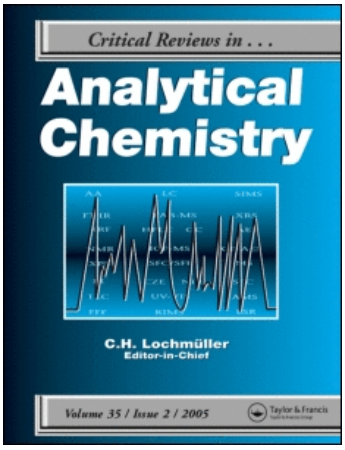

Critical Reviews in Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713400837

Analysis of Drinking Water for Trace Organics

C. J. Koester[a]; R. E. Clement[a]
[a] Laboratory Services Branch, Ontario Ministry of Environment and Energy, Etobicoke, Ontario, Canada

To cite this Article Koester, C. J. and Clement, R. E.(1993) 'Analysis of Drinking Water for Trace Organics', Critical Reviews in Analytical Chemistry, 24: 4, 263 — 316
To link to this Article: DOI: 10.1080/10408349308050555
URL: http://dx.doi.org/10.1080/10408349308050555

Critical Reviews in Analytical Chemistry, 24(4):263–316 (1993)

Analysis of Drinking Water for Trace Organics

C.J. Koester and R.E. Clement *

Ontario Ministry of Environment and Energy, Laboratory Services Branch, 125 Resources Road, Etobicoke, Ontario M9P 3V6, Canada

* Author to whom corresponding should be addressed.

ABSTRACT: The protection of drinking water quality is one of the most important mandates of government environment departments. During the past 2 decades, more and more attention has been spent on the trace organic chemical pollutants that may be present in potable water. Consequently, the detection, identification, and quantitation of trace organics in drinking water has been the subject of considerable analytical development work. Sophisticated methods based on gas chromatography-mass spectrometry (GC-MS) are now in routine use that can detect organics at parts per trillion concentrations. For some analytes, parts per quadrillion detection limits have been reported. Although these capabilities are largely due to the maturity of GC-MS as an analytical technique, recent developments in solid-phase extraction (SPE) and other reduced-solvent or even solvent-free extraction and concentration methods are leading the way to even greater analytical performance. Other methods based on liquid chromatography-mass spectrometry (LC-MS) may lead to concern over many other analytes not determined by GC-MS. The above and related techniques are reviewed to demonstrate the state of current analytical methods for the determination of trace organics in drinking water samples, and to discuss future developments. Throughout the 1980s, development of GC-MS instrumentation and chromatographic procedures were paramount, but attention has now shifted to improving sample preparation methods. Eventually, the development of fully automated methods from sampling to report generation will be realized.

KEY WORDS: drinking water, trace organics, gas chromatography-mass spectrometry (GC-MS), liquid chromatography-mass spectrometry (LC-MS), sampling, sample preparation, purge and trap (P & T), headspace analysis, solid-phase extraction (SPE), volatile organic compounds (VOCs), semivolatile organic compounds (SVOCs), polar organic compounds, chlorinated dibenzo-*p*-dioxins (PCDDs)

I. INTRODUCTION

If one considers the many different types of environmental samples that are analyzed for trace pollutants, aqueous samples seem to be among the simplest. Drinking water samples are likely to be viewed this way because potable water is assumed to contain no significant contaminants. This is true on a macro scale; however, because much greater purity is demanded of drinking water, the analytical chemist is required to produce valid, quantitative measurements at much lower detection levels than those required for other types of environmental samples. For example, we know that the by-products of chlorine disinfection treatment to produce potable water include low concentrations of some organic compounds thought to be harmful to humans when consumed over a long period of time; therefore, we must monitor these substances. Areas that rely on groundwater drinking water supplies are subject to potential contamination from a number of sources that include agricultural runoff, landfill leachates, and industrial activities. These groundwater supplies require constant monitoring for priority substances.

