elements 232
9. Heavy Metals 232
10. Rare-Earth Elements (Lanthanides) 234
11. Radionuclides 234
12. Other Inorganics 234
VII. Microorganisms 234
VIII. Natural Organic Matter 235
IX. Biological Samples 236
A. Organic Analyses 237
B. Inorganic Analyses 239
X. Field-Portable Mass Spectrometry 240
XI. Conclusions 240
XII. Acknowledgments 241
XIII. References 241

I. Introduction

This review covers applications of mass spectrometry to the environmental sciences. From the early applications of mass spectrometry to environmental research in the 1960s and 1970s, mass spectrometry has played an important role in aiding our understanding of environmental pollution and processes. Due to the tremendous amount of environmental research in the literature, this review must by necessity be selective. A brief historical perspective on the early impacts of mass spectrometry on environmental research will be presented, with the remainder of the review focusing mainly on the last 8–10 years of environmental research. Numerous papers and abstracts were consulted before choosing selected ones to present here. The organization of this review is somewhat different from most reviews that cover a shorter period of time. Air analyses are grouped together, and biological samples are grouped together, but because many of the same types of analytical methods were used for the measurement of pollutants in different media (e.g., drinking water, surface waters, groundwater, wastewater, and soils), those pollutants are organized into compound classes. For example, pesticide papers will be grouped together and dioxin papers are grouped together. It is anticipated that this organization would be helpful to the environmental scientist who wants an update on the types of mass spectrometry methods used for a particular pollutant. Geological measurements are included in this review, and they can be found in the Inorganic Analyses section. As there are many acronyms used throughout this review (such as GC/MS), a table of acronyms is provided for reference (Table 1).

II. Historical Perspective

A key finding in the early 1970s helped to launch the use of mass spectrometry for environmental analyses. In 1974, Rook discovered the first chemical disinfection byproduct (DBP) in drinking water—chloroform. Chloroform was formed when waters containing natural humic substances were chlorinated. Also in 1974, the U.S. Environmental Protection Agency (EPA) found 66 organics in New Orleans tap water. The next year, the EPA published the
of drinking water.10 surface waters,11 municipal wastewaters,12,13 and industrial wastewaters14 were also studied with these techniques (GC/MS, LC/MS, and GC/IR) to environmental problems. Her recent research has focused on the identification/characterization of drinking water disinfection byproducts (DBPs), with special emphasis on alternative disinfectants and polar byproducts.

Table 1. List of Acronyms

<table>
<thead>
<tr>
<th>Acronym</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>AAS</td>
<td>atomic absorption spectrometry</td>
</tr>
<tr>
<td>AED</td>
<td>atomic emission detection</td>
</tr>
<tr>
<td>AES</td>
<td>atomic emission spectrometry</td>
</tr>
<tr>
<td>APCI</td>
<td>atmospheric pressure chemical ionization</td>
</tr>
<tr>
<td>API</td>
<td>atmospheric pressure ionization</td>
</tr>
<tr>
<td>BTEX</td>
<td>benzene, toluene, ethylbenzene, and xylene isomers</td>
</tr>
<tr>
<td>CE</td>
<td>capillary electrophoresis</td>
</tr>
<tr>
<td>CI</td>
<td>chemical ionization</td>
</tr>
<tr>
<td>CID</td>
<td>collisionally induced dissociation</td>
</tr>
<tr>
<td>CLSA</td>
<td>closed-loop stripping analysis</td>
</tr>
<tr>
<td>CRIMS</td>
<td>chemical reaction interface mass spectrometry</td>
</tr>
<tr>
<td>DAI</td>
<td>direct aqueous injection</td>
</tr>
<tr>
<td>DBPs</td>
<td>disinfection byproducts</td>
</tr>
<tr>
<td>DCI</td>
<td>desorption chemical ionization</td>
</tr>
<tr>
<td>DNA</td>
<td>deoxyribonucleic acid</td>
</tr>
<tr>
<td>DNPH</td>
<td>2,4-dinitrophenylhydrazine</td>
</tr>
<tr>
<td>ECD</td>
<td>electron capture detection</td>
</tr>
<tr>
<td>ECNI</td>
<td>electron capture negative ionization</td>
</tr>
<tr>
<td>EDCs</td>
<td>endocrine disrupting chemicals</td>
</tr>
<tr>
<td>EDTA</td>
<td>ethylenediaminetetraacetic acid</td>
</tr>
<tr>
<td>EI</td>
<td>electron ionization</td>
</tr>
<tr>
<td>ELISA</td>
<td>enzyme-linked immunosorbent assay</td>
</tr>
<tr>
<td>EPA</td>
<td>Environmental Protection Agency</td>
</tr>
<tr>
<td>ESI</td>
<td>electrospray ionization</td>
</tr>
<tr>
<td>FAIMS</td>
<td>high-field asymmetric waveform ion mobility spectrometry</td>
</tr>
<tr>
<td>FAB</td>
<td>fast atom bombardment</td>
</tr>
<tr>
<td>GC</td>
<td>gas chromatography</td>
</tr>
<tr>
<td>HG</td>
<td>hydride generation</td>
</tr>
<tr>
<td>IC</td>
<td>ion chromatography</td>
</tr>
<tr>
<td>ICP</td>
<td>inductively coupled plasma</td>
</tr>
<tr>
<td>ICR</td>
<td>ion cyclotron resonance</td>
</tr>
<tr>
<td>IR</td>
<td>infrared spectroscopy</td>
</tr>
<tr>
<td>LAS</td>
<td>linear alkylbenzene sulfonates</td>
</tr>
<tr>
<td>LC</td>
<td>liquid chromatography</td>
</tr>
<tr>
<td>LDI</td>
<td>laser desorption ionization</td>
</tr>
<tr>
<td>MALDI</td>
<td>matrix-assisted laser desorption ionization</td>
</tr>
<tr>
<td>MB</td>
<td>2-methylisobornyl</td>
</tr>
<tr>
<td>MIMS</td>
<td>membrane introduction mass spectrometry</td>
</tr>
<tr>
<td>MS</td>
<td>mass spectrometry</td>
</tr>
<tr>
<td>MTBE</td>
<td>methyl tert-butyl ether</td>
</tr>
<tr>
<td>MX</td>
<td>3-chloro-4-(dichloromethyl)-5-hydroxy-2(5H)-furanone</td>
</tr>
<tr>
<td>NCI</td>
<td>negative chemical ionization</td>
</tr>
<tr>
<td>NDMA</td>
<td>N-nitrosodimethylamine</td>
</tr>
<tr>
<td>NMR</td>
<td>nuclear magnetic resonance</td>
</tr>
<tr>
<td>NOM</td>
<td>natural organic matter</td>
</tr>
<tr>
<td>PAHs</td>
<td>polynuclear aromatic hydrocarbons</td>
</tr>
<tr>
<td>PB</td>
<td>particle beam</td>
</tr>
<tr>
<td>PCBs</td>
<td>polychlorinated biphenyls</td>
</tr>
<tr>
<td>PCDDs</td>
<td>polychlorinated dibenzo-p-dioxins</td>
</tr>
<tr>
<td>PCDFs</td>
<td>polychlorinated dibenzofurans</td>
</tr>
<tr>
<td>PFBA</td>
<td>pentafluorobenzylalcohol</td>
</tr>
<tr>
<td>PFBOH</td>
<td>pentafluorobenzyl alcohol</td>
</tr>
<tr>
<td>REMPI</td>
<td>resonance-enhanced multiphoton ionization</td>
</tr>
<tr>
<td>SFC</td>
<td>supercritical fluid chromatography</td>
</tr>
<tr>
<td>SIMS</td>
<td>secondary ion mass spectrometry</td>
</tr>
<tr>
<td>SPE</td>
<td>solid phase extraction</td>
</tr>
<tr>
<td>SPME</td>
<td>solid phase microextraction</td>
</tr>
<tr>
<td>TCDDs</td>
<td>tetra- and dibenzo-p-dioxins</td>
</tr>
<tr>
<td>TOF</td>
<td>time-of-flight</td>
</tr>
<tr>
<td>TOC</td>
<td>total organic carbon</td>
</tr>
<tr>
<td>TOX</td>
<td>total organic halide</td>
</tr>
<tr>
<td>TSP</td>
<td>thermospray</td>
</tr>
<tr>
<td>VOCs</td>
<td>volatile organic chemicals</td>
</tr>
</tbody>
</table>

Early work presented at the 1975 Conference included results of the National Organic Reconnaissance Survey of volatile organics in drinking water and several other studies of organics in municipal drinking water supplies,3–5 Contaminants in groundwater,6–8 surface waters,9–11 municipal wastewaters,12,13 and industrial wastewaters14 were also studied with...
High-resolution gas chromatography, a technique that today we take for granted, was a relatively new technique during this time, allowing much improved separations over the traditional packed GC columns. 

In this second book, Keith states that “I think we have reached the stage in the evolution of analysis of organic pollutants in water where the easy methods and the easy compounds have been exploited. Now we will have to work harder and be more clever to produce newer and better methodology with which to uncover the more difficult organic pollutants.”

These were truly prophetic words, but the rapid rate at which new technologies would develop was probably not anticipated at this time.

Just 20 years later, we have a whole host of new mass spectrometry technologies available, which are helping us to “uncover the more difficult organic pollutants” and advance our knowledge of environmental chemistry in ways that could not have been fathomed 20 years ago. For example, liquid chromatography/electrospray ionization mass spectrometry (LC/ESI-MS) and capillary electrophoresis/mass spectrometry (CE/MS) have permitted the analysis of nonvolatile ionic pesticides, textile dyes, and surfactants in water; matrix-assisted laser desorption ionization mass spectrometry (MALDI-MS) has allowed the identification of pathogenic microorganisms; and high-resolution inductively coupled plasma (ICP)-MS has permitted the trace-level determination of inorganic species in environmental samples. LC/MS interfaces have improved over the years with the earlier developments of moving belt, thermospray, and particle beam interfaces to later developments of electrospray and atmospheric pressure chemical ionization (APCI) interfaces. Fast atom bombardment mass spectrometry (FAB-MS) and liquid secondary-ion mass spectrometry (SIMS) were also developed over this time.

There also have been a tremendous increase in the number of sample concentration and separation devices developed and used, often on-line, with mass spectrometry. Separation devices now coupled to mass spectrometry and used for environmental applications include LC, ion chromatography (IC), superf critical fluid chromatography (SFC), and capillary electrophoresis (CE). There have also been direct analysis methods developed, such as membrane introduction mass spectrometry (MIMS) and aerosol time-of-flight (TOF)-mass spectrometry, that have permitted the direct, real-time analysis of environmental samples, and many field-portable mass spectrometers have been developed to allow analyses to be performed at the site of contamination. Improvements in sample concentration have also taken place, with techniques such as solid-phase extraction (SPE) and solid-phase microextraction (SPME) allowing analytes to be concentrated with little or no solvent used. This review will attempt to cover the highlights of the use of these techniques for studying interesting and important environmental samples.

### III. General Reviews

Numerous reviews have been published that included environmental applications of mass spectrometry. Historical examples of reviews include ones by Alford, Freudenthal, Keith, Safe, and Schulten published in the 1970s and ones by Dougherty, Cairns et al., Bursey and Hass in the early 1980s. These reviews covered general reviews of environmental mass spectrometry applications, field-ionization and field-desorption-MS, NCI-MS, tandem mass spectrometry and reviews of mass spectrometry applied to specific analytes, such as dioxins, pesticides, and industrial chemicals.

More recent reviews include general environmental analysis reviews (which include mass spectrometry and other analytical techniques) and reviews of specific mass spectrometry techniques with environmental applications. Clement and co-authors have published a series of reviews for Analytical Chemistry entitled ‘Environmental Analysis’ that cover the years 1991–1999. Another series published in Analytical Chemistry, entitled ‘Water Analysis’, covers the years 1991–1999 and includes many environmental applications of mass spectrometry. Dietrich and co-authors have published a series on ‘Chemical Species’ in the journal Water Environment Research that covers the years 1993–1998. Lopez-Avila published a review on the trends in environmental analysis in 1999; Charles and Feinberg published a review on the key role mass spectrometry...
has played in advancing environmental research. Barcelo published a review on the use of mass spectrometry in environmental organic analyses, and Hites published a general review of mass spectrometry and environmental sciences. Koester and Clement published a review of the analysis of drinking water for trace organics, and Burlingame et al. published general reviews of mass spectrometry that contained a few environmental applications.

Several reviews covered the use of LC/MS for environmental studies. Berger et al. presented the use of LC with ion-trap mass spectrometry for structural elucidation and quantitation, and M¨oder and Popp presented the application of SPME-LC/MS for determining contaminants in environmental samples. In 1999, Niessen published an overview of the state-of-the-art in LC/MS. Several general overviews of LC/MS applications were also published, and earlier reviews in 1991–1996 covered environmental applications of thermospray and particle beam-LC/MS. Van Emon and Lopez-Avila published a review on immunoaffinity extraction with on-line LC/MS, which included applications to several environmental pollutants. Other reviews included environmental applications of membrane introduction mass spectrometry (MIMS), CE/MS, CE/I-CP-MS, GC/MS, GC/infrared spectroscopy (IR) and GC/MS, electron-capture (EC)-MS, and chemical ionization (CI)-MS.

Boyd reviewed quantitative trace analysis with chromatography–mass spectrometry, isotopic dilution-MS, GC/isotope ratio-MS, GC/carbon-isotope ratio-MS, and continuous-flow isotope ratio-MS were the subject of other reviews. Surface analysis with SIMS was reviewed by Benninghoven.

Many reviews on mass spectrometry techniques for trace element analysis were also published. In 1999, Bacon et al. presented a general review on atomic mass spectrometry and Haraguchi presented a review of multielement profiling analyses of biological, geochemical, and environmental samples as studied by atomic spectrometry. Mach et al. published a review of methods for metal speciation in 1996, and Bersier et al. compared advanced electroanalytical techniques to atomic absorption spectrometry, ICP-atomic emission spectrometry (AES), and ICP-MS for environmental analysis in a 1994 review. The state-of-the-art of GC coupled with optical and mass spectral detection for trace metal speciation was reviewed in 1994 by Lobinski and Cresser et al. provided a general review of atomic spectrometry for environmental analyses in 1993.

Several reviews covered ICP-MS specifically. Reviews in 1999 covered general applications of ICP-MS, metal speciation by SPME-combustion-ICP-MS, and the analysis of geological materials by ICP-MS. Reviews in 1998 covered the use of ICP-MS for elemental speciation studies and applications of multiple-collector-ICP-MS to cosmochemistry, geochemistry, and paleoceanography. Several other reviews were published from 1992 to 1997, including general environmental applications of ICP-MS and applications to radionuclides, rare-earth compounds, biological and environmental samples, and geochemistry and hydrology. Two reviews discussed chromatography coupled with ICP-MS. In 1995, Heumann et al. reviewed recent developments in thermal ionization-MS techniques for isotope analyses, Accelerator-MS applications were the focus of three reviews; one discussed applications for measurement of trace isotopes and elements, another discussed environmental geoscience measurements, and another discussed radionuclide dating and trace-element analysis. In 1992, Kopchak and Veber published a review on thermospray sample introduction to atomic spectrometry.

Reviews with an emphasis on the analysis of specific types of environmental pollutants included the use of LC/MS or GC/MS for measuring pesticides, LC/MS or CE/MS for measuring textile dyes, LC/MS and MS/MS for measuring surfactants, and LC/MS methods for measuring seafood toxins. Reviews were also presented on methods for determining mutagenic heterocyclic amines, carbonyl-containing compounds, and individual particles in environmental samples. I norganic application reviews included the determination of arsenic species in environmental and biological samples, LC/MS determinations of organotin compounds, and the determination of organomercurials in biological and environmental samples.

IV. Regulatory Methods

Many EPA-approved methods utilize mass spectrometry. There are too many to list here, but they can be found at the U.S. EPA's website: www.epa.gov/epahome/Standards.html. At this site, hundreds of EPA methods are listed, covering numerous organic and inorganic analytes and many sample matrices. From this website, there is a link to another important website: www.epa.gov/nerl/cwww/methmans.html, where a compendium called 'The Manual of Manuals' can be found. This site carries information for eight laboratory analytical chemistry method manuals that were published by the EPA laboratory in Cincinnati between 1988 and 1995. Examples of methods available include EPA Method 525.2, 'Determination of Organic Compounds in Drinking Water by Liquid–Solid Extraction and Capillary Column Gas Chromatography/Mass Spectrometry', and EPA Method 200.8, 'Determination of Trace Elements in Water and Wastes by Inductively Coupled Plasma-Mass Spectrometry'. In the last 2–3 years, there have been a few new regulatory methods published that utilize mass spectrometry. EPA Method 321.8, 'Determination of Bromate in Drinking Waters by Ion Chromatography Inductively Coupled Plasma-Mass Spectrometry', provides a lower detection limit for bromate of 0.3 μg/L and provides a degree of selectivity that was not available with former methodologies. EPA Method 1653, 'Chlorinated Phenolics in Wastewater by In Situ Acetylation and GC/MS', applies to certain pulp and paper mills regulated under the Pulp and Paper Cluster Rule that was promulgated in 1998. EPA Method 1666, 'Volatile Organic Compounds (VOCs) Specific to the Pharmaceutical Manufacturing Industry by Isotope Dilution GC/MS', represents a revised pharmaceutical method.
that is part of a compendium supporting the Effluents Guidelines Rule promulgated in 1998.130

V. Air Analyses

Many environmental mass spectrometry applications focused on air studies. These included studies and measurements of aerosols/particulate matter, industrial emissions, and biogenic emissions.