1040-8347/93/$.50

Accurate analytical results must be generated to assess the risk to the public to determine if costly cleanup of the water supply is necessary.

A. What is Trace?

The terms "trace" and "ultra-trace" have very different meanings depending upon the analytical application and historical time period. During the past 25 years, the meaning of "trace" organic analysis of environmental samples has changed from parts per million (ppm: 1 part in 10^6) to parts per billion (ppb: 1 part in 10^9), and, currently, to parts per trillion (ppt: 1 part in 10^{12}). Although parts ber billion concentration analyses are common for many organics in drinking water, the most sophisticated methods can achieve parts per trillion, or better, detection limits. The term "ultra-trace" is sometimes used to refer to parts per trillion analyses, but now should probably be reserved for sub-parts per trillion determinations. For example, chlorinated dibenzo-*p*-dioxins (PCDDs) and chlorinated dibenzofurans (PCDFs) in drinking water can be quantitatively determined at parts per quadrillion (ppq: 1 part in 10^{15}) concentrations.

B. Scope of Review

Given our definition of "trace", this review is concerned only with those techniques used for the determination of organic compounds in drinking water at parts per billion or lower concentrations. Further, the authors present the most effective methods presently in common use, and emerging technologies that may lead to significant future improvements in capabilities. We have avoided most historical references, and instead endeavor to present the reader with a "snapshot" of what the status of drinking water analysis is right now. Much of this review centers around methods promulgated by the U.S. Environmental Protection Agency (USEPA). This is simply a reflection of the work reported in the scientific literature, a significant proportion of which is devoted to the work of USEPA. Our coverage is not balanced. We have limited discussion in some areas where the methods employed are widely used but are "mature" enough that only minor improvements have been made in recent years, and given greater attention to a few emerging techniques that show great promise for the future. For those new to trace organic analysis, this review provides basic descriptions of the various techniques and why they are important. For those knowledgeable in this area, we present our views on the current status and future directions of the field.

II. OBJECTIVES OF DRINKING WATER ANALYSIS

The objectives of any analytical work affect the choice of methods employed by the analytical chemist. For example, suppose a large chemical spill occurred in a river just upstream of the intake to a water treatment plant. The urgency of this situation demands rapid and accurate determination of the target compound in the water output of the plant. The response of the analytical chemist would be much different if the same spill occurred in a remote area where there was no danger of contamination of potable water supplies. These applications are quite different from the one in which many analytes must be determined in monitoring work to determine general drinking water quality. The analytical methods chosen depend on the specific objectives of the analytical work. Some general guidelines to the choice of methods are given below.

1. *Emergency Response*. The speed of analysis is key. Emergency response is required when the quality of the drinking water supply is threatened. Generally, such situations arise from chemical spills. Detection limits and specificity are not usually key factors in the methods chosen because monitoring is only needed until concentrations of the spilled chemicals are below regulatory levels, which should be set well above the minimum detection

limits achievable by using established analysis methods.

2. *General Water Quality Monitoring Studies.* General water quality monitoring work is performed to ensure drinking water quality is within established regulatory norms. Methods used must be capable of quantifying target analytes at concentrations below those set by regulation. A good guideline is that method detection limits should be at least ten times lower than the maximum tolerable concentrations set by regulation. The speed of analysis for such routine work is not critical, and analyte specificity is not important unless specific contaminants are observed to exceed regulatory limits.
3. *Characterization Analysis.* Another type of study performed is a *characterization* of contaminants present in drinking water. This is done to ensure that no unsuspected "new" contaminants are present in drinking water supplies. Detection limits are not critical in a characterization analysis. Persistent, new contaminants, once identified, may be added to target compound monitoring lists. The key factor in this type of analysis is the ability of the analytical method to identify organic compounds at relatively low concentrations. Although instrumental techniques such as Fourier transform infrared spectroscopy (FTIR) and nuclear magnetic resonance (NMR) spectroscopy are excellent for compound identification, the analyte concentrations at which identifications must be performed preclude all techniques except mass spectrometry-based ones for this application.
4. *Research Studies.* The objectives of research studies are diverse, which may significantly affect the analysis requirements. The effectiveness of new water treatment systems is a common application that requires monitoring for selected contaminants at low detection limits.

An important reason for clarifying the overall objectives of a study is so that appropriate analytical methods can be selected. Cost constraints on projects generally preclude the strategy of always employing the state-of-the-art methods. For the analysis of trace organics in drinking water, the general instrumental method of gas chromatography-mass spectrometry (GC-MS) is almost always chosen when feasible. The type of GC-MS system, data quality objectives, and associated sampling and sample preparation methods are choices that significantly affect the speed, cost, precision, accuracy, and detection limits of the overall analysis procedure.

III. SAMPLING AND SAMPLE PRESERVATION

Regardless of the objectives of a drinking water analysis, it is always necessary to collect a representative sample and to ensure the integrity of that sample from the time of collection until the time of analysis. This guarantees that water quality will be accurately assessed. Contamination of the sample must be prevented and degradation of the analytes must be minimized. Practical aspects of environmental sampling and analysis, including discussions about the collection of aqueous samples, sampling strategies, and quality assurance and quality control issues, have been addressed by Keith[1] and by the American Society for Testing and Materials (ASTM).[2]

A. Sample Collection

The first step in any environmental analysis, after thorough planning, is sample collection. Exact sampling procedures should be determined by the objectives of the analysis and by the nature of the analytes. Sampling location, time of sampling, and the frequency at which samples are collected are some factors that must be considered when developing sampling strategies. The American Society for Testing and Materials describes procedures for collecting water samples from lakes, rivers, and pipes.[2] The USEPA[3] provides detailed descriptions of how to collect representative drinking water samples from

taps. For example, when sampling tap water, they recommend that the system be flushed at 500 ml/min for at least 10 min prior to sample collection. This removes sediments and gas pockets in the pipes and allows the water temperature to stabilize. The stability of the water temperature implies homogeneity of the sample. Measurements of pH and conductance also may be used to determine the representative quality of the sample.

The amount of sample collected also is important. The volume of water sampled should be sufficient to allow for replicate analyses, if necessary, and to meet required analyte method detection limits. In most cases, the sampling container should be completely filled because headspace affords the opportunity for volatile analytes to partition from the sample into the gas phase. However, if the sample is to be shipped, approximately 10% of the volume of the container may be left empty to allow for volume changes due to temperature fluctuations during transport.[2]

The selection of an appropriate sampling container affects sample integrity. The sample should be collected in a container which is compatible with both the analyte being determined and the sample matrix. Aqueous samples are typically collected in amber glass bottles (amber glass prevents light exposure) and sealed with inert, Teflon-lined caps. Plastic containers are not usually suitable when organic compounds (OCs) are to be analyzed because the analytes tend to sorb to the container walls and container materials, such as plasticizers, may leach into the sample. The bottles used to collect the samples (and all other glassware and materials that contact the sample or sample extract) should be precleaned to prevent sample contamination. Many follow the common practice of prerinsing sample containers with the drinking water to be sampled before the final sample is collected. This practice could lead to high results for some analytes that tend to adsorb to glass surfaces, although container prerinsing is an effective way of reducing the possibility of sample contamination. Although silanized glassware is not necessary for most analyses, the analyses of certain compounds, such as volatile sulfides, require silanized glassware for sample collection.[4] This prevents the adsorption of analytes to the glass surface.