A. Aerosols/Particulate Matter: Organics

Aerosols are, by definition, any particulate matter suspended in a gas (e.g., dust, fog, smoke, or smog);131 therefore, the terms aerosols and particulate matter will be used interchangeably throughout this section. A 1999 review by Suess and Prather discussed mass spectrometry analyses of aerosols.132 This review included an overview of laser probe MS, SIMS, and ICP-MS applications to aerosol research. Grohse reviewed trace element analysis of airborne particles by atomic absorption spectroscopy, ICP-emission spectroscopy, and ICP-MS.132 Mitra et al. developed a microtrap interface for on-line MS monitoring of air emissions which eliminated background moisture interferences.133 Brinkman et al. reported the use of ion-trap mass spectrometry for measuring trace VOCs in real-time.134 Shchekina et al. reported the development of a new desktop time-of-flight (TOF) mass spectrometer for measuring air samples,135 and Tobias and Ziemann reported the use of temperature-programmed thermal desorption particle beam-MS for identifying organic compounds in aerosols.136 Pelzing used Curie point pyrolysis-GC/MS to characterize organic compounds in airborne particulate matter.137

Indoor air was the focus of three studies reported here. De Bortoli et al. reported the results of a multilaboratory study involving 10 European countries, where the emission of VOCs from indoor building products were measured.138 In this study, GC/MS was used to measure VOCs emitting from carpet, cushion vinyl, and paint. Gorlo et al. used SPME with GC/MS to measure carbon tetrachloride, 1,1,1-trichloroethane, 1,1,2-trichloroethane, and other volatile organic compounds in airborne particulate matter.139

Several studies focused on reactions of ozone, hydroxyl radicals, and other ions with organic compounds in air. Grosjean and Grosjean used LC, LC/MS, and GC/MS to determine the major reaction products of unsaturated aliphatic oxygenates with ozone.140 The major products formed were methyl formate and methyl glyoxylate from methyl trans-3-methoxy acrylate, acetaldehyde and 2-oxobutanal from 4-hexen-3-one, propanal and succinic dialdehyde from cis-4-heptenal, hydroxyacetalddehyde and acetone from 3-methyl-2-buten-1-ol, and ethyl formate and acetaldehyde from cis- and trans-ethyl-1-propenyl ether. Anderson and Hites developed a system to measure relative rate constants of reactions of semivolatile organic compounds with hydroxyl radicals.142 Letzel et al. used LC/ATCI-MS to separate and identify 29 different polar degradation products of benzo[a]pyrene with ozone; some reaction products were reported for the first time.143 Aschmann and Atkinson used GC and atmospheric pressure ionization (API)-MS/MS to identify products of gas-phase reactions of hydroxyl radicals with n-butyl methyl ether and 2-isopropoxyethanol.144 Spanel and Smith studied reactions of H2O2, NO2, and O3 with aromatic and aliphatic monosubstituted halocarbons.145

Yu et al. used pentafluorobenzylhydroxylamine (PFBHA) derivatization and GC/MS to identify airborne carbonyl compounds formed by the photooxidation of isoprene.146 The use of pentafluorobenzyl bromide (PFBBr) and pentafluorobenzyl alcohol (PFBOH) as derivatizing agents for measuring airborne organic compounds was the focus of three papers.147–149 The first paper discussed the analysis of carboxylic acids and phenols with PFBBr derivatization and GC/ion-trap-MS using a novel chemical ionization reagent, PFBOH.147 This method allowed the first-time measurement of methacrylic acid from the oxidation of isoprene in indoor and outdoor smog. The second paper discussed the successful measurement of hydroxy carbonyls and other carbonyls in ambient air through the use of PFBOH as a chemical ionization reagent.148 In this study, methyl vinyl ketone, methacrolein, methylglyoxal, hydroxyacetone, glyoxal, and 3-hydroxy-2-butanalone were identified in air from Davis, CA. The third paper detailed the formation of unique ions (PFBOH derivatives) under chemical ionization MS conditions that aid in the identification of oxygenated polar organics in air.149

Two papers discussed the use of 2,4-dinitrophenylhydrazone (DNPH) as a derivatizing agent with LC/MS for measuring carbonyl compounds in ambient air.150,151 The first paper by Kölliker et al. detailed the structural elucidation of DNPH-derivatized carbonyls in air and presented detailed fragmentation pathways obtained through MS/MS/MS and MS/MS/MS/MS with only 1–10 ng of material.150 The second paper by Grosjean et al. detailed results from the study of 78 carbonyls derivatized by DNPH and analyzed with both diode array-ultraviolet (UV) spectroscopy and APCI-MS.151 Thomas et al. used derivatization with 2-hydroxymethylpiperezidine (coated in a denuder tube), recovery by thermal desorption, and analysis by GC/MS to measure formaldehyde in air.152 Tsai and Hee discussed the use of a new solid sorbent passive sampler for measuring aldehydes in air.153 and Zurek et al. presented an LC/APCI-MS method for analyzing carbonyls in air, including automobile exhaust.154

Polynuclear aromatic hydrocarbons (PAHs) and nitro-PAHs were the focus of several studies. Cecinato et al. studied the distribution of n-alkanes, PAHs, and nitro-PAHs between fine and coarse fractions of inhalable dust particles in downtown Rome.155 Preferential accumulation was observed on fine particles. Niederer used GC/ion-trap-MS/MS to measure PAHs, nitro-PAHs, and oxy-PAHs in urban airborne particulate matter and soil.156 Nitro-PAHs
were found to be less persistent in soil than nonsubstituted PAHs, and they were 10–100 times lower in concentration than oxy-PAHs and the parent PAHs in air. PAHs, nitrogen-PAHs, and hydroxy-PAHs were also measured by SFC with GC/MS,\textsuperscript{157} laser desorption ionization (LDI)-TOF-MS,\textsuperscript{158} and on-line LC-GC-ion-trap-MS.\textsuperscript{159} Hachimi et al. used laser microprobe at short wavelengths and low energy to allow the in-situ desorption of high molecular weight PAHs and nitro-PAHs.\textsuperscript{160} Vincenti et al. used GC/electron capture-MS/MS to determine nitro-PAHs at sub-ppb levels in airborne particulate matter and soils.\textsuperscript{161} Haefliger et al. used laser desorption/laser photoinization-TOF-MS to measure aromatic compounds in urban aerosols over the course of a day.\textsuperscript{162} Yang and Baumann studied the seasonal variations of PAHs in street dust collected from highways, urban streets, a gas station, pedestrian tunnels, a civil house, and a parking deck in German cities, using SFE-GC/MS.\textsuperscript{163} In this study, it was found that PAH concentrations showed distinct variations with the sampling area and were 2–12 times higher in the winter than in the summer and that fluoranthene, pyrene, and phenanthrene were the highest in concentration. GC/MS was also used to measure PAHs and oxygenated PAHs in other studies. Koeber et al. used LC/MS to determine benzo[a]pyrene diones, which are photooxidation products of benzo[a]pyrene, in air particulate matter.\textsuperscript{167} Asano et al. used parallel monitoring for multiple-targeted compounds with ion-trap mass spectrometry to measure trace explosives in air (2,4-dinitrotoluene, 2,4,6-trinitrotoluene, and 2,4,6-trinitrophenyl-methyl nitramine).\textsuperscript{158}

Several air studies focused on the measurement of organic compounds in automobile exhaust. Two studies reported the real-time characterization of organics in automobile exhaust using ion-trap-MS\textsuperscript{169} or aerosol TOF-MS.\textsuperscript{170–172} The development of aerosol TOF-MS by Prather et al. has enabled the real-time analysis of single particles.\textsuperscript{173–176} GC/MS was used by other authors to quantify toxic hydrocarbons in engine exhaust and air,\textsuperscript{177} and to measure benzene and alkylated benzene from vehicular emissions\textsuperscript{176} and PAHs and dioxin-receptor ligands in diesel exhaust particulate extracts.\textsuperscript{177} Franzen et al. developed a new procedure using resonant multiphoton ionization and TOF-MS to enable the dynamic study of combustion processes.\textsuperscript{178} Other studies focused on the detection of VOCs in ambient air. Yassaa et al. reported the use of chiral GC for analyzing VOCs in the ambient air of Algiers.\textsuperscript{179} The cyclodextrin column used allowed good separations of aromatic hydrocarbons and p- and m-xylene. Hassoun et al. used thermal desorption-GC/MS to study urban hydrocarbons in Leeds, U.K.\textsuperscript{180} This method permitted the simultaneous measurement of 68 C6–C12 hydrocarbons at ppb levels. Wedel et al. used a new on-line GC/MS technique to measure VOCs in a nationwide study in Germany of photooxidants formed by the reaction of organic plant emissions with hydroxyl radicals in air.\textsuperscript{181} In this study, approximately 250 C6–C15 hydrocarbons and C4–C12 oxygenated VOCs and aldehydes were monitored. Fernandez-Martinez et al. developed a new method using thermal desorption-GC/MS for determining C6–C9 VOCs and applied it to urban and rural air in Northwest Spain.\textsuperscript{182} Chai and Pawliszyn used SPME-GC/ion-trap-MS to measure VOCs in air at ppt to sub-ppb levels.\textsuperscript{183} Two studies reported the measurement of VOCs in arctic air. One used serial GC/MS to study variations of 11 halocarbons, 3 hydrocarbons, and acetone in arctic air,\textsuperscript{184} and the other used GC/MS to study the seasonal variation of four natural halocarbons and three anthropogenic halocarbons in the arctic troposphere.\textsuperscript{185} Oliver et al. reported a method using sorbent preconcentration, cryofocusing, and GC/MS analysis for measuring toxic VOCs in air.\textsuperscript{186} This method produced detection limits less than 0.10 ppb and was linear over a range of 1–40 ppb. MIMS was used by Cisper et al. for the on-line detection of VOCs in air at ppt (ng/L) levels.\textsuperscript{187} Finally, Haunold et al. reported an improved sampling strategy for VOCs based on cooled sampling and analysis by thermodesorption-GC/MS.\textsuperscript{188}

Halogenated organic compounds were studied by several researchers. Airborne concentrations of toxaphene congeners were measured in Ontario using GC/electron capture-negative-ion (ECNI)-MS.\textsuperscript{189} Ulrich and Hites measured enantiomeric ratios of chlordane-related compounds in air near the Great Lakes using chiral GC with ECNI-MS.\textsuperscript{190} In this study, 48 air samples were taken near Lake Erie, 5 air samples were taken near Lake Michigan, and 6 air samples were taken near Lake Superior. Differing enantiomeric ratios were found—e.g., for cis-chlordane, the overall enantiomeric ratio was 1.05 (racemic mixture), but for trans-chlordane, it was 0.88, indicating that trans-chlordane and cis-chlordane may be degraded differently in the environment. Takasuga et al. reported that chlordane-related compounds were potential interferences to polychlorinated dibenzofurans (PCDFs) in the GC/high-resolution-MS analyses of ambient air.\textsuperscript{191} Koester et al. compared high-resolution electron ionization (EI)-MS and low-resolution ECNI-MS for measuring dioxins and furans in air\textsuperscript{192} and reported how wet and dry deposition contribute to the observed dioxin and furan profiles between sources and sinks.\textsuperscript{193} Yang and Baumann used SFE-GC/MS to study PCBs in street dust in Germany.\textsuperscript{194} and Unwin and Groves used GC/MS to measure bis(chloromethyl)ether in air at ppb levels.\textsuperscript{195} Methyl halides were measured in marine atmospheres using canister sampling and GC/MS.\textsuperscript{196} In this study, methyl chloride levels were found to increase at night and were negatively correlated with surface ozone concentrations. Engen et al. used GC/high-resolution-MS to measure brominated compounds in the background air of rural Montana.\textsuperscript{197} In this study, most of the brominated compounds were identified at sub-ppt levels; the method permitted detection down to ppq (pg/L) levels. Sharp et al. also measured organobromine compounds in air using adsorbent trapping and GC/MS, with detection limits of 0.1–0.2 ppt.\textsuperscript{198}

In other air studies, GC/NCI-MS was used to measure peroxyacetyl nitrate at ppt levels in air,\textsuperscript{199} and EI- and NCI-MS were used to measure arylalkyl
nitrates in urban air. In the latter study, the following arylalkyl nitrates were identified in urban air: benzyl nitrate, xyllyl nitrate, phenyl-n-propyl-1-nitrate, and phenyl-n-propyl-2-nitrate, with benzyl nitrate being the dominant compound of this group. Glasius et al. used LC/ion-trap-MS to determine polar terpene oxidation products in aerosols, which allowed the identification of three new compounds, tentatively identified as 10-hydroxy-pinonic acid, 9-hydroxynorpinonic acid, and pinalic-4-acid. IC-GC/MS was used to determine mono- and dicarboxylic acids in aerosol particles, and GC/ion-trap-MS was used to determine muramic acid, which is a chemical biomarker for bacterial peptidogycan. In this study, muramic acid was monitored in airborne dust collected in a horse stable and in a dairy. Jonsson et al. used derivatization with PFBBr or BF3/methanol, followed by GC/MS analysis, to determine organic anhydrides in air, and Sturaro et al. used GC/MS to determine vinyl acetate at ppt levels in air.

Karlsson et al. used LC/MS to determine aliphatic isocyanates and amines in air at 20 nmol/L detection limits with good linearity over 50–500 nmol/L. Nolte et al. used trimethylsilation derivatization with GC/MS to determine highly polar compounds in meat smoke. In this study, silylation enabled the detection of monoglycerides and enhanced the detection of cholesterol. Finally, Shao et al. used accelerator-MS to study the source identification of aerosols in China.

B. Aerosols/Particulate Matter: Inorganics

Many air studies involved the measurement of inorganics in air particulate matter. Sich and Russow used GC/MS to measure nitric oxide and nitrous oxide in air, and Reiner et al. used mass spectrometry with chemical conversion/ion–molecule reactions for aircraft-borne measurements of peroxy radicals in the troposphere over South Germany. Iodine-129 was measured in atmospheric samples using accelerator-MS, and HOCI was measured using API-MS, which permitted air analyses at higher pressures—up to 1 atm in air. Arsenic and vanadium were measured in airborne reference materials using ICP-MS. Multiple-element analyses were the focus of four papers using ICP-MS methods. One of these studies measured the atmospheric deposition of 18 elements, and another study measured 33 elements deposited on 495 moss samples collected in a nationwide Norwegian study. In the latter study, it was found that there was a decreased contribution of most long-range transported elements in Southern Norway, as compared to studies conducted in earlier years.

D. Biogenic Air Emissions

Two recent studies focused on biogenic air emissions. Helming et al. used GC/MS to study the emissions of biogenic VOCs from the dominant vegetation species found in Atlanta, GA, Rhinelander, WI, and Hayden, CO. Fall et al. measured VOCs emitted after leaf wounding, using proton-transfer-reaction MS. In this study, a family of hexenal compounds and their metabolites were identified from the wounding of aspen leaves.

VI. Drinking Water, Surface Waters, Wastewater, and Soil

The analysis of drinking water, surface waters, wastewaters, and soils are combined in this section due to the similarity of the methods and the chemicals studied for these sample media. Organic chemi-
icals are grouped according to type—general organic analyses (involving multiple types of chemicals), pesticides, PAHs and PCBs, dioxin, textile dyes, surfactants, disinfection byproducts, VOCs, and other organic pollutants. Inorganic analyses are also organized in this way, with disinfection byproducts and groups of elements organized together. The types of organic and inorganic compounds studied have not changed much over the years, but the types of methods and measurements have advanced significantly, permitting increasingly lower detection limits (ppt and sometimes ppq) and the direct analysis of ionic and polar species that in previous years was not possible. Improved low- or no-solvent extraction techniques, such as solid-phase microextraction (SPME), have become more important as researchers and regulators seek environmentally friendly and more rapid methods. There has also been an increase in the use of on-line separation techniques with mass spectrometry, including LC/MS, SFC/MS, IC/ICP-MS, and LC/ESI-MS, CE/MS, and CE/ICP-MS. ESI-MS and APCI-MS have also been extremely beneficial for the measurement of highly polar pesticides, such as diquat and paraquat. Before the advent of LC/MS techniques, polar compounds were difficult and sometimes impossible to measure. Now they can be measured at very low detection levels. There has also been a recent push to separate enantiomeric forms of chemicals due to differences in their degradations in the environment. Chiral cyclodextrin columns have made these measurements possible. Thus, although many of the chemicals and elements that are being measured now have not changed, the level of information that can be obtained has changed significantly.

A. Organic Analyses

1. General Organic Analyses

Two studies combined the use of infrared spectroscopy (IR) with GC/MS. One used GC/IR and GC/MS (high-resolution EI- and CI-MS) to identify drinking water contaminants in connection with a suspected childhood cancer cluster in Toms River, NJ. Two other studies used GC/IR/MS to analyze contaminated water, clay, and soil samples. Benfenatia et al. compared GC/MS, LC/nuclear magnetic resonance spectroscopy (NMR), and LC/MS for identifying chemicals in an industrial landfill leachate. and Fuoco et al. used on-line SFC-cryotrap-GC/MS to analyze priority pollutants in sediment reference samples and seawater. Several studies used toxicity measurements to direct MS analyses. Kuehl et al. used in vitro reactions of chemicals with deoxyribose nucleic acid (DNA) as an analytical technique to detect and identify genotoxic contaminants in aqueous environmental samples. This new method involves the incubation of DNA with the contaminated aqueous samples, followed by enzymatic hydrolysis of the DNA to deoxynucleosides and LC/MS analysis of the resulting solution. In this work, it was found that adduct formation was linear with both contaminant concentration and electrophilic reactivity potential. Three studies used toxicity-directed fractionation of effluents using the bioluminescence of Vibrio-fischeri, followed by GC/MS detection or LC/MS detection. This approach was shown to be beneficial for expanding the number of toxicants identified in wastewater effluents. Castillo et al. evaluated enzyme-linked immunoassay (ELISA) kits followed by LC/APCI-MS for determining organic pollutants in industrial effluents.

Several studies used LC/MS techniques to measure organic chemicals in environmental samples. Castillo and Barcelo presented an overview of analytical methods for measuring endocrine disrupting chemicals (EDCs) in industrial effluents, which included a discussion of the use of LC/MS for identifying the more polar EDCs. Castillo et al. used SPE with LC/MS (APCI and ESI) to identify polar, ionic, and highly water-soluble pollutants in untreated waste water. Hughes et al. and Schröder used LC/MS to identify polar organic pollutants in waste treatment processes and river samples, respectively. Shumate and Hill applied electrospray ion mobility spectrometry for continuous monitoring of organic compounds with detection limits of 5 fmol/s. Particle beam-LC/MS and thermospray-LC/MS, FAB-MS, and fast ion bombardment-MS have also been used to identify organic pollutants in water and wastewater.