B. Sample Preservation

Once the sample is collected, measures must be taken to preserve its integrity until the time of analysis. Because some changes in the sample are likely to occur, certain physical and chemical parameters of a water sample (temperature, pH, alkalinity, conductivity, dissolved gases, etc.) should be measured in the field to ensure accurate values are obtained. Drinking water samples are typically refrigerated (4°C) for transport to the laboratory and while in storage before analysis. It is critical that samples be stored in a location away from solvent vapors to minimize contamination. For hydrophobic analytes such as the PCDDs and PCDFs, it may not be necessary to refrigerate samples before analysis, because at cooler temperatures hydrophobic analytes may be adsorbed more strongly to the walls of the sample container, and therefore great care must be taken to thoroughly rinse all container surfaces in the extraction step. However, no definitive study has been reported to examine this factor.

The sample preservation necessary after collection depends on the stability of the analytes. For many analytes in drinking water samples, no special preservation procedures are necessary. When sample preservation is thought to be needed, common procedures call for pH adjustment or the use of additives at the sampling site. Samples of nonchlorinated waters are often acidified to retard bacterial growth and to prevent biological degradation of the analytes, to prevent acid or base catalyzed decomposition, or to improve extraction efficiencies. To prevent analyte oxidation, preservatives such as ascorbic acid (typical concentration 25 mg/l) and sodium thiosulfate (3 mg/l) are often added

to samples to remove free chlorine. This hinders the formation of trichloromethane and other by-products of chlorine reactions.[5]

Mercuric chloride ($HgCl_2$) inhibits bacterial growth in water samples. For example, $HgCl_2$ prevents degradation of benzene compounds.[6] Ethyl benzene recoveries as low as 43% have been observed when a sample was stored for more than 2 d at 4°C without this preservative. However, preservative use has several disadvantages. In addition to presenting waste disposal problems because of its high toxicity, $HgCl_2$ can also interfere with sample extraction and analysis. In closed loop stripping, $HgCl_2$ is coextracted with the analytes and is adsorbed on the activated charcoal used to trap analytes.[7] This causes poor recoveries for some compounds. In addition, $HgCl_2$ elutes as a broad GC peak which interferes with the determination of certain analytes. Therefore, the effects of using preservatives on all analytes must be carefully determined before using them in routine applications. Of course, it is also important to determine the purity of all preservatives before use. For analyses performed at trace levels, even "high purity" grade chemicals may result in some sample contamination.

The analysis of polynuclear aromatic hydrocarbons (PAH) provides another example of the importance of preservative use. Several PAH, including benzo(*a*)pyrene and 7,12-dimethylbenz(*a*)anthracene, are unstable in chlorinated water; the addition of $Na_2S_2O_3$ (a reducing agent) to collected water samples was found to be an effective method of sample preservation.[8] Phenolic compounds are also susceptible to chemical degradation. Low recoveries (0 to 40%) for phenolic compounds have been observed when using USEPA Method 625 to analyze groundwater samples.[9] In that study, evidence suggested that manganese oxides in groundwater were oxidizing the phenolic surrogates. The addition of $Na_2S_2O_3$ to the water samples increased phenolic surrogate recoveries. Adjusting the pH to 2 before extraction prevented the formation of manganese oxides, which also resulted in increased recoveries of the phenolic surrogates.

During the study of phenolic compounds, it was demonstrated that the presence of analytical artifacts, in this case, iodocyclohexanol, could indicate chemical changes in the sample.[9] Iodocyclohexanol is formed by the reaction of cyclohexene (sometimes present as an inhibitor in the extraction solvent CH_2Cl_2) and iodine (formed by the oxidation of iodide). Finding iodocyclohexanol in the sample confirmed the presence of an oxidizing agent in the water. Thus, the presence of artifacts in the sample can indicate that reactions have occurred.

The use of preservatives does not always guarantee the prevention of analyte degradation. Recovery data for 147 analytes monitored during the National Pesticide Survey (U.S.) show that significant losses, in some cases 100%, were observed for 26 of the 147 analytes studied.[10] These losses occurred even when water samples were biologically inhibited with $HgCl_2$ or monochloroacetic acid buffer and stored at 4°C for 14 d, as specified by USEPA methods. However, analytes were generally stable when stored as extracts. This suggests that it is prudent to extract samples as soon as possible after sample collection.