MIMS has been useful for the direct detection of organic compounds in water, with one paper reporting ppq (pg/L) detection limits. Vincenzi and co-authors recently developed a derivatization method that enables highly polar compounds with multiple hydroxyl, carboxyl, and amine groups to be extracted and analyzed by GC/MS. This method involves the use of n-hexyl chloroformate, which permitted 10–100 μg/L detection limits, or octafluoropropyl chloroformate, which permitted 30–300 fmol detection limits. Large-volume injection-GC/MS has been used to inject water samples (up to 1 mL) or organic extracts directly onto a gas chromatograph. In the first study, over 20 compounds were identified in river water at a detection limit of 0.01 μg/L. GC/MS is still used extensively for measuring organic pollutants in environmental samples, due to the low detection limits and high degree of separation that can be achieved. Butlerman et al. used on-line trace enrichment GC/MS to measure organic contaminants in water samples, and Lega et al. developed a quantitative GC/MS method for the simultaneous determination of organochlorine pesticides, PCBs, PAHs, phthalates, chloroaromatics, phenolics, phenoxy acids, and other base/neutral compounds in sewage sludge. Ding et al. used GC/EI-MS, GC/CI-MS, and GC/MS/MS to identify organic residues in treated wastewater effluents. Castillo et al. used high-temperature-GC/MS to identify organic pollutants in industrial effluents. GC/MS has also been shown to be useful for determining organic compounds in oil field wastewater samples that were high in sulfide. SFE-GC/MS has been useful for identifying organic pollutants in sewage, and SPME-GC/MS has been useful for measuring hydrophilic compounds. Dias and Freeman used SPME to facilitate the measurement of stable carbon isotope compositions of organic compounds in water. Finally, GC was used with simultaneous atomic emis-
tion and mass spectral detection (GC/AED/MS) for analyzing nontarget organic compounds in municipal wastewater. 275

2. Pesticides

Due to the nature of their toxicity and concerns about their effects on the environment, pesticides represent the dominant class of pollutants investigated in environmental studies. An interesting development in recent years has been the use of immunoaffinity chromatography with LC/MS or GC/MS to selectively determine pesticides. 276–278 This method enables on-line extraction, preconcentration, and positive confirmation of pesticides in as little as 10 min, 276 and it makes it possible to detect low levels of pesticides in complex environmental samples without interferences from matrix components. Another interesting development is in the use of chiral chromatography, which allows the stereospecific determination of pesticides. 280 MALDI-MS 282 and LDI-ion-trap MS 283 and have also recently been used to identify pesticides, such as diquat, 282 paraquat, 282 and DDT. 283 A few researchers have applied CE/MS to analyze highly polar or ionic pesticides. 284–287 This analytical method is not yet considered rugged—achieving optimal results and good reproducibility can be difficult—but it shows a great deal of analytical promise due to the extremely high number of theoretical plates that can be achieved in separations. Thus, it has the potential to offer increased separations of highly polar and ionic pesticides, as compared to LC/MS. Ionic pesticides, paraquat and diquat, have been measured by CI-ESI-MS 284 and CE/TOF-MS; 285 sulfonylureas have been measured by CE/ion spray-MS; 286 and chlorinated acid herbicides have been measured by CE/ESI-MS. 287

Numerous LC/MS methods have recently been developed for analyzing pesticides in environmental samples. Electrospray and APCI methods are becoming the most popular of the LC/MS methods, due to improved ease of operation, long-term operating stability, and better detection limits and analytical precision that can be achieved, as compared to earlier thermospray and particle beam methods. Ferrer and Barcelo reviewed LC/MS methods for the trace determination of pesticides in environmental samples. 288 Aguera and Fernandez-Alba reviewed GC/MS and LC/MS studies of pesticide degradation products generated through advanced oxidation processes. 289 Hogenboom et al. reported accurate mass determinations of pesticides from different compound classes using on-line SPE-LC-ESI-orthogonal-TOF-MS, 290 and Lin and Voyksner used ESI-ion-trap-MS/MS to determine pesticides in water. 291 Hogenboom et al. used on-line single-short-column LC combined with APCI-MS/MS for rapid analyses (10–15 min) of herbicides, with a linear range of 0.1–10 μg/L. 292

Several ESI- or APCI-MS methods were developed for simultaneously determining multiple groups of pesticides. Some of these methods also used tandem mass spectrometry to provide additional structural information. 293–296 Carbamate, triazine, phenylurea, phenoxy acid, and nitrophenol pesticides 293 were the focus of one study; polar pesticides and their trans-formation products were the focus of another. 294 and organophosphates, carbamates, phenylureas, and triazines were the focus of another. 295 Aguilar et al. monitored a group of pesticides and metabolites of different chemical groups in water samples from the Ebro Delta area (Spain). 297 The most frequently detected pesticides were betazone, molinate, metolachlor, simazine, atrazine, and dealkylated metabolites, desisopropilatrazine and deethylatrazine (at levels ranging from 0.03 to 2.4 μg/L). 297 Hu et al. measured water from a public waterworks treatment plant in J apan for 31 thermolabile and/or polar pesticides; 8 pesticides were detected in treated water and 10 in the raw, untreated water. 298 J cannot and Sauvard analyzed surface waters in the Center Region of France for a priority list of 40 pesticides; 299 and Molina et al. analyzed estuarine water from the Elorn River in France for triazine, phenylurea, and other priority pesticides. 300 Doerge and Bajic developed an APCI-MS method for 17 pesticides from five chemical classes (triazines, phenylureas, carbamates, organophosphates, and others) that were from the U.S. EPA’s National Pesticide Survey of groundwater contaminants. 301 Rodriguez and Orescan developed an LC/ESI-MS method for quantifying 16 selected sulfonylurea, imidazoline, and sulfonamide herbicides in surface water. 302 and Crescenzi et al. developed a method for analyzing 45 widely used pesticides in drinking water, groundwater, and river water. 303 The latter method provided detection limits ranging from 0.06 (malathion) to 9.0 ng/L (butoxy-carboxim) for drinking water analyses. 303 Aguilar et al. compared automated APCI-MS to particle beam-MS for determining a priority group of pesticides; 304 Giraud et al. developed a method to determine six pesticides (atrazine, hydroxyatrazine, carbofuran, promecarb, linuron, and monolinuron) in drinking water.305

Organophosphorus pesticides were the focus of several studies using APCI- or ESI-MS. 306–309 One of these studies utilized SPE followed by LC-ESI-MS for detection limits of 0.01 μg/L. 306 Another study utilized on-line IC with ESI-MS, which required no sample preparation. 309 Sulfonylurea 310–315 or phenylurea 316 herbicides were the focus of other studies using API-MS. Three studies also utilized tandem mass spectrometry. 310–312 One of these involved the study of the degradation rate of metsulfuron-methyl in soil over 2 years. After application of this herbicide, its degradation was found to be very rapid, with a half-life of 6.5 days. 311 Atrazine and other triazine herbicides were measured in other studies. 317–319 One study followed atrazine and its six major degradation products with SPE and LC-ESI-MS. 317 Another study utilized ESI-ion mobility mass spectrometry, which allowed the direct sampling of atrazine in high humic waters, 318 and the last study involved the use of ultrahigh-pressure LC/TOF-MS, which permitted the separation of triazine herbicides and benzodiazepines in less than 60 s. 319 Three API-MS studies focused on imidazolinone herbicides. 320–322 Imidazolinone herbicides are a relatively new class of herbicides that are applicable to several different crops but require lower doses and have reduced environmental risk. 320
One method reported detection limits of 2–5 ng/L with recoveries higher than 89% in different aqueous matrices; other methods reported ppb level detection limits in soil. API-MS methods were also developed for acidic herbicides, quaternary ammonium herbicides, carbofuran and methio-carb, ionic chloroacetanilide herbicide metabolites, mothproofing agents such as sulcoturon and flucuron, and marine antifouling herbicides such as diuron, 2-thiocyanomethylthiobenzothiazole, Irgarol, and chlorothalonil.

The degradation of pesticides was the focus of several API-MS studies. Five papers studied the photolytic degradation of various pesticides under controlled conditions. One study also involved the use of a photocatalyst (TiO₂) and two studies involved the use of natural sunlight and temperatures. In one of these studies involving organophosphorus pesticides, the following half-lives were observed: methyl-parathion, 3 days in groundwater and 4 days in estuarine and river water; ethyl-parathion, 2 days in groundwater and estuarine water; fenitrothion and pentachlorophenol, 2 days or less in all types of water. In another study, half-lives varied between 4 and 12.5 days for carbofuran and methio-carb under natural sunlight conditions. Finally, the reductive halogenation of atrazine with Fe⁰ was studied using LC/MS/MS. In this study, a previously unidentified degradation was found—2-(ethylamino)-4-isopropylamino-1,3,5-triazine.

Particle beam-LC/MS was also used in several pesticide studies. PB-MS produces EI spectra that can be searched with commonly used library databases, which was one of the reasons for its early popularity. However, ESI- and APCI-MS generally provide lower detection limits; thus, the development of these latter techniques has significantly curbed the number of PB-MS studies. One of the earlier uses of PB-MS for measuring pesticides involved the determination of urea and carbamate pesticides. A more recent paper in 1997 involved the determination of neutral and acidic pesticides with on-line SPE and LC/PB-MS. Other studies involved the determination of 18 acidic pesticides, 32 base/natural and 13 acidic pesticides, diquat and paraquat, phenylurea herbicides, and rotenone. The following detection limits were achieved in these studies: 0.1–1 ppb for acidic pesticides, 5–10 ppb for diquat and paraquat, and 0.03–0.05 ppb for phenylurea herbicides.

Thermospray (TSP)-LC/MS has also been used in several studies of pesticides. However, like PB-MS, it is one of the earlier LC/MS techniques and suffers from lower sensitivity as compared to more recent ESI and APCI techniques. Jones et al. discussed results from three interlaboratory U.S. EPA studies, including a TSP-LC/MS study of chlorinated herbicides, a TSP-LC/MS study of carbamate pesticides, and a PB-LC/MS study of benzidines. Volmer et al. used TSP-LC/MS to determine 128 pesticides having a wide range in structure and polarity. Sennert et al. used on-line enrichment and TSP-LC/MS to analyze for 51 polar pesticides in water, and Chiron et al. used on-line SPE with TSP-LC/MS to determine 34 pesticides and their transformation products in river and groundwater.
in Canadian lake sediment cores from the last 60 years. Sanchez-Rasero et al. used chiral GC-ion-trap-MS to simultaneously determine enantiomeric forms of mecoprop and dichlorprop in soil samples.

Several GC/MS studies were designed to simultaneously measure different classes of pesticides. Sensenman et al. published a pesticide survey of surface water in Arkansas conducted in 1989–1991 in which 59–62 lake and river/stream sites were sampled eight times and screened for 17 commonly used pesticides. Using SPE with GC/MS and UV detection, 256 detections of pesticides were made, representing 14 pesticides. Metolachlor represented 25% of the total detections, atrazine, 25%, norflurazon, 16%, and cyanazine, 14%. A total of 5% of the detections were above health advisories.

3. PAHs and PCBs

PAHs and PCBs continue to be pollutants of interest in environmental studies. GC/MS methods are mostly used, but newer LC/MS methods have been introduced, along with some innovative approaches. Two particularly innovative approaches involved the use of immobilized copper-IC/APCI-MS and capillary column-SFC-MS with APCI. Using the IC-MS method, the copper-coated column was used to separate portions of PAH extracts into a number of fractions, each containing a homologous series of different PAH classes. Using the SFC-MS method, a complex mixture of PAHs was investigated, and a detection limit of 40 pg was obtained for chrysene. Brincourt et al. published a method using Rydberg electron capture-MS to measure environmental contaminants, including PAHs, PCBs, and one dioxin.

Anadeto et al. evaluated three LC/MS interfaces for analyzing complex mixtures of PAHs—moving belt, particle beam, and APCI. In this evaluation, the moving belt interface was found to be too me-
chanically awkward and limited the use of different mobile phases. The particle beam interface provided useful EI spectra, but detection limits were poor (low ng range) and calibration curves nonlinear. The APCI interface produced both molecular ions (M+•) and protonated molecular ions (M + H)+ and provided detection limits in the low pg range with linear calibration curves. Using APCI-MS, 17 target PAHs could be detected and quantified in a complex coal tar reference material, whereas PB-MS only detected 7 of the 17 PAHs. Thomas et al. used LC-APCI-MS/MS to determine polycyclic aromatic heterocycles in sediment samples, and Pace and Betowski used PB-LC/MS to measure high molecular weight PAHs. In the latter study, detection limits were found to range from 0.15 to 0.60 ng for PAHs with molecular weights up to 352 and from 2 to 4 ng for PAHs with molecular weights greater than 352. Linear calibration curves were obtained for PAHs with molecular weights of 300–352, and curves were nonlinear for PAHs of higher molecular weight.

Pyle et al. reported the analysis of PAHs with GC/ion-trap-tandem mass spectrometry. The collisionally induced dissociation (CID) spectra obtained showed differences in the relative abundances of progeny ions of isomers, which made the identification of specific isomers possible—an advantage over traditional EI-MS. On-line microwave extraction with GC/MS was evaluated for analyzing PAHs in sediment samples, and GC/MS was used for the compound-specific analysis of alkylated and parent PAHs in water, sediment, and aquatic organisms. Potter and Pawliszyn used SPME-GC/MS to rapidly determine PAHs and PCBs in water, with detection limits exceeding the regulatory requirements of EPA Method 525. Using GC/MS, Bodzek et al. reported the identification of nitro-PAHs in sewage sludge in an industrialized region of Poland. Bernstein et al. used IR and GC/MS to study the photolysis products of PAHs in ice; alcohols, quinones, and ethers were found to be the primary products formed. Disdler et al. used GC/MS to identify monocyclic and polycyclic aromatic hydrocarbons formed in thermolyzed waste products, and Spitzer and Takeuchi reported advances made in determining benzanthrone and other polycyclic aromatic ketones in environmental samples. Beriset and Holzer reported an SFE-GC/MS method for quantifying PAHs, PCBs, and organochlorine pesticides in sewage sludge.

PCBs have also been analyzed using multidimensional GC/MS with NCI detection, an in-line catalytic derivatization method with GC/laser-based resonance-enhanced multiphoton (REMPI)-TOF-MS, and electrothermal vaporization-ICP-MS. The multidimensional GC/MS method permitted the complete separation of coplanar PCB congeners in environmental and biological samples, which simplified the amount of sample pretreatment required. The REMPI-TOF-MS method selectively detected PCB isomers, and the ICP-MS method allowed organic and inorganic chlorine to be differentiated. High-resolution EI-MS was used in two methods. One combined the use of fast chromatography and two-dimensional GC with high-resolution MS to measure PCBs, PCDDs, and PCDFs. The other method used GC/high-resolution MS to measure polychlorinated naphthalenes in groundwater.

GC/EI-MS and GC/NCI-MS methods were compared for measuring PCBs in soils or sewage sludge. Another paper compared GC/MS to GC/electron capture detection (ECD) and GC/AED for determining PCBs in highly contaminated marine sediments. This comparison revealed that GC/MS (both low and high resolution) and GC/ECD measurements suffered from interferences from the complex matrix, whereas GC/AED in the chlorine-selective mode provided good PCB profiles without interferences. Two papers reported the use of microwave-assisted extraction with GC/MS for measuring PCBs in soil or sewage sludge. Siefert and Andersson developed a method for separating polychlorinated dibenzo- and polychlorinated dibenzofurans from PCDDs and PCDFs using low-resolution MS, and Werther et al. developed chemometric tools for deconvoluting GC/MS peaks of PCBs. Finally, GC/MS response factors and EI mass spectra were published for all 209 PCB congeners.

4. Dioxin

Dioxin measurements in waters and soil will be detailed here; dioxin measurements in biological samples can be found in the later section on Biological Samples. Dejong and Liem published a review of the use of GC/MS for ultra-trace detection of PCDDs and PCDFs in environmental and biological samples. Plomley et al. developed a rapid screening technique for tetrachlorodibenzo-p-dioxins (TCDDs) in complex environmental samples using GC/MS/MS with an ion-trap mass spectrometer. This method, TCDDs could be detected at 500 fg/L in extracts from fish, air, and soil. Sandell et al. used an activated carbon column as a rapid cleanup method prior to GC/high-resolution-MS for measuring PCDDs and PCDFs in soil and sediment; this method produced extraction efficiencies> 98%. Wunderli et al. used GC/high-resolution-MS to determine PCDDs and PCDFs in solid residues from wood combustion, and van Bavel reported results from an international intercalibration of PCDDs, PCDFs, and PCBs in fly ash extracts. Steinwandter reported a fast micromethod for determining 1,2,3,4,6,7,8-heptachlorodibenzo-p-dioxin and octachlorodibenzo-p-dioxin in sewage sludge, and Marbury et al. discussed the development and applications of an MS/MS method for quantifying PCDDs and PCDFs. Charles et al. presented an appraisal of MS/MS analyses of PCDDs and PCDFs using new data on collision energy. This evaluation revealed that in the absence of interferences, MS/MS and high-resolution MS provided similar data for these compounds. Takasuga et al. presented experiences with mass peak profile monitoring of dioxins. Finally, Umlauf et al. presented an extensive study of recent dioxin levels (1994–1995) in Seveso, Italy, where the largest accidental exposure of dioxin took place in 1976. GC/high-resolution-MS was used to measure dioxin in soil, plants, and earthworms in the area. An interesting finding was that the highest
concentrations of dioxin were found not at the sites of maximal concentration in 1976 but northwest of that area, where there were initially lower concentrations after the accident. It was not clear whether this was due to insufficient remediation or other reasons.

5. VOCs

Traditionally, VOCs have been measured by headspace GC/MS and purge-and-trap-GC/MS. Recently, several MIMS applications have also been reported. Ojala et al. compared MIMS to purge-and-trap-GC/MS and static-headspace GC for measuring VOCs (toluene, benzene, trichloroethene, and volatile sulfur-containing compounds). Both MIMS and purge-and-trap-GC/MS were used for detection limits <1 μg/L, whereas headspace GC detection limits were in the low μg/L range. MIMS has been used to directly measure VOCs in water, drinking water, and seawater. The combination of MIMS with mass-selective ion storage (using an ion-trap MS) was found to enhance sensitivity so that ppq levels of some VOCs could be measured directly in aqueous solution. Detection limits of VOCs in seawater were in the ppt range, with detection limits of 300 ppt for chlorobenzene and 190 ppt for trans-1,2-dichloroethene. MIMS has also been used to study the photocatalytic degradation of phenol and trichloroethylene in a continuous manner. Purge-and-membrane MS was used in a few studies to measure VOCs in water and soil. This procedure involves the purging of VOCs from a water or soil sample with an inert gas and directing the stream through a membrane into the mass spectrometer for analysis. It offers an advantage in that complex samples, such as soils and sludge, can be directly analyzed.

GC with direct aqueous injection (DAI)-MS has also been used to analyze VOCs in water. In one of these studies, 24 VOCs could be separated and analyzed in 12 min, with detection limits of 20 ppb and no preconcentration. Schwengkofler and Niessner reported a GC/MS/atomic emission spectroscopy (AES) method for determining siloxanes and VOCs in landfill gas and sewage gas. Pawliszyn et al. developed the use of SPME for concentrating analytes without the use of a solvent and described the detection of substituted benzenes in water at pg/ml levels using SPME with GC/ion-trap-MS. Two papers reported the development of SPME-GC/MS methods for determining VOCs in wastewater and sewage-polluted water and drinking water/surface water. The latter method reported the analysis of 55 VOCs with concentrations as low as 0.05 ppb detected. Buszka et al. determined ng/L levels of VOCs in water using GC/selected ion monitoring-MS to define groundwater flow directions in a Texas aquifer. GC/MS has been used to determine VOCs in plant leaves and purge-and-trap-GC/MS was used to measure VOCs from a hydrothermal site in the Gulf of California.