Derivatization of analytes while the sample is in transport to the laboratory can be an alternative to sample preservation. Aldehydes, such as formaldehyde, glyoxal, methyglyoxal, and acetaldehyde (all formed by the reaction of ozone, used in water treatment, and naturally occurring organic matter in raw water), can be derivatized as they are collected and stored in bottles containing *o*-2,3,4,5,6-pentafluorobenzylhydroxylamine.[11] Results obtained by this method of sample treatment were comparable to those obtained when samples were preserved with $HgCl_2$ and NH_4Cl and stored before derivatization. In addition to the advantage of having a derivatized analyte upon arrival at the laboratory, this method eliminates the hazards of using and disposing of $HgCl_2$.

Table 1 summarizes sample preservation strategies for the analysis of OCs employed

TABLE 1
Sample Preservation Strategies for Various Organic Compounds

Compound class	Preservative	Storage	Ref.
Base / neutral extractables	Adjust to pH 2	Store sample at 4°C; analyze within 33 d	13–16
	Adjust pH > 2, sodium thiosulfate	Store sample at 4°C; extract within 7 d; analyze extract within 30 d of collection	3
Carbamate pesticides	Adjust to pH 3 with monochloroacetic acid buffer, sodium thiosulfate	store at 4°C from sample collection, store sample at −10°C; extract and analyze within 28 d	5
Chlorinated acids	Mercuric chloride or sodium thiosulfate	Store sample at 4°C; extract within 14 d; store extract at 4°C; analyze within 28 d	3
Chlorinated dioxins and furans	Sodium thiosulfate	Store sample at 4°C; extract within 7 d	17
	None	Store sample at ambient conditions; extract within 90 d; analyze within 40 d after extraction	5
Diquat and paraquat	Sodium thiosulfate adjust to pH 2, with sulfuric acid	Store sample at 4°C; extract within 7 d; analyze within 30 d	5
Endothall	None	Store sample at 4°C; derivatize and analyze within 7 d	5
Glyphosate	Sodium thiosulfate	Store sample at 4°C; analyze within 14 d; samples stable for 18 months if frozen	5
Haloacetic acids	Ammonium chloride	Store sample at 4°C; extract within 28 d; store extract at 0–4°C; analyze within 48 h	5
Neutral chlorinated extractables	None / chloroform	Store sample at 4°C; extract and analyze within 6 weeks; chloroform increases storage time to 15 weeks	18
	Sodium sulfate or sodium arsenate, adjust to pH < 2 with HCl	Store sample at 4°C; extract within 7 d; analyze extracts within 30 d	3
Organohalide pesticides	Sodium thiosulfate	Store sample at 4°C; extract within 7–14 d; store extract at 4°C until analysis	3
Organophosphorous pesticides	None	Store sample at 4°C; for 6 weeks	19
	Mercuric chloride or sodium thiosulfate	Store sample at 4°C; extract within 14 d; store extract at 4°C; analyze within 14 d	3
Phenolics	Chloroform or sulfuric acid	Samples may be stored for 3 weeks	20
Phenoxy acid herbicides	Adjust to pH 2 with sulfuric acid	Store sample at 4°C; samples stable for 50 d	12
Phenylurea pesticides	Adjust to pH 5–9	Store sample at 4°C; extract within 7 d, analyze extract within 40 d	12
Phthalate and adipate esters	Sodium thiosulfate	Store sample at 4°C; extract within 14 d; store extract at 4°C; analyze within 14 d	5
Polychlorinated biphenyls	None	Store sample at 4°C; extract sample within 14 d; store extract at 4°C; analyze within 30 d	3
Polycyclic aromatic hydrocarbons	Sodium thiosulfate, adjust to pH < 2 with HCl	Store samples at 4°C; extract within 7 d; analyze within 30 d of extraction	3
Triazine herbicides	Adjust to pH 5–9	Store sample at 4°C, extract within 7 d; analyze extract within 40 d; or extract in ethyl acetate and store at room temperature for up to a year	21
	Sodium thiosulfate or ascorbic acid	Store samples at 4°C; analyze within 14 d	3
Volatile organics, non-halogenated	None	Store sample at 4°C; analyze within 56 d	12
	Sodium thiosulfate or ascorbic acid	Store sample at 4°C; analyze within 14 d	3

Note: All recommendations are based on actual methods used by USEPA or those recommended by Neaves and Fong[12] based on a literature survey.

by USEPA and recommended as a result of a comprehensive literature review funded by the Ontario Ministry of the Environment and Energy.[12] Many preservation strategies are available. Ultimately, the selection of an appropriate preservation method should be determined by considering the properties of both the sample matrix and the analytes and by considering the limitations that the use of a preservative may impose on an analysis.

IV. EXTRACTION OF ANALYTES

Effective extraction of trace analytes from drinking water samples is not simple because no single extraction technique will effectively recover all organic analytes. Hennion[22] and Onuska[23] have recently summarized sample preparation procedures for the analysis of OCs in aquatic samples. Extraction techniques must be selected based on the physical and chemical properties of the analytes to be determined. For this review, we will consider that all organic compounds fall into three categories: volatiles (VOCs), semivolatiles (SVOCs), or polar compounds. VOCs have vapor pressures of about 10^{-1} to 10^{3} torr (20°C), and boiling points of −30 to 180°C (760 torr), and, for analysis, are typically extracted and concentrated in the gas phase. SVOCs, which have lower vapor pressures and higher boiling points, are most often extracted from water by partitioning into an organic solvent or by adsorption onto a solid sorbent. Polar compounds are also extracted by adsorption onto a solid sorbent or by liquid-liquid extraction. An excellent book describing the analyses of trace organics in aquatic systems has been published.[24]

A. Volatile Organic Compounds (VOCs)

Volatile organic compounds are primarily extracted by either static or dynamic headspace methods. All headspace methods rely on the establishment of equilibrium partitioning of an analyte between dissolved and gas phases to facilitate extraction. In static headspace methods, the closed airspace above the water is sampled and analyzed directly. In dynamic headspace methods, the most common of which are purge and trap (P & T) and closed loop stripping, the analytes are actively removed from the water as an inert gas is bubbled through the sample. Liquid-liquid extraction, solid sorbents, and other miscellaneous techniques have also been employed for the extraction of VOCs from aqueous media. An excellent review of the analysis of VOCs found in water has been written by Oliver.[25] Thomas has reported sampling protocols and approaches to determining VOCs.[26]

1. Purge and Trap

a. Introduction

The P & T method is most commonly used for extracting VOCs from water. The wide use of P & T is reflected by the results of a recent survey in which 633 laboratories were questioned about the number of analyses that they routinely performed using USEPA protocols.[27] Of a total of 39 USEPA methods used by these laboratories, five of the top ten most commonly used methods (602, 624, 601, 502.2, 524.2) were P & T analyses. This illustrates the importance of P & T techniques in assessing the quality of drinking water.

Figure 1 shows a typical P & T device. In P & T, a water sample is placed in a purge vessel and VOCs are extracted by passing an inert gas (usually helium or nitrogen) through the sample. The extracted, vapor-phase analytes are then collected on an adsorbent trap and thermally desorbed and introduced into a gas chromatograph for separation and detection. During extraction, a needle sparger or a glass frit is used to produce purge gas bubbles of < 3 mm in diameter. Commonly used trap adsorbents include a 2,6-diphenylene oxide polymer (Tenax), Carbopack-B/Carbosieve, and a combination of Tenax, silica gel, and charcoal. The retention characteristics of volatile compounds on Tenax TA have been described.[29] Several commer-