6. Textile Dyes

Textile dyes have been an environmental concern for several years. Millions of pounds of dyes are used each year by the textile industry, and it is estimated that approximately 15% of the total dye is lost in the manufacturing and application process, with most being discharged in the textile mill effluents. Sulphonatedazo dyes make up a significant portion of the textile dyes used, and there is information that both the intactazo dye molecule and the aromatic amine metabolites cause cancer in laboratory animals. With the advent of FAB-MS in the early 1980s, nonvolatile sulphonatedazo dyes could be measured intact for the first time. Monaghan and co-authors published the first FAB-MS analyses of sulphonatedazo dyes and soon other reports followed. Later, studies using liquid SIMS-MS/MS for analyzing sulphonatedazo dyes, reactive dyes, and cationic dyes were published. Liquid SIMS is a technique identical to FAB except that fast ions (usually cesium) are used to bombard the sample instead of fast atoms (usually argon), and detection limits are generally a little better than with FAB. Because FAB-MS and liquid SIMS generally form only molecular ions, the use of tandem mass spectrometry has been important for obtaining structural information for these dyes. Continuous-flow FAB-MS, which was developed later, allowed samples to be analyzed continuously, without having to replenish a sample on a traditional static probe. Although newer LC/MS methods have been developed, some groups are still using FAB-MS for analyzing sulphonatedazo dyes. One recent study involved the monitoring of river water that was polluted with dye wastes.

Thermospray, particle beam, APCI, and electrospray LC/MS and LC/MS/MS have also been used for the analysis of sulphonatedazo dyes. In 1992, Straub et al. evaluated thermospray-, particle beam-, and electrospray-LC/MS for analyzing and characterizing 14 commercialazo and diazo dyes. LC/ESI-MS/MS has also been used for determining Remazol textile dyes in effluents and determining the behavior of dyes in wastewater treatment processes. Rafols and Barcelo used LC/APCI-MS to determine disulphonatedazo dyes, and LC/ESI-MS has been used to trace polar benzene- and naphthalene-sulphonates in treatment works and in industrial effluents. CE/MS has been used to study the photodegradation of textile dyes and to measure textile dyes in groundwater and industrial effluents. Fournier transform ion cyclotron resonance (FT-ICR)-MS has been used to determine 3,3-dichlorobenzidine and its degradation products. The aromatic amines that originate from azo dyes have been determined by chemical reduction combined with LC/MS or GC/MS. GC/MS has also been used with SPME to determineazo dyes or with SPE to determine naphthalenesulphonates.

7. Surfactants

Like textile dyes, surfactants are generally non-volatile (and many surfactants are ionic), causing them to be difficult to analyze until techniques such as FAB-MS and LC/MS techniques were developed. Millions of tons of surfactants are used every year, mostly through the use of household detergents. Many surfactants in use now, such as linear alkyl-
benzene sulfonates (LAS), are biodegradable and can be removed in municipal wastewater treatment plants. There is also renewed interest in nonylphenol polyethoxylates and their metabolites, due to their weakly estrogenic properties. Four reviews have been published on mass spectrometry methods and determinations of surfactants. Reemtsma reviewed methods of analysis for polar aromatic sulfonates (including LAS) in aquatic environments. In 1998, DiCorcia reviewed LC/MS methods for characterizing surfactants and their biointermediates. Marcomini and Zanette presented chromatographic procedures available for determining alcohol polyethoxylates in environmental samples. Cserhati and Forgacs reviewed chromatographic techniques for the separation and quantitation of nonionic surfactants used as pesticide additives.

Ventura et al. published one of the earlier methods using FAB-MS and FAB-MS/MS for measuring different classes of industrial surfactants in raw and drinking water extracts. This method permitted the measurement of anionic, nonionic, cationic, and amphoteric surfactants. Desorption chemical ionization (DCI)-MS was another earlier technique used for determining nonionic surfactants. Later, LC/MS and LC/MS/MS techniques were used to measure linear alcohol ethoxylates, alkyl ethoxysulfates, linear alkyl benzene sulfonates (LAS), and cationic ammonium surfactants. Using LC/MS, alkylphenol ethoxylates have been detected in river water in the United Kingdom at levels of 5.6 μg/L, in drinking water samples at ppt levels, in tannery wastewaters at levels of 0.03–3.0 mg/L, and in marine sediments. LC/MS was used to investigate the fate of linear alkyl benzene sulfonates and their coproducts in controlled laboratory degradation studies and in natural marine water. In the latter study, it was found that the biodegradation of LAS is a slow process in a marine environment that is deficient in oxygen and highly contaminated with other organic substrates.

One paper has reported the use of CE/ESI-MS for measuring alkyl sulfonates, and recently, MALDI-TOF-MS has been used to measure nonylphenol ethoxylates, with detection limits in the μg/L range. Both ESI-MS and MALDI-TOF-MS techniques offer an advantage over GC/MS techniques in that higher molecular weight surfactants (with 10–20 ethoxylate units) can be measured. GC/MS has also been used in some studies to measure surfactants—mostly through derivatization. Field et al. developed a method for analyzing secondary alkane sulfonates and linear alkylbenzene sulfonates in sewage wastewaters using SPE and injection-port derivatization-GC/MS. This method required no sample cleanup steps and permitted recoveries of 92–98% from raw sewage and >85% from primary and secondary sewage effluents, respectively. Ding and Chen analyzed LAS in water samples using large-volume injection-port derivatization and GC/MS. This method produced reproducible results and detection limits of 0.1 μg/L for 200-mL water samples. Ion-pair chromatography was used with GC/MS to determine aromatic sulfonic acids in industrial wastewater and anion exchange-SPE was used with GC/CI-MS to determine nonylphenol polyethoxylate metabolites in paper mill effluents, municipal sewage treatment plant effluents, and river water. Finally, Lee and Peart used GC/MS to measure 4-nonylphenol in effluents and sludge from sewage treatment plants; samples collected from the Toronto area showed concentrations from ~1 to 30 μg/L in the effluents and >100 μg/g in sludge.

8. Disinfection Byproducts

As discussed earlier in the Historical Perspective section, drinking water disinfection byproducts (DBPs) were one of the earliest chemicals of concern in the environment. DBPs are formed when a disinfectant, such as chlorine or ozone, reacts with natural organic matter present in the water. There is concern over DBPs because several have been shown to cause cancer in laboratory animals. There is also renewed concern due to results of recent epidemiological studies that have linked DBPs to adverse reproductive effects, such as significant increases in early miscarriage. Although there are justifiable concerns about the risks of DBPs, the benefits gained by disinfecting drinking water should not be forgotten. Until the early 1900s, waterborne diseases, such as cholera and typhoid, caused death on a significant scale in industrialized nations. When chlorine was introduced with filtration for disinfecting drinking water, the incidence of waterborne diseases dramatically declined. Thus, removing microorganisms remains a primary concern. At the same time, however, the chemical byproducts produced from chlorine and other disinfectants are also of significant concern.

Richardson published a review of drinking water DBPs in 1998 which summarized all of the known DBPs from the commonly used disinfectants, discussed analytical methods used to identify them, and discussed any known health effects. Glaze and Weinberg published a report in 1993 on the identification and occurrence of ozonation byproducts in drinking water. Weinberg also published a recent article detailing the analytical challenge in identifying DBPs in drinking water, particularly for polar and nonvolatile DBPs. In this article, Weinberg explains how only a portion of the total organic halide (TOX) in chlorinated drinking water has been identified and seeks input from the greater analytical community to identify ways to uncover the DBPs that are being missed.

Drinking water DBP studies generally focus on one of four areas: (1) identification of new DBPs that have not been previously reported, (2) identification of a targeted DBPs, such as those that are regulated, (3) identification of DBPs from the reaction of natural organic matter or model compounds with disinfectants, and (4) development of new methods for measuring particular DBPs. Mass spectrometry has been a key tool for all of this work. Several early studies are mentioned in the Historical Perspectives section. More recent papers include those that have looked at several disinfectants for treating drinking water. Krasner et al. reported the occurrence of DBPs in U.S. drinking water in a 1989 study.
 involving the targeted analysis of DBPs from chlorine, ozone, and chloramine. This study used GC/MS and GC/ECD. Richardson et al. published a recent study that identified several new ozone, chlorine, and chloramine DBPs and also DBPs formed by the combination of ozone and secondary chlorination or chloramination. GC/IR and GC/MS (with high- and low-resolution EI and CI) and derivatization with PFBHA or BF3-methanol were used to identify these new byproducts. A separate paper studied the effect of elevated bromide levels on DBPs produced by the same disinfectants. In this study, an entire family of bromo- and mixed bromochloro-panones were found to be formed by chlorine and chloramine. DBPs from chlorine have also been the focus of other studies. One of these studies involved the GC/MS identification of chlorination DBPs from 10 drinking water treatment plants.

Mass spectrometry has also played a key role in the identification of a DBP called 'MX' [3-chloro-4-(dichloromethyl)-5-hydroxy-2(5H)-furanone]. This compound was found to be responsible for 20–50% of the total mutagenicity of chlorinated drinking water, making it the most mutagenic DBP ever identified in drinking water. It was termed ‘Mutagen X’ before its complete structure was solved. A recent study has shown that MX is not only mutagenic but also causes cancer in laboratory animals. MX was first identified in pulp mill effluent, and later it was found to be a byproduct of the chlorination of humic material and a chlorination byproduct in several drinking water samples taken from Finland, Great Britain, the United States, and Spain. MX has also been found to be formed by monochloramine. In 1992, Charles et al. developed a new high-resolution MS method for determining MX in water at ppt (ng/L) detection limits. In 1995, mass spectrometry was used to identify brominated forms of MX that are formed in chlorinated drinking water when natural levels of bromide are present.

Several studies of ozone DBPs have also utilized mass spectrometry. In 1989, Glaze et al. reported the improvement of an aqueous-phase PFBHA derivatization method that enabled the extraction and identification of polar carbonyl DBPs, such as formaldehyde. Glaze et al. later reported the use of PFBHA derivatization, closed-loop stripping analysis, and nonionic resin accumulation with GC/MS for identifying new ozone DBPs. Other studies followed, including those that focused on the formation of brominated DBPs when water containing elevated levels of bromide was ozonated. Coleman et al. used GC/MS with EI and Cl to identify DBPs from ozonation/post-chlorination of drinking water. LeLacheur et al. used GC with EI-MS and positive- and negative-ion CI-MS to identify carbonyl ozone DBPs. In 1997, Weinberg and Glaze presented a unified approach for analyzing polar organic DBPs from ozone. This approach involves the simultaneous recovery and preconcentration of mono- and multifunctional carbonyl-containing species from a single aqueous sample. Recently, LC/ESI-MS has also been applied to identify ozone DBPs in drinking water.

Relatively few studies of chlorine dioxide DBPs have been conducted using mass spectrometry. Colclough et al. conducted the first comprehensive analysis of organic DBPs from chlorine dioxide using GC/MS with EI and CI. Richardson et al. used a combination of GC/MS techniques (low- and high-resolution EI and CI) and GC/IR to identify several new DBPs from chlorine dioxide and also from chlorine dioxide/post-chlorination. GC/MS and GC/IR have also been used to identify DBPs from an experimental TiO2/UV treatment of drinking water and TiO2/UV followed by secondary chlorination. This experimental treatment has been used for wastewater and has potential for drinking water. UV disinfection has been shown to kill microorganisms, and TiO2 is used as a photocatalyst to degrade pollutants, such as pesticides, that are present in the raw drinking water, as well as potentially degrade DBPs as they are formed. In this study, only a single DBP was detected—a diketone—from TiO2/UV treatment with several chlorinated DBPs formed after post-treatment with chlorine.

Controlled laboratory studies of the reaction of disinfectants with humic material or with model compounds has helped in the understanding of mechanisms involved in the formation of DBPs. Carlson and Lin used GC/MS to characterize products from the reaction of hydroxybenzoic acid and hydroxycinnamic acids (as model compounds) with chlorine, chlorine dioxide, and chloramine. In this study, chlorine dioxide was found to efficiently convert p-hydroxybenzoic acids to p-benzoquinones; whereas use of chlorine alone would lead to further oxidation. Therefore, chloramine appeared to mediate and limit reactions of chlorine. Many studies have used GC/MS to study the reaction of chlorine with humic acid, fulvic acid, and amino acids. In one of these studies, Coleman et al. found that nine types of halogenated DBPs found from the reaction of chlorine with humic acid accounted for about 25% of the total organic halogen (TOX) formed. These compounds included trihalomethanes, -acetic acids, -acetonitriles, -propanones, -propenals, -propenenitriles, -propenes, -phenols, and -thiophenes. The similarity of these compounds to those previously identified in drinking water suggested that the reaction of chlorine with natural aquatic humic material is a likely source of mutagen formation in drinking water. In another study by Christman et al., the reaction of chlorine with isolated humic acid was studied and products identified with GC/MS. The main classes of products formed were non-chlorinated substituted aromatics, non-chlorinated straight-chain acids, and chlorinated straight-chain acids. The most abundant compounds identified were found to be dichloroacetic acid, trichloroacetic acid, and 2-chloropropanionic acid. Because the haloacids have also been found in reactions of the model compounds, resorcinol and 3-methoxy-4-hydroxycinnamic acid, it was postulated that the reaction mechanism involved a ring rupture of activated...
GC/MS has also been used to study the reaction of ozone with humic acid,\textsuperscript{588} fulvic acid,\textsuperscript{589–591} or amino acids.\textsuperscript{592,593} In one of these studies, Killops found that carboxyl- and carbonyl-containing compounds were produced from the reaction of ozone with humic and fulvic acids.\textsuperscript{588} Anderson et al. also observed the formation of carboxylic acids from the reaction of ozone with fulvic acid.\textsuperscript{589} and Lawrence observed the formation of carboxylic acids and cyclic ketones. LeLacheur and Glaze studied the formation of byproducts from the reaction of ozone or hydroxyl radicals with serine.\textsuperscript{593} They found that reactions of ozone with serine under radical-scavenging conditions (O$_3$ reaction route) led to the formation of carboxyl and carboxylic acid byproducts, whereas radical-promoting conditions (OH$^-$ reaction route) led to the formation of hydroxyl, carbonyl, and carboxylic acid byproducts.\textsuperscript{593} In a later study, Hureiki et al. studied the reaction of ozone with several amino acids and found that the molecular ozone reaction pathway (O$_3$ reaction route) favored the formation of aldehydes, such as formaldehyde, acetaldehyde, glyoxal, and glyoxal derivatives, and that the amino acid side chains appeared to be the main sites responsible for the high ozone reactivity with polypeptides.\textsuperscript{592} The reaction of monochloramine with fulvic acid\textsuperscript{594} and resorcinol (as a model compound)\textsuperscript{595} have also been studied with GC/MS.

Recent methods that have been developed to analyze DBPs in water include a new ESI-high-field asymmetric waveform ion mobility spectrometry (FAIMS)-MS method.\textsuperscript{596} This FAIMS instrument is an ion filter that can be tuned to continuously transmit selected ions from a complex mixture. The ESI–FAIMS-MS method developed allowed the measurement of six haloacetic acids at detection limits ranging from 0.5 to 4 $\mu$g/L and offered a significant reduction in the chemical background.\textsuperscript{596} SPE-GC/MS\textsuperscript{597} and SPME-GC-ion-trap-MS\textsuperscript{598} methods have also been developed for determining haloacetic acids in drinking water. Detection limits for the SPME method were reported to be 10–200 ng/L.\textsuperscript{598} Merkel et al. also recently reported an SPME-GC/MS method for determining drinking water DBPs.\textsuperscript{599} and Prakash et al. reported the performance of a purge-and-trap-GC/ion-trap-MS method for the routine analysis of cyanogen chloride in several hundred drinking water samples.\textsuperscript{600} The latter method was used to analyze drinking water samples collected as part of an 18-month national survey associated with the Information Collection Rule and produced detection limits of 0.02 $\mu$g/L with a linear dynamic range of 0.1–20 $\mu$g/L.\textsuperscript{600}

9. Taste and Odor Compounds

GC/MS methods have been published for measuring geosmin and 2-methylisoborneol (MIB), which are metabolites of biological organisms (actinomycetes, blue-green algae) that are often responsible for earthy-musty odors in drinking water.\textsuperscript{601–603} One of these methods utilized microextraction with hexane and analysis with GC/ion-trap-MS and measured a number of odor-causing organic compounds in addition to geosmin and MIB.\textsuperscript{601} Another method used isotope dilution high-resolution MS for measuring geosmin and MIB\textsuperscript{602} and the third method used SPME with GC/MS, which involved shorter analysis times but comparable sensitivity to closed-loop stripping analyses (CLSA).\textsuperscript{603} Khiari et al. used sensory GC with MS to identify chemicals responsible for septic and decaying vegetation odors in natural waters and reference samples.\textsuperscript{604} In this study, dimethyl disulfide, dimethyl trisulfide, and 2-isobutyl-3-methoxypyrazine were found to be the principal contributors to decaying vegetation odors whereas dimethyl trisulfide and indole were strongly associated with septic odors.\textsuperscript{604} Kenefick et al. used GC/MS with CLSA to analyze odor-causing compounds in the Athabasca River in Alberta, Canada, and found that compounds from a bleached kraft mill effluent were detectable 950 km downstream and were responsible for the odors.\textsuperscript{605} Brownlee et al. used olfactory GC with GC/MS to identify a variety of sulfury odors in extracts of bleached kraft pulp mill effluent; compounds that were identified include dimethyl disulfide, dimethyl trisulfide, 3-methylthiophene, and thioanisole.\textsuperscript{606} Romero et al. studied odor-causing compounds in river waters and groundwaters in Spain, using CLSA, flavor profile analysis, and purge-and-trap with CI-MS and EI-MS/MS.\textsuperscript{607} Compounds that were found to be the most significant in river water and groundwater were 2-alkyl-5,5-dimethyl-1,3-dioxanes and 2-alkyl-4-methyl-1,3-dioxolanes, with a threshold odor of 10 ng/L for 2-ethyl-5,5-dimethyl-1,3-dioxane, the most malodorous compounds. These byproducts were found to originate from a company that manufactures resins, and discharge of these dioxanes and dioxolanes into the river was found to impact the aquifer.\textsuperscript{607} Hassett and Rohwer reported the analysis of odorous compounds in water using closed-loop stripping with a multichannel silicone rubber trap followed by GC/MS.\textsuperscript{608} This technique allowed absorbed compounds to be directly thermally desorbed from the rubber trap, eliminating the solvent extraction step that is used with CLSA analyses.

10. Algal and Bacterial Toxins

Algal and bacterial toxins have been responsible for large fish kills, the poisoning of shellfish, and illness of swimmers, forcing the temporary closing of many beaches used for recreation. ‘Red tide’ algae are the better known of these toxin-producing organisms. Mass spectrometry has been an important tool in identifying these hazardous compounds. Sirén et al. reported methods using CE and micellar electrokinetic chromatography with ESI-MS/MS for identifying cyanobacterial hepatotoxins in water.\textsuperscript{609} Takino et al. used on-line derivatization with LC/ESI-MS for identifying anatoxin-a, which is produced by cyanobacterial blooms in freshwaters.\textsuperscript{610} Derivatization was carried out with fluorenyl methylchloroformate; recoveries were found to be 76%, with detection limits of 2.1 ng/L. Sherlock et al. reported the use of a similar method involving derivatization of microcystins with 2-aminoethanethiol and analysis with ESI-MS.\textsuperscript{611} Using this method, the authors reported
the first identification of microcysts in Irish lakes. Kaya and Sano used GC/Cl-MS to determine microcysts in water, and Dembitsky et al. used serially coupled capillary columns with consecutive nonpolar and semipolar stationary phases to separate and identify hydrocarbons and other VOCs from blue-green algae. Using this procedure, more than 130 metabolites were identified, with the most abundant family of hydrocarbons being derivatives of cyclohexane and cyclopentane. Pleasance et al. compared ion spray-MS methods to analyze paralytic shellfish poisoning toxins. In this study, flow injection analysis (FIA), LC, and CE separation techniques were evaluated; tandem mass spectrometry was also used to obtain structural information on these toxins. Gallacher et al. used LC, CE/MS, and immunoassay techniques to determine paralytic shellfish toxins; evidence was obtained for their production by specific bacteria. James et al. used LC/MS and LC/MS/MS to identify new pectenotoxin-2 analogues from marine phytoplankton and shellfish. These toxins have been shown to be responsible for diarrhetic shellfish poisoning and were isolated from toxic marine phytoplankton in waters off the coast of Ireland. Hua et al. reported an on-line LC/ESI-MS method for separating and identifying brevetoxins that are associated with ‘red tide’ algae. Brevoxins, which have a polyether structure, are responsible for many fish kills and pose health risks to humans. Detection limits of this method were <600 fmol, 1 pmol, and 50 fmol, respectively, for the three brevetoxins analyzed PbTx-9, PbTx-2, and PbSx-1.

11. Other Organic Pollutants

This section covers the measurement of such compounds as pharmaceuticals, phenolic compounds, various chlorinated compounds, nitrosamines, other amines, carboxylic acids, alcohols, phosphates, phthalates, chemical warfare agents, and petroleum products. A few recent studies have focused on the measurement of pharmaceutical compounds in environmental samples. Hartig et al. reported the detection and identification of sulfonamide drugs in municipal wastewater using LC/ESI-MS/MS. In this study, 13 sulfonamide drugs were measured and sulfamethoxazole and sulfadiazine were found in concentrations ranging from 10 to 100 ng/L in primary and secondary municipal wastewater effluents. Hirsch et al. used LC/ESI-MS/MS to determine penicillins, tetracyclines, sulfonamides, and macrolid antibiotics down to the lower ng/L range. Ternes et al. used LC/ESI-MS/MS and GC/MS to determine neutral drugs and betablockers in wastewater, river, and drinking water. Muller et al. studied the enantioselectic degradation of ibuprofen and the herbicide meprop in surface waters and sewage using chiral GC/MS. Both enantiomers of ibuprofen were found to degrade efficiently in raw sewage, with the S-enantiomer degrading faster; the same effect was observed in lake water. Huppert et al. developed a method using SPME with GC/MS to determine ibuprofen in wastewater. Daughton and Ternes published a review in 1999 that discussed the environmental origin, distribution and occurrence, and effects of pharmaceuticals and personal care products in the environment.

Phenolic compounds were the subject of several papers. Lafont et al. used CE/MS to quantify several phenolic compounds in olive mill wastewater with detection limits of 1–390 pg. Other papers reported the use of LC/ESI-MS for measuring phenolic compounds. Motoyama et al. used column-switching semi-microcolumn LC/ESI-MS to measure trace levels of bisphenol A and nonylphenol in river water. This method produced detection limits of 0.5 and 10 µg/L for bisphenol A and nonylphenol, respectively. Puig et al. reported the ppt level determination of 19 priority phenols in water using on-line liquid/solid extraction followed by LC/APCI-MS. With this method, three compounds—phenol, methylphenol, and 2,4-dimethylphenol—could not be detected by APCI-MS unless a porous graphite carbon column was used with 100% methanol elution. Puig et al. compared three different LC/MS interfaces—TSP, APCI, and ion spray—for determining priority phenolic compounds in water. APCLI offered an order of magnitude improvement in sensitivity, with detection limits ranging from 3 to 180 ng in full-scan mode and 0.001 to 0.085 ng with selected ion monitoring. Johnson et al. used LC/ESI-MS to identify the products and intermediates of the electrochemical incineration of 4-chlorophenol. Alimpiev et al. reported a laser ionization-TOF-MS procedure for analyzing phenol in tap water; this method allowed detection down to 1 µg/L.

Phenolic compounds have also been measured by a variety of GC/MS procedures. Bolz et al. developed an SPE-GC/MS method for determining phenolic xenoestrogens in surface water and sewage. Cheung and Wells used SPE-GC/MS with direct on-column benzoylation and negative-ion CI-MS to analyze eight phenolic compounds in sewage effluents. This method utilized a nonionic polystyrene divinylbenzene polymeric sorbent, which was superior to graphitized carbon black, and allowed detection limits at ppt levels. Crespin et al. used GC/MS in the EI and NCI modes to discriminate the structural isomers of chlorinated phenols in water. Baltussen et al. reported a thermal desorption-GC/MS method for determining phenols in water; derivatization with acetic anhydride was used, and detection limits of 1–5 ng/L were obtained. Geissler and Scholer reported a GC/MS method for determining phenol, methylphenols, chlorophenols, nitrophenols, and nitroquinones in water at 0.1 µg/L levels. This method used continuous liquid–liquid extraction, derivatization with diazomethane or trimethylsulfonium hydroxide, and analysis by GC/MS. Finally, Zapf and Stan reported a GC/MS method using online methylation with trimethylsulfonium hydroxide and large-volume injection for analyzing organic acids and phenols in water. Using this procedure, carboxylic acids and phenols could be detected in 5 mL of tap water at concentrations of 0.04–0.1 µmol/L in the full-scan mode.

Chlorinated compounds were also the focus of several papers. Sinkkonen published a review of the environmental analysis of chlorinated aromatic thio-
ethers, sulfoxides, and sulfones. Polychlorinated dibenzothiophenes and diphenylsulfides have been found in pulp mill effluents and in waste combustion processes; chlorinated sulfoxides and sulfones have been found to be metabolites or oxidation products of different chlorinated aromatic compounds. SPE and LC/MS or LC with electrochemical detection was used to determine chlorobenzenes in industrial effluents. The difficulty in analyzing organic compounds in industrial effluents is the high total organic carbon (TOC) and particle content. In this study, several different polymeric solid-phase extraction cartridges were evaluated to extract chloroanilines and chlorobenzenes from industrial effluents ranging in TOC from 1 to 70 mg/L. Microwave-induced plasma-MS was evaluated as an element-selective detector for SFC for the determination of halogenated compounds; detection limits for 1-chloronaphthalene and 1-bromo-2-methylnaphthalene were found to be in the low pg range, with linear ranges over 3 orders of magnitude. Curie-point pyrolysis-GC/tandem MS was used to selectively determine macromolecular chlorogenic acids (MW >1000) in river water and drinking water. This method was used for measuring chlorogenic acids in the River Rhine (Germany) and for studying the removal of these compounds in drinking water treatment. Trigg et al. used automated SPE with GC/MS for determining organochlorine compounds in sludge and sediment, with μg/kg detection limits, and Wang and Lee used SPE with GC/MS to determine chlorobenzenes in drinking water, river water, and groundwater at detection limits ranging from 0.01 to 0.042 μg/L. SPME-GC/MS was used to determine chloroethers in river water, with 100 ng/L detection limits and high precision (2.5% RSD).

Nitrosamines have been the subject of new methods using mass spectrometry. Volmer et al. developed an LC/ESI-MS method, coupled on-line with a photolysis reactor, to measure several N-nitosodimethylamines. Plomley et al. developed a GC/tandem mass spectrometry method using a quadrupole ion storage mass spectrometer to determine N-nitrosodimethylamine (NDMA) in complex environmental matrices. Using this method, concentrations were found to be comparable to those obtained by high-resolution MS, and interferences that can be problematic with GC/low-resolution-MS were not detected with this method. Taguchi et al. reported an isotope-dilution high-resolution-MS method for measuring NDMA in aqueous environmental samples. Using this procedure, NDMA could be detected as low as 1.0 ppt in water and a precision of 4% was obtained.

Different mass spectrometry techniques have been used to study amines. Zhao et al. developed CE and CE/ESI-MS methods for analyzing heterocyclic amines and Sacher et al. developed GC/MS methods for determining aliphatic amines, based on the derivatization of the amines directly in water with 2,4-dinitrofluorobenzene or benzenesulfonyl chloride. The GC/MS methods were used to measure aliphatic amines in industrial wastewaters and to determine the rate of occurrence of these amines in the aquatic environment. Peters and Vanduivenbode developed a GC/MS method for analyzing pyridine in soil and water using a distillation-extraction procedure. Detection limits were found to be 0.01 mg/kg for soil samples and 0.2 μg/L for water samples.

Methyl tert-butyl ether (MTBE) has become a pollutant of concern due to its use as an additive in gasoline, which has caused its transport throughout the hydrologic cycle. There have been documented impacts to surface and groundwaters, the latter from leaking underground storage tanks. MTBE is used as an oxygenated additive to meet Clean Air Act mandates for reduced emissions and as an octane booster, replacing alkylllead. However, when MTBE migrates into groundwater, there are aesthetic concerns because of low taste and odor thresholds and potential health impacts. Because of these concerns, there are moves to phase out the use of MTBE in gasoline; the U.S. EPA is now encouraging the use of ethanol in place of MTBE. As a result of recent interest in measuring MTBE in environmental samples, several analytical methods have been developed, including those using mass spectrometry. Lopez-Avila et al. used automated MIMS to directly analyze MTBE in water at low ppb levels with fast analysis times (5 min). Koester et al. developed a purge-and-trap GC/MS method that can detect MTBE at ppt levels in raw drinking waters. This method was used to measure several raw drinking waters in California. No detectable MTBE was found in deep groundwater (>1000 ft), but more shallow groundwaters (<250 ft) contained MTBE at concentrations of nondetect to 1300 ppt. In rivers and lakes, MTBE ranged from nondetect to 3500 ppt, and East San Francisco Bay area rainwater contained approximately 80 ppt of MTBE. Hong et al. used direct aqueous injection-GC/MS to analyze MTBE and its degradation products in water at mg/L detection limits.

Several mass spectrometry methods were reported for determining carboxylic acids. CE/ESI-MS, LC/API-MS, LC/MS, MIMS, and GC/MS methods have been published. CE/ESI-MS allowed the determination of small carboxylic acids at 1–10 ppm with little or no sample preparation, IC/API-MS permitted the analysis of small carboxylic acids and other anions with low ng detection limits, LC/ESI-MS was used to identify carboxylic acids containing several carboxyl groups in water, and LC/APCI-MS was used to determine several aliphatic, alicyclic, and aromatic carboxylic acids in groundwater.

Methods for measuring ethylenediaminetetraacetic acid (EDTA) were also reported. One used boron trifluoride–methanol derivatization with GC/MS for measuring EDTA and nitrilotriacetic acid in river water and sediment at 4–12 μg/L. Another used a method that converts the EDTA to a nickel–EDTA chelate, followed by automated SPE extraction and CE/ion spray-MS/MS.
analysis. Detection limits using the latter method were 0.15 μg/L for a 5 mL water sample.

MIMS was used to determine ammonia, ethanol, and acetate acid in aqueous solution, and derivatization with hexyl chloroformate was used to determine ethylene glycol in aqueous matrices, with a 0.1 mg/L detection limit in tap water. A GC/MS method, using derivatization with PFBBr on a polymeric phase-transfer catalyst, was developed for measuring dialkyl phosphates in aqueous samples. Methods were also developed for phthalates using CI-MS/MS and GC/MS. One of these papers reported results from a sampling campaign for the determination of phthalates in freshwaters and sediments of rivers and lakes in central Italy, which showed a direct relation between phthalate levels and the input of urban or industrial treated wastewaters. Polystyrene was measured in polluted sediments using pyrolysis-GC/MS, and terpenes were measured in water with MIMS, and organic contaminants were measured in water using SPME and GC/MS. In the latter study, 30 representative surface water samples were collected from rivers, lakes, and canals in Berlin, and synthetic musks were found at μgL/L levels.

Chemical warfare agents were also the subject of several papers. Positive- and negative-ion LC/APCI-MS was used to rapidly screen for hydrolysis products of chemical warfare agents in aqueous samples. In this study, negative-ion APCI provided selective detection of acidic analytes and allowed differentiation of alkyl alkylphosphonic acids from isomeric dialkyl alkylphosphonates. Limits of detection were in the range of 10–100 ng/mL. CE/ion spray-MS methods were developed to identify organophosphonic acids, which are the primary hydrolysis products of nerve agents. Nitroaromatics, which are explosives, and nitramines, which are degradation products of explosives, were measured using GC/MS after liquid–liquid extraction or SPE extraction or LC/thermospray-MS/MS. The latter method was applied to the measurement of nitroaromatic explosives and their degradation products in unsaturated-zone water samples collected in the United States.

Characterization of petroleum products from contaminated sites and identifying their source through isotopic fingerprinting has been the focus of several papers. Measuring these types of compounds in water, soil, and sediment often can link hydrocarbon pollution to previous oil spills. In 1995, Whittaker et al. reviewed methods for characterizing petroleum hydrocarbons in contaminated soil and water. In 1993, Krahn et al. published a review of LC methods for screening aromatic compounds in sediment, bile, and tissue samples; this review included discussions of the role that LC and GC/MS chromatographic patterns play in determining the source of contamination (e.g., crude oil, diesel fuel, or pyrogenic contaminants). Xie et al. compared a new GC/MS method to EPA Method 418.1 and to a rapid field method for quantifying petroleum product contamination. Havenga and Rohwer developed a headspace SPME-GC/MS method for screening soil samples polluted by coal tar or refined petroleum products. Reddy and Quinn developed a GC/MS method for measuring total petroleum hydrocarbons and PAHs in seawater samples after the North Cape Oil spill. In this study, more than 50 seawater samples were analyzed, and total petroleum hydrocarbon and PAH concentrations were as high as 3940 and 115 μgL/L respectively.

Isotope ratio-MS was used in several studies to determine the source of hydrocarbon pollution. In one of these studies, bitumen pollution along the coastlines of the Northern Territory in Australia was linked to oils originating from the Central Sumatra Basin. Wang and Fingas reported the differentiation of the source of spilled oil using GC/MS, and Munoz et al. developed a new approach using GC/high-resolution-MS and metastable reaction monitoring GC/MS/MS. White et al. reported the pyrolysis-GC/MS analysis of contaminated soils from Alaska and discussed complications from the presence of natural organic matter (NOM). In this study, the background interference from natural organic matter could be removed by quantifying biogenic indicators. SPME was used with GC/continuous flow-isotope ratio-MS for the molecular and isotopic analysis of gasoline hydrocarbons and isotope ratio-MS was used to determine isotopic fingerprints of shallow gases in the Western Canadian sedimentary basin. Beneteau et al. used isotope ratio-MS to link a groundwater plume of dissolved tetrachloroethylene emanating from a dry cleaner to a particular tetrachloroethylene manufacturer. GC/isotope ratio-MS was also used for the compound-specific isotope analyses of fatty acids and PAHs in aerosols. These compounds were investigated as potential tracer species for the products of biomass burning. Naraoka et al. used the carbon isotopic differences of saturated fatty acids to distinguish between terrestrial and marine sediments, and Bird et al. used carbon isotopic differences to link hydrocarbons found in marine sediments to terrestrial sources. Baylis et al. used GC/combustion-isotope ratio-MS to measure C1 to C5 compounds in natural gases without any sample preparation, and Dempster found that GC/combustion-isotope ratio-MS could be used to link BTEX (benzene, toluene, ethylbenzene, and xylene isomers) contamination to a specific manufacturer from distinct differences found in the δ13C values.

Finally, Zeng et al. reported the application of GC/combustion-isotope ratio-MS to carbon isotopic analyses of methane and carbon monoxide in environmental samples, including those from biomass burning.

### B. Inorganic Analyses

#### 1. Disinfection Byproducts

Several mass spectrometry methods have been published for measuring inorganic drinking water DBPs. Many of these methods have focused on bromate, which has been shown to be a potent rodent carcinogen and will be regulated by the U.S. EPA under the Stage 1 DBP Rule. Health effects data suggested that bromate should be regulated below 10 ppb; however, early methods could not reliably
meet this level. Therefore, many groups have worked to develop new methods that could accomplish lower detection limits. Some methods utilize IC (with no mass spectrometry), but other methods utilized mass spectrometry. Creed et al. developed an IC/ICP-MS method for bromate and obtained detection limits of 0.1–0.2 μg/L (ppb).699 This method was later updated to include isotope dilution. The revised method effectively separated bromate from interferences, such as bromide and brominated haloacetic acids, and produced detection limits of 0.3 μg/L.700 This method was later published as an EPA Method.128 Diemer and Heumann published a negative thermal ionization isotope dilution-MS method and an IC/ICP-MS method for measuring bromate.701 These methods produced detection limits in the range of 0.03–0.09 μg/L. Yamanaka et al. developed an IC-postcolumn derivatization/ICP-MS method for analyzing bromate and iodate in ozonated drinking water, with detection limits of 0.45 and 0.034 μg/L, respectively.702 Nowak and Seubert developed a microbore IC/ICP-MS method, with 0.05–0.065 μg/L detection limits and no sample pretreatment.703 This method also allowed short run times of 8–15 min. Charles et al. developed an earlier IC/ESI-MS/MS method for determining bromate at 0.1 μg/L, which at the time lowered the detection of bromate by a factor of 10.704 Charles and Pepin developed an IC/ion spray-MS/MS method for determining bromate, chlorate, iodate, and chlorite in water.705 The coupling of IC with ion spray-MS/MS allowed the detection of all four oxyhalides in a single run with high specificity and sensitivity. Buchberger and Ahrer published a method using suppressed and nonsuppressed IC with API-MS for determining bromate, iodate, sulfate, and thiosulfate in water.706 With this method, absolute detection limits of 0.4–0.7 ng were achieved.706 Barnett et al. reported a new method using ESI–FAIMS-MS which produced ppt detection limits for bromate, chloride, and iodate, with significantly improved signal-to-background ratios.707

Scifenti et al. evaluated three analytical techniques for measuring cyanogen chloride, which is a DBP primarily formed in chloraminated drinking water.708 In this study, purge-and-trap-GC/MS, headspace-GC/ECD, and micro-liquid/liquid extraction with GC/ECD were compared and determined to produce comparable results for cyanogen chloride analysis. Gazda et al. used MIMS to confirm the existence of bromochloramine and N-bromo-N-chloromethylamine as products of the reaction of monochloramine with bromide ion or hypobromous acid.709 Finally, Shang and Blatchley used MIMS to differentiate and quantify free chlorine, monochloramine, and trichloramine in drinking water and wastewater.710 Linear response curves over several orders of magnitude were obtained with detection limits of 0.06–0.1 mg/L.

2. Perchlorate and Dissolved Gases

In 1997, perchlorate was discovered to be a significant groundwater contaminant in northern California and subsequently has been detected by the California Department of Health Services in wells throughout California.711 Due to health concerns, many of these wells were shut down. Most commonly used methods for measuring perchlorate involve the use of IC; however, IC measurements are subject to interferences and newer mass spectrometry methods have been developed to provide added specificity needed to make unequivocal identifications. Urban-sky and Magnuson used ESI-MS with organic complexing agents to improve the detection of perchlorate in water.712 Using this method, distinctive high mass anions allowed for the specific and unique identification of perchlorate and detection limits were comparable to IC methods. Clewell and Tsui developed another ESI-MS method for determining perchlorate in water.713 Mass spectrometry methods have also been developed for dissolved gases. Kana et al. used MIMS to rapidly and precisely determine N₂, O₂, and Ar in environmental water samples.714 With this MIMS method, 20–30 samples could be measured per hour, with small sample sizes (<10 mL) and no sample preparation or degassing.

3. Multiple Elements

Groups of elements have been measured in environmental samples using a number of mass spectrometry techniques. Two of the newer techniques, CE/ESI-MS715,716 and CE/ICP-MS,717,718 have been used to measure metals and organometallic complexes with low μg/L detection limits. Rottmann and Heumann reported an on-line isotope dilution LC/ICP-MS method for accurately quantifying elemental species.719 IC/ICP-MS methods for measuring multiple elements have also been reported.720,721 Using one of these methods,720 trace elements were determined in seawater at 1–50 ng/L detection limits. Another paper reported the off-line separation of elements by IC and confirmation with ICP-MS for measuring 31 elements in radioactive waste sludge.722 Two papers reported methods using SFC/ICP-MS for determining multiple elements.723,724 One of these reported 3 pg detection limits for diethylmercury, 0.5 pg for tetrabutyllead, and 10 pg for tributyllead acetate.724 Gerdin et al. developed a thermal desorption-MS method for the rapid screening of contaminated soil samples,725 and several papers reported methods using electrothermal vaporization-ICP-MS for measuring metals in sediments, fresh water and seawater.726–730 One of these methods reported detection limits of 0.01–0.08 μg/L for As, Se, and Sb in freshwater,727 and another reported detection limits of 0.001–0.005 μg/L for Cd, Hg, and Pb in seawater.728 Several methods using on-line preconcentration with ICP-MS have also been published.731–736 One method utilized a hydroxyquinoline-based chelating ion-exchanger and ICP-MS to analyze 32 elements at low ng/L levels in seawater.731

Stetzenbach et al. developed an ICP-MS method that could determine 54 trace elements directly in groundwater at ppt levels.737 Using this method, elements were measured in four springs in Nevada and concentrations spanned almost 7 orders of magnitude. In another study, a dynamic reaction cell was coupled with ICP-MS to remove Ar-related spectral interferences in the analysis of multielements at sub-
ppt levels. Bayon et al. developed an alternative GC/ICP-MS interface design for the analysis of trace metals and organometallic compounds. Several papers published analyses of multiple elements in environmental samples using various ICP-MS methods. One paper reported the use of cold plasma conditions, another reported the use of laser ablation with ICP-MS for determining trace elements in geological samples, and another reported the use of continuous-flow hydride-generation with ICP-MS for determining Se, Sb, As, and Ge in seawater. Yi et al. developed a multiple-collector ICP-MS method for the precise determination of cadmium, indium, and tellurium in geological materials, and Hall discussed the capabilities of production-oriented laboratories in water analysis using ICP-MS and ICP-emission spectrometry. The latter paper discussed round-robin analyses of 22 lake water samples by eight laboratories.

4. Arsenic and Selenium

Several methods have been developed for measuring arsenic and selenium. ICP-MS has been used with ultrasonic nebulizers, membrane desolvation, and postcolumn reaction to improve the sensitivity for As(III), As(V), Se(VI), and Se(IV) with detection limits of 0.1 ng/L. LC/ICP-MS was used to simultaneously determine arsenic, selenium, and antimony species with detection limits of 0.5–4.5 µg/L. Flow injection-electrothermal vaporization-ICP-MS has been used to determine As and Se in seawater at 7 and 70 pg detection limits, respectively, using 0.5 and 10 mL samples. Arsenic and selenium were also determined in reference materials (oyster tissue, sediment, urine, water, and tomato leaves) using high-resolution ICP-MS; a resolution of 7500 enabled 75As and 77Se to be separated from ArCl interferences. Pergantis et al. developed an LC/ESI-MS/MS method for determining 10 organoarsenic compounds in environmental samples at low pg detection limits. Using this method, low µg/L levels of arsenobetaine were measured in undiluted urine.

Many papers have also been published on methods for arsenic species only. Recently developed CE/ICP-MS methods have allowed ng–µg/L detection limits for As(III), dimethyl arsenic acid, monomethyl arsine acid, As(V), arsenobetaine, and arsenocholine. Several methods were developed for the measurement of multiple metals in seawater. Saleh and Wilson analyzed metal pollutants in the Houston, TX, shipping channel using ICP-MS; this method provided 0.08–16 ng/L detection limits for the measurement of multiple metals in seawater. Saleh and Wilson determined heavy metals in groundwater using ICP-MS, and Gueguen et al. used UV irradiation to enable the ICP-MS analysis of metals bound to humic materials. ICP-MS methods were also used to determine trace elements in snow and ice. One of these studies sampled snow and ice cores from Greenland, Antarctica, and the Alps to assess the past natural background concentrations of metals and to determine their present levels. Another paper reported the use of ultraclean field and laboratory procedures and ICP-MS to measure trace element concentrations and total mercury in northern Alaskan snow. Two papers reported measurements of colloids. These studies used on-line flow-field-flow fractionation with ICP-MS to determine colloidal size and element distributions for 28 elements in natural waters. Gabler et al. used isotope dilution ICP-MS to determine the interchangeable heavy-metal fraction in soils, and two papers reported the analysis of metals in municipal landfill gas by ICP-MS and GC/ICP-MS. Katoh et al. used isotope dilution ICP-MS to determine six elements (Ni, Cu, Zn, Cd, Ti, and Pb) in atmospheric particles located in a remote mountainous region in Japan. Wang et al. reported two new SIMS methods for measuring metals in geological materials, and Hall discussed the capabilities of production-oriented laboratories in water analysis using ICP-MS and ICP-emission spectrometry. The latter paper discussed round-robin analyses of 22 lake water samples by eight laboratories.
been determined in 15N-enriched nitrite and nitrate isotope dilution-MS. Results of this study showed that isotopic compositions of materials at 0.01 pg, and the linear dynamic range spanned 2 orders of magnitude. Derivatization reagents have also been used with GC/MS to measure selenium. One of these methods reported ng detection limits after preconcentration. Haygarth et al. compared hydride generation (HG)-ICP-MS to HG-atomic absorption spectrometry (AAS), HG-ICP-atomic emission spectrometry (AES), radiochemical neutron activation analysis (RNAA), and fluorimetry for determining total selenium in environmental samples. For samples of low Se concentration, HG-ICP-MS and RNAA methods were found to be superior. Two GC/MS methods were developed for determining Se speciation; one used SPE for 1.4–900 ng/L detection limits for Se(VI), Se(IV), dimethylselenide, dimethylselenide, and diethylselenide; the other reported detection limits of 0.02 μg/L. GC/ICP-MS offered the advantage of transferring the total analyte into the ICP-MS without loss of analyte through nebulization. Finally, McCurdy et al. reported a hydride generation-ICP-MS method for determining selenium in digested sediment reference materials at 0.01–1.0 μg/L levels.

5. Lithium, Boron, Nitrogen, Sulfur, and Halogens

Lithium isotopic compositions have been measured in geological materials using multiple collector-sector-ICP-MS, which allowed small sample sizes (40 ng of Li) and rapid analyses (two samples/hour). 11H has been determined in 15N-enriched nitrite and nitrate in aqueous samples after reduction to NO and analysis by continuous flow-MS. Trace amounts of boron have been determined in rainwater using ICP-isotope dilution-MS and negative thermal ionization-isotope dilution-MS. Results of this study showed that there was significant dependence of the boron concentration in rainwater on the meteorological conditions but not on the season of sampling or on the altitude of the sample collection site. Other papers reported methods using high-resolution-ICP-MS for tracing the anthropogenic input of boron into surface and groundwater or isotope dilution-MS for determining boron in silicate rock samples. An ESI-MS method has been developed for measuring specific sulfur species and was demonstrated for measuring sulfate in wastewater. High-resolution ICP-MS has permitted the analysis of sulfur isotope ratio measurements with a high sample throughput and minimal sample preparation, and ICP-MS has permitted the separation and detection of sulfide, sulfite, sulfate, and thiosulfate. Iodine, bromine, fluorine, and chlorine were measured in geological reference materials using ICP-MS with IC, and ICP-MS has been used to measure I-129 and I-127 in environmental samples. The latter method was used to study the sources of radioactive iodine in soils; coniferous forest soils were found to have higher I-129 concentrations, and most of this iodine was retained in the first 10 cm.

6. Group IIIA Elements

Measurements of aluminum have included a new LC/ICP-MS method that permitted 0.3–0.6 μg/L detection limits in percolating water of forest soils and a flow injection-ICP-MS method that allowed the reactive aluminum fraction in water to be determined. Measurements of thallium have included the use of flow injection-hydride generation-ICP-MS, isotope dilution-MS, and multiple collector-ICP-MS. With the isotope dilution-MS method, Schielbauer and Heumann discovered the first evidence for the existence of dimethylthallium species in the ocean. With the multiple collector method, thallium was measured in geological materials and meteorites.

7. Group IVB and VB Elements

LC/ICP-MS has been used to determine vanadium species in seawater and river water, and ICP-MS has been used to determine titanium, vanadium, gallium, and indium in seawater and river water. One of these papers utilized hydroxyquinoline resin preconcentration for detection limits in the sub-ppt range, and another study used isotope dilution with electrothermal vaporization-ICP-MS for low pg measurements.

8. Group IIA Elements

Strontium has been measured in environmental samples using ICP-MS and accelerator mass spectrometry. One of these studies used quadrupole-based ICP-MS to measure 87Sr/86Sr isotope ratios in rock samples to provide information on the timing of geological events that affected the rocks over several millions of years after their initial formation. Barium has been measured in environmental samples (rocks, river water, rainwater, and seawater) using isotope dilution-ICP-MS.

9. Heavy Metals

Chromium species have also been determined using mass spectrometry. Recent IC/ICP-MS methods have been developed that allow the simultaneous detection of Cr(III) and Cr(VI) in water samples and in wastewater sludge incinerator emissions. In water, detection limits of 0.1 μg/L are possible and analyses can be completed in <3 min. LC/ICP-MS methods have also been recently developed for measuring chromium. Detection limits as low as 30–180 ng/L could be achieved when using a direct injection nebulizer with LC/ICP-MS. SFC–ICP-MS has also been used to determine organochromium compounds at pg detection levels.

GC/ICP-MS has been used to determine Ni(CO)₅, Fe(CO)₅, Mo(CO)₆, and W(CO)₆ in sewage gas from a municipal sewage treatment plant. This method provided useful speciation information for volatile transition metals that was not possible with previous...
methods. Double-focusing ICP-MS has been used to determine cadmium in environmental and biological reference materials, and isotope dilution-ICP-MS has been used to determine nickel in environmental waters. Isotope dilution-double-focusing ICP-MS has permitted high sensitivity and accuracy for determining iron in seawater. This method also used Mg(OH)₂ coprecipitation to preconcentrate iron from seawater, which permitted detection limits of 0.085 nM. Isotopic compositions of copper and zinc in rocks and biological materials have also been measured using ICP-MS.

The measurement of organometallic compounds in environmental samples has become important due to the toxic forms that can be present in the environment. For example, organotins have been widely used as the active ingredient in antifouling marine paints and have been identified in seawater samples in harbors. Concerns have arisen due to the toxicity of organotin compounds to marine organisms. Organotins are also used as fungicides, herbicides, and insecticides. GC/ICP-MS and GC/glow discharge-MS methods have enabled the separation and identification of organometallic compounds of tin, mercury, and lead in seawater and sediment. One method reported rapid analysis times (10 min) and low detection limits (0.13–3.7 ng/L as metal) with small sample sizes (25 mL of water, 0.5 g of sediment). Recent LC/MS methods have also been developed for measuring organotin compounds in seawater and sediment. LC has been coupled to ICP-MS to measure organotins and inorganic tin species in seawater and sediment. Using LC/ICP-MS, separations can be completed in less than 6 min, with detection limits in the range of 2.6–16 pg. Various GC/MS methods have been developed for measuring organotins in environmental samples. One of these methods has explored the use of ion-trap mass spectrometry, which provided a wide linear dynamic range (over 3 orders of magnitude) and pg sensitivity. GC/NCI-MS permitted detection limits of 20 pg/mL for tributyltin and triphenyltin, and detection limits in the range of 2.6–16 pg. Another method explored the use of microplasma spectrometry, which provided a wide linear dynamic range (over 3 orders of magnitude) and pg sensitivity. GC/ICP-MS methods have been developed for measuring organotins and inorganic tin species in seawater and sediment. GC/ICP-MS methods have provided sub-fg level measurements. Another interesting study of organotins in harbor sediment and water used GC/ICP-MS to measure butyltins in two marinas from the coastal area of The Netherlands, two years after their ban of tributyltin. Sediment concentrations showed no trend of decrease between 1992 and 1995, and levels were extremely high in the marina sediments from tidal action (17.5 μg/g) but much lower in the marina with tidal action (0.117 μg/g). ICP-MS has also been used to measure total tin in sediment reference materials.

Mercury compounds have been determined in environmental samples using LC/ICP-MS. GC/ICP-MS, ICP-MS, and ICP-MS methods have enabled the separation and identification of organotin compounds to marine organisms. Organotins are also used as fungicides, herbicides, and insecticides. GC/ICP-MS and GC/glow discharge-MS methods have enabled the separation and identification of organometallic compounds of tin, mercury, and lead in seawater and sediment. One method reported rapid analysis times (10 min) and low detection limits (0.13–3.7 ng/L as metal) with small sample sizes (25 mL of water, 0.5 g of sediment). Recent LC/MS methods have also been developed for measuring organotin compounds in seawater and sediment. LC has been coupled to ICP-MS to measure organotins and inorganic tin species in seawater and sediment. Various GC/MS methods have been developed for measuring organotins in environmental samples. One of these methods has explored the use of ion-trap mass spectrometry, which provided a wide linear dynamic range (over 3 orders of magnitude) and pg sensitivity. GC/NCI-MS permitted detection limits of 20 pg/mL for tributyltin and triphenyltin, and detection limits in the range of 2.6–16 pg. Another method explored the use of microplasma spectrometry, which provided a wide linear dynamic range (over 3 orders of magnitude) and pg sensitivity. GC/ICP-MS methods have been developed for measuring organotins and inorganic tin species in seawater and sediment. GC/ICP-MS methods have provided sub-fg level measurements. Another interesting study of organotins in harbor sediment and water used GC/ICP-MS to measure butyltins in two marinas from the coastal area of The Netherlands, two years after their ban of tributyltin. Sediment concentrations showed no trend of decrease between 1992 and 1995, and levels were extremely high in the marina sediments from tidal action (17.5 μg/g) but much lower in the marina with tidal action (0.117 μg/g). ICP-MS has also been used to measure total tin in sediment reference materials.

Mercury compounds have been determined in environmental samples using LC/ICP-MS. GC/ICP-MS, ICP-MS, and ICP-MS methods have enabled the separation and identification of organotin compounds to marine organisms. Organotins are also used as fungicides, herbicides, and insecticides. GC/ICP-MS and GC/glow discharge-MS methods have enabled the separation and identification of organometallic compounds of tin, mercury, and lead in seawater and sediment. One method reported rapid analysis times (10 min) and low detection limits (0.13–3.7 ng/L as metal) with small sample sizes (25 mL of water, 0.5 g of sediment). Recent LC/MS methods have also been developed for measuring organotin compounds in seawater and sediment. LC has been coupled to ICP-MS to measure organotins and inorganic tin species in seawater and sediment. Various GC/MS methods have been developed for measuring organotins in environmental samples. One of these methods has explored the use of ion-trap mass spectrometry, which provided a wide linear dynamic range (over 3 orders of magnitude) and pg sensitivity. GC/NCI-MS permitted detection limits of 20 pg/mL for tributyltin and triphenyltin, and detection limits in the range of 2.6–16 pg. Another method explored the use of microplasma spectrometry, which provided a wide linear dynamic range (over 3 orders of magnitude) and pg sensitivity. GC/ICP-MS methods have been developed for measuring organotins and inorganic tin species in seawater and sediment. GC/ICP-MS methods have provided sub-fg level measurements. Another interesting study of organotins in harbor sediment and water used GC/ICP-MS to measure butyltins in two marinas from the coastal area of The Netherlands, two years after their ban of tributyltin. Sediment concentrations showed no trend of decrease between 1992 and 1995, and levels were extremely high in the marina sediments from tidal action (17.5 μg/g) but much lower in the marina with tidal action (0.117 μg/g). ICP-MS has also been used to measure total tin in sediment reference materials.
orders of magnitude. Three papers reported pre-ng/mL sensitivity, with a dynamic range over 4 environmental samples. LC/ICP-MS permitted sub-ng/mL sensitivity, with a dynamic range over 4 orders of magnitude. Three papers reported pre-concentration methods for rare-earth elements using a flow injection-on-line precipitation system, a hydroxyquinoline-immobilized hollow fiber membrane, or by chelating resin preconcentration. An isotope dilution-ICP-MS method reported detection limits of 1–10 ppb. Another paper reported levels of rare-earth elements in Dutch drinking water and their sources. In this study, raw and treated drinking water from 18 groundwater stations and two surface water stations were sampled; significant amounts of rare-earth elements were found in the raw water from eight locations and in drinking water from three locations. Two of the drinking water samples contained rare-earth elements at levels exceeding admissible concentrations.

10. Rare-Earth Elements (Lanthanides) LC/ICP-MS and ICP-MS methods have been developed to measure rare-earth elements in environmental samples. LC/ICP-MS permitted sub-ng/mL sensitivity, with a dynamic range over 4 orders of magnitude. Three papers reported pre-concentration methods for rare-earth elements using a flow injection-on-line precipitation system, a hydroxyquinoline-immobilized hollow fiber membrane, or by chelating resin preconcentration. An isotope dilution-ICP-MS method reported detection limits of 1–10 ppb. Another paper reported levels of rare-earth elements in Dutch drinking water and their sources. In this study, raw and treated drinking water from 18 groundwater stations and two surface water stations were sampled; significant amounts of rare-earth elements were found in the raw water from eight locations and in drinking water from three locations. Two of the drinking water samples contained rare-earth elements at levels exceeding admissible concentrations.

11. Radionuclides Although liquid scintillation is still widely used for measuring radionuclides in environmental samples, mass spectrometry techniques are also commonly used. Quadrupole-based ICP-MS, double-focusing ICP-MS, electrothermal ICP-MS, and thermal ionization-MS methods have been used to measure radionuclides in environmental samples. Detection limits for one of these methods (ICP with quadrupole MS) was reported to be 0.012–0.11 ng/L for 226Ra, 230Th, 237Np, 238U, 239Pu and 241Am. Becker and Dietze reviewed the performance of double-focusing sector field ICP-MS for determining long-lived radionuclides. Hodge and Laing presented a new ICP-MS method for measuring radium-226 in drinking water, which provided fast analysis times (<3 min) and low detection limits (1 ppb). High-resolution ICP-MS enabled determinations of 226Ra in ground- and soil water at levels 10 times lower than could be attained with liquid scintillation. High-precision and high-accuracy isotopic measurements of uranium were made using ICP-multiple collector-MS. ICP-MS was used to measure the concentrations of uranium in soil and in air particulate matter in Kuwait following the 1991 Gulf War. In this study, it was found that average uranium concentrations in soil were one-half of what was found in particulate matter. Uranium concentrations in tap water were found to be very low (0.02 pg/L). High-resolution ICP-MS has enabled the determination of trace levels of plutonium in environmental samples (1–5 fg/mL for 239Pu, 240Pu, and 242Pu). In one of the more interesting studies of radionuclides, isotopic compositions of plutonium were measured in Irish Sea sediments using ICP-MS and thermal ionization-MS. Ion exchange preconcentration prior to ICP-MS analysis enabled the measurement of Tc-99 in seawater at 0.03 ng/L detection limits. Beals reported an isotope dilution-ICP-MS method for measuring Tc-99 in aqueous samples that was faster than radiometric techniques, was less subject to interferences, and had equal or better detection limits. Moran et al. used thermal ionization-MS to study the depth profiles of Th-230 and Th-232 in the Norwegian Sea and Denmark Strait. SIMS has also been used for measuring radionuclides in environmental samples. In one of these papers, SIMS was used to measure the distribution of dissolved and particulate Th-230 and Th-232 in seawater from the Gulf of Mexico and Cape Hatteras.

12. Other Inorganics Makishima et al. developed a rapid and accurate flow injection-ICP-MS method for determining zirconium, niobium, hafnium, and tantalum in geological materials at 0.1–40 ng/g detection limits. McKelvey and Orians developed an isotope dilution-ICP-MS method for determining dissolved zirconium and hafnium in seawater. Anbar et al. developed a chemical extraction-negative thermal ionization-MS method for determining iridium in natural waters. Finally, Klinkenberg et al. used LC/ICP-MS for determining tellurium in industrial wastewater; this method was used to monitor tellurium removal from wastewater.

VII. Microorganisms The measurement of microorganisms has long been an environmental concern due to pathogenic or toxin-producing organisms that can be present in drinking water supplies and ecosystems. Mass spectrometry has played a minor role in the past through the use of pyrolysis-GC/MS but is beginning to play a more important role with the advent of MALDI-MS and API-MS techniques. These techniques are allowing important protein and other biomarkers (and the entire organism itself) to be measured, enabling more specific information about the microorganisms than traditional microscopic techniques can offer. Saraf and Larsson published two reviews on the identification of microorganisms by mass spectrometry; the first is a general review, and the second is on the use of GC/ION-TRAP-MS for identifying microorganisms. Fenselau published an earlier review in 1994 on the characterization of microorganisms by mass spectrometry. In 1994, Cain et al. published a paper on the use of MALDI-MS for differentiating bacteria according to their protein profiles and Larsson published a paper on the use of GC/MS for determining chemical markers of microorganisms. In 1996, Siuzdak published the first report of a mass spectrum (by ESI-MS) of a complete, intact virus. His results demonstrated that ESI-MS could be used to determine biomolecules with molecular weights over 40 million Da and that the native biomolecular structure could be conserved through the electrospray process. Siuzdak proved...
that the viral structure remained intact in the mass spectral analysis by collecting the ions after passage through the mass analyzer and analyzing them by transmission electron microscopy. Transmission electron microscopy revealed that rice yellow mottle virus and tobacco mosaic virus retained their respective spherical and rodlike structures, and the viability of the isolated tobacco mosaic virus was confirmed by inoculation and infection of tobacco plants. Siudzak later used mass spectrometry to identify viral protein posttranslational modifications, such as myristoylation, phosphorylation, and disulfide bridging, and demonstrated that viruses are highly dynamic particles.\textsuperscript{931} Also in 1996, Holland et al. provided the first report of the identification of intact whole bacteria using MALDI-TOF-MS and reported the presence of species-specific mass spectral ions.\textsuperscript{932} Later in 1996, Claydon et al. published the rapid identification of intact bacteria using MALDI-TOF-MS.\textsuperscript{933} In this paper, intact Gram-negative and Gram-positive microorganisms were analyzed, and their mass spectra allowed the identification of microorganisms from different genera, different species, and different strains of the same species. Krishnamurthy et al. also published papers in 1996, reporting the MALDI-TOF-MS identification of intact whole cells of bacterial pathogens.\textsuperscript{934,935} This method enabled the direct measurement (in 10 min) of intact whole cells with no desalting and minimal sample preparation and allowed the assignment of biomarkers specific to the genus and species (and sometimes the strain) of the particular organism. More recently, Krishnamurthy et al. applied MALDI-TOF-MS to detect Cryptosporidium parvum oocysts and Giardia lamblia cysts.\textsuperscript{936} These waterborne pathogens have been responsible for many outbreaks of gastrointestinal illness in the United States and in other countries due to ingestion of drinking water that contained these treatment-resistant organisms. Welham et al. characterized bacteria using MALDI-TOF-MS and found species- and strain-specific biomarkers for the organisms studied.\textsuperscript{937} Demirev et al. also developed a MALDI-TOF-MS method for rapidly identifying microorganisms and correlated each ion to a protein by searching an Internet-accessible protein database.\textsuperscript{938} Saenz et al. investigated the reproducibility of MALDI-TOF-MS for replicate bacterial culture analysis,\textsuperscript{939} and Lynn et al. used MALDI-MS to identify Enterobacteriaceae bacteria, including Salmonella and E. coli.\textsuperscript{940} Holland et al. identified proteins from whole cells of bacteria using MALDI-TOF-MS,\textsuperscript{941} and Winkler et al. reported the direct analysis and identification of Helicobacter and Campylobacter species using MALDI-TOF-MS.\textsuperscript{942} MALDI-MS was also used to rapidly type Bacillus subtilis strains through the identification of secondary metabolites.\textsuperscript{943} Bundy and Fenselau used lectin-based affinity capture with MALDI-MS to isolate and analyze bacteria,\textsuperscript{944} and Goodacre applied ESI-MS to characterize strains of intact Gram-negative and Gram-positive bacteria.\textsuperscript{945} Krishnamurthy et al. used LC/microspray-MS for identifying protein biomarkers specific to particular microorganisms.\textsuperscript{946} This electrospray method was as effective as earlier MALDI-MS methods but offered an advantage in that liquid samples could be directly analyzed and tandem mass spectrometry could be used to obtain further structural information.

Birmingham et al. used corona plasma discharge for measuring biomarkers from bacteria, spores, and viruses,\textsuperscript{947} and Hendrick et al. used in situ thermal hydrolysis and methylation with a field-portable membrane-inlet quadrupole-ion-trap mass spectrometer for characterizing pathogenic bacteria.\textsuperscript{948} Barshick et al. used pyrolysis-ion-trap-MS with chemical ionization to differentiate five pathogenic Gram-negative bacteria,\textsuperscript{949} and Goodacre et al. used Curie-point pyrolysis MS and Fourier transform IR spectroscopy to detect the dipicolinic acid biomarker in 36 strains of aerobic endospore-forming bacteria.\textsuperscript{950} Bacterial carbohydrates were measured in two studies through the use of GC/MS/MS\textsuperscript{951} and GC/MS with automated derivatization.\textsuperscript{952} Saraf et al. used quadrupole GC/MS and ion-trap GC/MS/MS to determine components of Gram-negative bacterial endotoxins (3-hydroxy fatty acids) in household dust.\textsuperscript{953} In this study, 30 dust samples were analyzed and it was found that both methods allowed the acids to be distinguished, but the GC/MS/MS method provided additional specificity and required only sub-mg amounts of dust.

**VIII. Natural Organic Matter**

Natural organic matter (NOM) is a complex mixture of substances, such as amino acids, carbohydrates, lipids, lignins, waxes, organic acids, humic acids, and fulvic acids. Humic substances are complex macromolecular structures that generally have molecular weights over 2000 Da. A variety of functional groups have been reported in humic substances, including COOHs, phenolic OHs, enolic OHs, quinones, hydroxyquinones, lactones, ethers, and alcoholic OHs, and various nitrogen, phosphorus, and sulfur functional groups.\textsuperscript{954} However, even today, with all of the analytical and spectroscopic tools that are available, we still cannot definitively characterize the complete structure of NOM. Its complex structures still elude precise identification. One of the reasons that makes the understanding of NOM structure important is that NOM is the precursor material to drinking water disinfection byproducts (DBPs). NOM is transported from humus materials in soil to rivers and lakes that serve as much of our source water for drinking water. If NOM were better understood, it is possible that DBPs could be minimized or even eliminated. For example, better ways of removing NOM from the water prior to disinfection could be developed or treatment conditions could be altered so that the formation of DBPs is reduced. However, this is only one example of why understanding the structure of NOM is important. Mass spectrometry has always played an important role in the characterization of NOM throughout the years that it has been studied. NOM, as a whole, complete structure has been
studied using pyrolysis-GC/MS, and NOM has also been cleaved by chemical reaction into smaller structures that could be analyzed by GC/MS.

Two recent reviews discussed the characterization of NOM by pyrolysis-GC/MS. Christy et al. carried out a study of NOM in nine water samples using reverse osmosis and evaporation techniques to isolate the NOM and high-temperature pyrolysis-GC/MS to characterize the NOM. Four main types of products were observed—biopolymer carbohydrates, proteinaceous materials, N-acetylamino sugars, and polyhydroxy aromatics. Schnitzer discussed the use of pyrolysis GC/MS, along with SFE and $^{13}$C NMR spectroscopy, for obtaining information on the major humic components of NOM. Harrington et al. used pyrolysis-GC/MS and $^{13}$C NMR spectroscopy to characterize hydrophobic extracts of NOM from five water supplies. In this study, carbon dioxide and phenol peak areas from pyrolysis-GC/MS correlated with $^{13}$C NMR estimates of carboxylic acid content and aromatic carbon content and the phenol peak area from pyrolysis GC/MS was found to be a qualitative indicator of chlorine consumption and DBP formation.

Schmitt-Kipplin et al. used pyrolysis-field ionization-MS, along with CE, gel permeation chromatography, Fourier transform-IR spectroscopy, and one- and two-dimensional NMR spectroscopy, to characterize the structural changes in dissolved humic acid during photolytic degradation (by UV–vis light). This study revealed that there was selective degradation of dissolved humic material, especially under an oxygen atmosphere. Lignin and lipid structures were found to be the most labile, as compared to carbohydrates, alkylbenzenes, or N-containing structures. Under a nitrogen atmosphere, the carboxylic acids were fairly stable. Schulten and Gleixner used pyrolysis-field ionization-MS, Curie-point pyrolysis-GC/MS, and for the first time Curie-point pyrolysis-GC/combustion-isotope ratio-MS to characterize organic matter from freeze-dried surface water, natural fulvic and humic acids, and ultrafiltrate samples. The results provided information on 10 classes of characteristic molecular building blocks of NOM—carbohydrates, phenols and lignin monomers, lignin dimers, lipids, alkyaromatics, aromatic nitrogen compounds, sterols, peptides, suberins, and loosely bound fatty acids. Peverauvori et al. characterized lake aquatic humic matter using pyrolysis GC/MS and found that the quantities of thermal degradation products were strongly correlated with the various humic matter fractions. Krüge et al. characterized NOM in bottom sediments from western Lake Ontario by pyrolysis-GC/MS and found that sediment samples containing high amounts of NOM were relatively rich in aliphatic hydrocarbons and pyrrolic nitrogen compounds while samples with less NOM were more aromatic and pyridinic. White and Beyer used pyrolysis GC/MS to analyze organic matter in three Antarctic soils.

Newer techniques, such as ESI-MS, LD-MS, and FAB-MS, have also recently been applied to the study of NOM. Brown et al. compared FAB-MS and LD-MS to study fulvic acids, finding that LD-MS methods did not suffer from the background problems of FAB methods. Novotny et al. evaluated different experimental parameters for analyzing fulvic acids by FAB-MS, and Soluiki et al. applied a gas-phase hydrogen/deuterium-exchange technique to determine the number of active hydrogens in fulvic acid ions using ESI–Fourier transform-ion cyclotron resonance (ICR)-MS. Brown and Rice also used ESI–ICR-MS to study four reference fulvic acids. In this study, the pH, ionic strength, and concentration of multivalent cations had little or no effect on the observed m/z distributions. Lignins were analyzed using either ESI-MS to determine their molecular weights and provide structural information or pyrolysis-GC/MS with lignin permethylation to quantify marker compounds (phenols and their methylated derivatives).

Several studies focused on understanding the chemical processes involved in soil organic matter. Boutton et al. used stable isotopes of H, C, and O to document changes in ecosystem structure and function in a subtropical savanna ecosystem. Gleixner et al. used Curie-point pyrolysis GC/MS and isotope ratio MS to determine the individual turnover rates of specific carbohydrates, lignins, lipids, and N-containing compounds from French arable soils. McTiernan et al. studied the short-term changes in $^{13}$C and $^{15}$N signatures of water discharged from grazed grasslands, and Schweizer et al. studied isotopic $^{13}$C fractionation during plant residue decomposition and its implications for soil organic matter studies. Seibert et al. used NMR and GC/MS to characterize soil organic nitrogen after the addition of biogenic waste composts. Boon et al. used direct temperature-resolved ammonia CI-MS to characterize microgram quantities of oceanic colloidal organic matter, and Vilge-Ritter et al. used pyrolysis GC/MS to study the removal of NOM from Seine River water by coagulation–floculation.

**IX. Biological Samples**

The analysis of biological samples has always been important because it provides information on the uptake and metabolism of environmental pollutants in the human body as well as in other terrestrial and aquatic animals. For example, fatty tissues have been a primary source of bioaccumulation for hydrophobic pollutants, such as PAHs, PCBs, and dioxin, and the ingestion of fish that have been exposed to these hazardous contaminants can provide a concentrated exposure of pollutants to humans who consume them. Mass spectrometry has played an important role in measuring the bioaccumulation of pollutants such as these, as well as providing insights into mechanisms of action of these pollutants in humans and other organisms, through the analysis of polar metabolites, DNA and protein adducts, and other biomarkers of exposure. Improved extraction techniques, along with recent advances in mass spectrometry (e.g., ESI-, APCI-, and MALDI-MS), are dramatically changing this area. These new developments are enabling the analysis of highly polar metabolites and other biomarkers of exposure at extremely low levels in complex biological fluids and tissues.
A. Organic Analyses

Several excellent reviews have been published on the MS detection of carcinogen–DNA adducts, protein adducts, and hemoglobin adducts. Qu et al. discussed the use of ESI- and MALDI-MS for nucleotide and protein adduct detection and sequencing and the use of ESI- and MALDI-MS for nucleotide and quantitative determination of these adducts through the use of GC/MS and GC/MS/MS for quantitative determinations of carcinogen-modified nucleic acid bases and protein amino acids. Qu et al. discussed the use of chromatography/MS, along with immunological assay, fluorescence techniques, and P-32-postlabeling, for determining DNA adducts. In a 1992 review, Chiarelli and Lay discussed the use of FAB- and DCI-MS for analyzing carcinogen–DNA adducts, and in a 1995 review, Hemminki reported methods for detecting excreted urinary ribonucleic acid (RNA) and DNA adducts. Apuzzese and Vouros reviewed the use of capillary methods coupled to mass spectrometry for analyzing DNA adducts, McClure et al. reviewed the use of GC/MS for analyzing hemoglobin adducts formed by exposure to the aromatic amine herbicides, propanil and fluometuron, and Sweetman discussed the leading role that mass spectrometry has played in the structural and quantitative determination of these adducts through the use of ESI- and MALDI-MS for nucleotide and protein adduct detection and sequencing and the use of GC/MS and GC/MS/MS for quantitative determinations of carcinogen-modified nucleic acid bases and protein amino acids. Qu et al. discussed the use of chromatography/MS, along with immunological assay, fluorescence techniques, and P-32-postlabeling, for determining DNA adducts. In a 1992 review, Chiarelli and Lay discussed the use of FAB- and DCI-MS for analyzing carcinogen–DNA adducts, and in a 1995 review, Hemminki reported methods for detecting excreted urinary ribonucleic acid (RNA) and DNA adducts. Apuzzese and Vouros reviewed the use of capillary methods coupled to mass spectrometry for analyzing DNA adducts, McClure et al. reviewed the use of GC/MS for analyzing hemoglobin adducts formed by exposure to the aromatic amine herbicides, propanil and fluometuron, and Sweetman discussed the leading role that mass spectrometry has played in the structural and quantitative determination of these adducts through the use of ESI- and MALDI-MS for nucleotide and protein adduct detection and sequencing and the use of GC/MS and GC/MS/MS for quantitative determinations of carcinogen-modified nucleic acid bases and protein amino acids. Qu et al. discussed the use of chromatography/MS, along with immunological assay, fluorescence techniques, and P-32-postlabeling, for determining DNA adducts.

CE/MS has been used recently to identify styrene oxide adducts in DNA and DNA components. LC/ESI-MS has also been used to identify glutathione conjugates of 1-nitronaphthalene and hemoglobin adducts of methyl bromide. Arylamine–DNA adducts have been identified using FAB-MS/MS and LD-TOF-MS. Immunoassay with mass spectrometry is increasing in use for biological samples. MALDI-TOF-MS has been used to identify antigens for toxins, following capture by immunoassay, and GC/NCI-MS has been used to identify protein adducts formed by exposure to perchloroethylene, following immunoaffinity chromatography. GC/MS has been used in several studies for identifying DNA, hemoglobin, and protein adducts. Using GC/MS, benz[a]pyrene metabolites and DNA adducts have been identified in human cervical tissues and hemoglobin adducts of acrylamide and glycidamide have been identified in humans. GC/MS has also permitted the identification of alachlor–protein adducts, DNA and protein adducts of halogenated olefins, a glutathione adduct of trichloroethylene, DNA adducts of 4-aminobiphenyl, and a new DNA adduct of benz[a]pyrene. NCI-MS has been used in many of these studies to provide added sensitivity.

LC/MS and GC/MS techniques have been used to identify metabolites of pollutants in humans and animals. LC/ESI-MS has been used to determine metabolites of benz[a]pyrene, benzene, and naphthalene in urine. GC/MS and GC/MS/MS have been used to determine metabolites of the insecticide pirimicarb, nitropyrene, styrene, polychlorinated aryl methyl sulfones, and chloral hydrate in urine, plasma, and tissue.

Two major incidents of dioxin exposure have made the measurement of dioxin in human tissues and serum important. In 1976, an explosion at a chemical plant near Seveso, Italy, resulted in the largest incident of dioxin exposure ever recorded for humans. The other major incident involved the exposure of Vietnam War soldiers to dioxin through the aerial spraying of Agent Orange, which was used as a defoliant. Schecter published an historical review of congener-specific human tissue measurements as specific biomarkers of exposure to dioxins and related compounds. The majority of PCDD and PCDF measurements are accomplished through the use of GC/high-resolution-MS, which provides specificity and ppq sensitivity. Mocarelli et al. presented data from a long-term health monitoring (1976 to 1996) of groups of people in Seveso, Italy, affected by the TCDD accident that occurred in 1976. Recent advances have enabled the measurement of TCDD blood lipid content in serum samples that have been kept frozen since the accident. From these samples and from newly collected samples, exposure to TCDD could be correlated with health effects observed during those years. Chloracne was the only clinical effect that could be positively correlated to the TCDD contamination, but there was a significant modification of the sex ratio during 1977–1984 with an excess of females associated with high TCDD exposure of both parents. However, this effect decreased with time, so that today, there are no longer significant differences.

Early studies of human tissue from Vietnam War veterans were published by Gross et al. and Schecter et al. Later studies include those by Schecter el al., Wolfe et al., and Michalek et al. In one of these studies, the half-life of TCDD was found to change significantly with body fat and age in 337 members of Operation Ranch Hand, the U.S. Air Force unit responsible for the aerial spraying of Agent Orange in Vietnam. The half-life of TCDD was found to increase significantly with increasing percent body fat and decrease significantly with increasing relative change in percent body fat and age; the median half-life was found to be 11.3 years. Another study focused on whether paternal exposure to Agent Orange and its dioxin contaminant (TCDD) during the Vietnam War is related to adverse reproductive outcomes after the war. Results from this study indicated no meaningful elevation in risk for spontaneous abortion or stillbirth but some elevation in the risk of birth defects. However, after review of clinical descriptions, these birth defects were found not to be biologically meaningful. There was an increase in nervous system defects in Ranch Hand children with increased paternal dioxin, but this was based on sparse data.

Rosenberg et al. measured PCDD and PCDF levels in the blood of workers at a pulp and paper mill and found no statistically significant differences in the total lipid-adjusted PCDD/PCDF concentrations between these workers and the controls (61 vs 49 pg/g). Because there is a distinct distribution of PCDDs and PCDFs that results from chlorine-based pulping, measurements such as these can be used to determine whether the PCDD or PCDF levels found in human body fluids is linked to such an exposure.
PCDD and PCDF levels have also been measured in human milk from women in Norway, Sweden, and Denmark.\textsuperscript{1017} Four of the locations sampled had different PCDD and PCDF sources. It was found that there were no geographical differences in total dioxins measured. Mean values were 15–18 pg/g in Norway and Denmark and 20–24 pg/g in Sweden, with the highest values of PCDD congeners found in industrialized areas of Sweden and the highest values of PCDFs found in a Norwegian area known for dioxin contamination from a magnesium-producing factory.\textsuperscript{1017} Anderson et al. studied human blood for dioxin contamination from a magnesium production factory.\textsuperscript{1017}

Values of PCDFs found in a Norwegian area known for dioxin contamination from a magnesium-producing factory.\textsuperscript{1017} Anderson et al. studied human blood for dioxin contamination from a magnesium production factory.\textsuperscript{1017}

The overall mean toxic equivalents for dioxins, furans, and coplanar PCBs were greater than selected background levels in the general population (dioxins, 1.8 times; furans, 2.4 times; and coplanar PCBs, 9.6 times).\textsuperscript{1018} PCDDs and related compounds have also been measured in polar bear milk in Norway\textsuperscript{1019} and in harp seals in the Greenland Sea.\textsuperscript{1020} Concentrations ranged from 0.2 to 1.6 pg/mL in the polar bear milk\textsuperscript{1019} and 4–10 pg/g in the seal blubber.\textsuperscript{1020} PCDDs have also been measured in human milk in The Netherlands\textsuperscript{1021} and in fish from the Great Lakes.\textsuperscript{1022}

Finally, Boggess et al. reported the measurement of dioxins and PCBs in rat tissues using GC/high-resolution-MS and isotope dilution.\textsuperscript{1023}

Volatile organics have been measured in human samples (blood, urine, and breath) for a number of years, but the application of recent mass spectrometry techniques has greatly improved specificity and detection. Plebani et al. developed an optimized GC/MS method for analyzing benzene in exhaled breath using collection with Tedlar bags and cryotrapping.\textsuperscript{1024} Riedel used microwave desorption coupled with GC/MS to determine benzene after trapping exhaled air in graphitized charcoal tubes.\textsuperscript{1025} Headspace-GC/MS,\textsuperscript{1026} headspace-SPME-GC/MS,\textsuperscript{1027} and SPE-GC/MS methods\textsuperscript{1028} have been used to measure benzene and related aromatic compounds in urine. The SPME method required only 2 mL of urine and produced detection limits of 12–34 ng/L, with a linear dynamic range up to 5000 ng/L.\textsuperscript{1027} SPME-GC/MS has also been used to determine ppb levels of monocyclic aromatic amines in human milk.\textsuperscript{1029} On-line MIMS was used to analyze the time persistence of monochloramine in human saliva and stomach fluid.\textsuperscript{1030} Monochloramine is a popular drinking water disinfectant, and residual levels in drinking water are commonly maintained to prevent microbial regrowth in distribution systems. The results of this study indicated that the decay of monochloramine in saliva from 0.7 ppm to below the limit of detection (100 ppb) took approximately 5 min; from a level of 1.8 ppm, the decay time was approximately 50 min, and at higher monochloramine levels (3.6–15 ppm), monochloramine did not decay completely. These results indicated that most of the monochloramine ingested through drinking water reaches the stomach intact. In contrast to its reaction in saliva, monochloramine was found to decay rapidly in contact with stomach fluid—at concentrations of 0.7–15 ppm, the decay occurred in approximately 30 s.\textsuperscript{1030}

GC/MS has been used to measure pesticides in human body fluids and tissues following fatal poisonings.\textsuperscript{1031,1032} Pauwels et al. reported GC/MS methods for measuring organochlorine pesticides in human serum and tissues.\textsuperscript{1033,1034} Williams et al. used GC/MS to measure chlorinated naphthalenes in human adipose tissue collected during autopsies in Canadian municipalities within the Great Lakes basin.\textsuperscript{1035} 1,2,3,4,6,7- and 1,2,3,5,6,7-hexachloronaphthalenes were found in all tissue samples, together with an unidentified pentachloronaphthalene. Levels ranged from 0.1 to 25 ng/g fat. Pauwels and Scheepens developed a method using gel permeation or adsorption chromatographic cleanup with GC/MS for measuring PCBs and other organochlorine hydrocarbon residues in human serum and adipose tissue.\textsuperscript{1036} Liu et al. developed a method using headspace SPME-GC/MS for determining dichlorobenzene isomers in human blood.\textsuperscript{1037} With this method, each compound was detected at a level of at least 0.02 μg per 1 g of whole blood.

Pollutants have also been measured in aquatic animals. SFE-GC/high-resolution-MS has been used to determine PCBs in Antarctic krill.\textsuperscript{1038} GC/MS and GC/MS/MS have been used to determine polychlorinated terphenyls in shellfish;\textsuperscript{1039} toxaphene congeners in marine mammals, penguins, eggs of seabirds, and fish;\textsuperscript{1040} organochlorine and organophosphorus compounds in whale tissue;\textsuperscript{1050} seals and sea lions;\textsuperscript{1051} porpoise and fish;\textsuperscript{1052} PCBs in dolphins;\textsuperscript{1053} PAHs in fish;\textsuperscript{1054} PCDDs and PCDFs in crab;\textsuperscript{1055} polychlorinated paraffins in fish;\textsuperscript{1056} halogenated fatty acids in marine mammals, fish, and bivalves;\textsuperscript{1057} dichloromyrystic acid in lobster;\textsuperscript{1058} brominated diphenyl ethers in fish and seal;\textsuperscript{1059,1060} and VOCs in fish.\textsuperscript{1061} An important finding in one of these studies was that toxaphene levels were found to be constant in trout samples taken from Lake Superior over the time period of 1982–1992 (despite its ban in 1982), while levels decreased by a factor of 1.4–5 in trout from the other Great Lakes.\textsuperscript{1046} This suggested that toxaphene concentrations in very large and very cold lakes (such as Lake Superior) decrease much more slowly than they do in relatively small and warm lakes (such as Lake Ontario).\textsuperscript{1046} In a study involving the identification of extractable organically bound chlorine (EOBC) in lobsters, dichloromyrystic acid was found to account for approximately 20% of the EOBC in the lipid tissue.\textsuperscript{1058} GC/high-resolution-MS has been used to measure brominated and chlorinated dioxins and furans in osprey and salmon.\textsuperscript{1062} GC/ECNI-high-resolution-MS has been used to analyze C\textsubscript{14}–C\textsubscript{17} polychloro-n-alkanes in fish\textsuperscript{1063} and chlorodane components in Antarctic penguin, Baltic fish and seal, and Arctic seal.\textsuperscript{1064} LC-APCI-MS was used to determine sulfadiazine residues in salmon,\textsuperscript{1065} and CE/MS/MS has been used to measure tetramine toxin in whelks.\textsuperscript{1066} This toxin has been responsible for numerous incidents of human intoxication in Japan, Europe, and Canada due to the consumption of whelks.
Mass spectrometry has also been used to measure pesticides and other contaminants in foods. LC/ESI-MS has been used to determine pesticides in apples and pears, and tomato juice as well as plant growth regulators in grain. GC/MS has been used to determine pesticides in 10 different types of fruits and vegetables. GC/MS has been used to measure carbamate insecticides in 10 different green vegetables, and DiCorcia used LC/ESI-MS to measure benzothiazole in 10 different types of fruits and vegetables. GC/MS has been used to determine carbamate insecticides in 10 different green vegetables. MS has been used to determine lead isotope ratios in whole blood, pottery, and leaded gasoline in residents of a small town in Mexico. This study revealed that the predominant source of lead in this population was the ceramic ware used for cooking. Mercury has been measured in whole blood and urine using ICP-MS and in hair using cold vapor atomic adsorption-ICP-MS. High-resolution ICP-MS has been used to determine radionuclides in human body fluid samples, and flow injection-ICP-MS has been used to determine uranium in urine and serum. MacLellan et al. investigated two analytical procedures (alpha spectrometry and ICP-MS) for discriminating between environmental and occupational sources of uranium, and Lewis and Schweitzer compared liquid scintillation and ICP-MS for measuring $^{99}$Tc. In the latter study, it was found that both techniques gave accurate results, but the precision of ICP-MS was superior to liquid scintillation.

Mass spectrometry methods have also been used to measure inorganics in aquatic organisms, plants, and foods. ICP-MS and laser ablation-ICP-MS have been used to determine trace elements in shellfish. ICP-MS has also been used to determine trace elements in lichens, with 0.2 μg/g detection limits. Arsenic appears to be the most frequently measured element in biological samples. Newer LC/ICP-MS methods have been used to measure arsenic species in fish, marine algae, bivalves, crustaceans, and mushrooms. One of these papers reported the measurement of arsenic from mussels collected from the Barcelona harbor; typical concentrations for the seven arsenic species were 1–7 mg/kg. Other organoarsenical compounds, believed to be arsenosugars, were found in a concentration range of 0.3–1.5 mg/kg. In another study that measured arsenic species in fish caught in coastal waters around Plymouth, U.K., arsenic levels were found to range from 1.0 to 187 mg/kg. Electrothermal vaporization-ICP-MS was used to determine arsenic in standard reference materials of plant origin, and microscale flow-ICP-MS was used to reduce background interferences and improve the detection of As in wines. Using this microscale flow method, concentrations of arsenic were found to be between 7 and 13 pg/μL for all wines examined, which were significantly lower than maximum permissible limits.

Several studies have focused on the measurement of arsenic and organoarsenic species in body fluids. LC/ICP-MS has been used to determine organoarsenic species in the blood plasma of patients undergoing dialysis, and LC/MS and LC/ICP-MS have been used to identify and quantify arsenic species in the urine of rats chronically exposed to dimethylarsinic acid. CE/ESI-MS has been used to measure arsenic species in urine samples. GC/MS analysis following derivatization with thioglycol methylate or LC/ESI-tandem MS has been used to determine dimethylarsinic acid and monomethylarsenic acid in human urine. ICP-MS has been used to determine total arsenic in finger nails as a method of assessing chronic exposure to arsenic. Analytical methods using double-focusing ICP-MS have been used to determine 50 elements in digested human blood in one study. SPME-GC/MS was used to simultaneously determine Hg(II) and alkylated Hg, Pb, and Sn species in human urine, providing detection limits of 7–22 ng/L. High-resolution ICP-MS has been used to determine copper, zinc, cadmium, and lead in human urine from workers occupationally exposed to cadmium. Results revealed cadmium levels 7–8-fold greater than for nonexposed workers, along with slight increases in lead.
reference materials. Lee et al. developed a method for determining heavy metals in calcified tissues, and Bargagli et al. reported results from the measurement of metals in a variety of mosses in Italy and northern Antarctica. Slaets et al. optimized the coupling of multicapillary GC with ICP-MS for mercury speciation in biological materials and reported detection limits of 0.2 ng/g for methylmercury. Finally, atomic fluorescence spectrometry (AFS) was compared to GC/ICP-MS for determining methylmercury in ringed seal and buluga whale. Detection limits were 0.25 and 0.9 pg for AFS and GC/ICP-MS, respectively.

X. Field-Portable Mass Spectrometry

In recent years, field-portable mass spectrometry has gained importance for on-site measurements of environmental contaminants. This MS equipment generally involves a small, mobile instrument that can be transported to collect field data on-site or MS equipment that is housed in a mobile laboratory (usually a bus equipped with instrumentation). These field-portable mass spectrometers offer real advantages for characterizing contaminated field sites. Traditional analyses involve the collection of a few representative samples from a contaminated site and transporting them back to an off-site, permanent laboratory for analysis. Field-portable mass spectrometers are enabling rapid, on-site collection of data that allows more samples to be taken and can result in a more complete characterization of the contaminated site. In this way, complex gradients and plumes can be more efficiently mapped and studied and changes can be monitored in real-time. There have been several excellent reviews on field-portable mass spectrometry. Baykut and Franzen published a review in 1994 entitled 'Mobile Mass Spectrometry—A Decade of Field Applications'; Poppiti published a review in 1994 on the role of field testing in environmental measurements, and Kotiaho published a 1996 review on on-site environmental and in-situ process analysis by mass spectrometry. Wise et al. reviewed the use of direct MS analysis of environmental samples, and Eckenegro reviewed applications of field-portable GC/MS. The latter paper also discussed the trend toward integrated miniaturization. More recently, Badman and Cooks published a review on miniature mass analyzers.

Chambers et al. reported the development of an ion-store TOF-MS that can be used for real-time measurement of VOCs in air, and Cameron reported the effects of air and helium on the performance of an ion-trap-MS when used for real-time monitoring of atmospheric pollutants. Also mentioned earlier in the section on Air, Prather et al. developed aerosol-TOF-MS to measure automobile exhaust emissions and other samples in the field in real-time. Liu developed a method using a transportable purge-and-trap GC/MS system for VOC analyses in air, water, and soil in a mobile laboratory. Schuetz et al. compared the quality of data produced by on-site GC/MS to GC/MS data collected at an off-site, permanent laboratory. Virkki et al. described a MIMS method for on-site environmental analysis in a mobile laboratory. Results showed that many environmentally significant compounds could be measured directly from water samples at sub-ppb levels, with response times of 1–2 min and linear dynamic ranges of 4 orders of magnitude. Reiner et al. developed an aircraft-borne triple-quadrupole MS for studies of ions in the upper troposphere and lower stratosphere. McClennen et al. used a Roving GC/MS instrument to perform on-site sampling and analysis in <10 min. This mobile GC/MS system was designed specifically for the rapid analysis of hazardous organics in fire and chemical accidents. Gudsteyn et al. designed an in-situ sampling device capable of thermally desorbing organics bound to subsurface soils at depths up to 20 m, and Almirall et al. reported the field recovery of explosive residues using SPME-GC/MS. Matz et al. developed a field GC/MS method for evaluating total petroleum hydrocarbons. In another study, Matz et al. compared solvent-less sample preparation methods for use with a mobile GC/MS system. These preparation methods included membrane extraction with a sorbent interface, thermal membrane desorption, and purge-and-trap. Thermal desorption-GC/MS was used in two separate studies for on-site determinations of PAHs and other pollutants.

XI. Conclusions

The importance of protecting our environment became a prime issue in the early 1970s, and mass spectrometry played a key role in that early movement. Mass spectrometry allowed the precise identification of pollutants and has enabled a better understanding of environmental processes. With the advent of GC/MS, complex environmental samples could be effectively separated and individual pollutants unequivocally identified. The development of computers later simplified the data analysis process, and even today, computers continue to advance so that rapid analyses can be processed and huge data sets can be handled in an automated fashion. The many advances that have occurred over the years in mass spectrometry are a tribute to the bright and innovative scientists who continue to develop new ideas and improve our ability to measure pollutants. Just when researchers begin to think that the field of mass spectrometry has matured and all of the analytical techniques have been fully explored, a new analytical tool is created. Examples of these include the development of MALDI-MS, which is now enabling specific information for microorganisms that was not possible with traditional microscopic techniques. API-MS techniques are also enabling the analysis of highly polar pesticides and other pollutants that was not possible a few years ago. The development of ‘softer’ ionization techniques such as FAB-MS and later MALDI- and API-MS are now enabling very large (~1000 Da), nonvolatile, macro-molecular complexes to be studied for the first time. It is expected that these MS techniques will soon...
rapidly expand our understanding of natural organic matter, carcinogen—DNA adducts, and mechanisms of carcinogenicity and toxicity of pollutants—to name a few. As Keith stated in his 1981 book Advances in the Identification & Analysis of Organic Pollutants in Water, "Now we have to work harder and be more clever to produce newer and better methodology with which to uncover the more difficult organic pollutants"—it is true that we are now addressing those "more difficult organic pollutants". What an exciting time this is.

XII. Acknowledgments

The author thanks Janice Sims and Brandy Manders for their invaluable assistance during the reference acquisition period. This paper has been reviewed in accordance with the U.S. Environmental Protection Agency’s peer and administrative review policies and approved for publication. Mention of trade names or commercial products does not constitute endorsement or recommendation for use by the U.S. EPA.

XIII. References