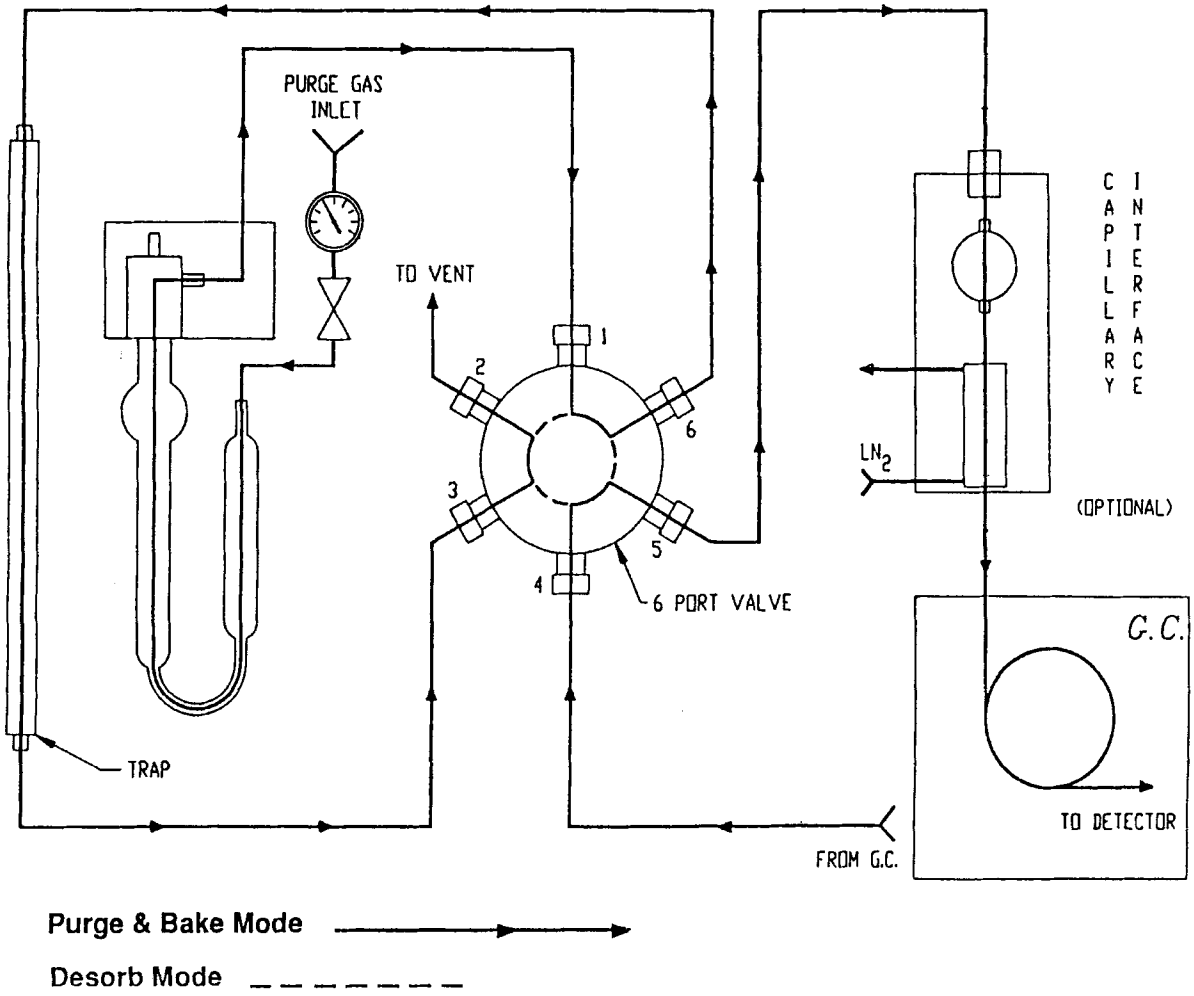

FIGURE 1. A typical P & T system. ("From Fundamentals of Purge and Trap," Tekmar, Publ. Note B121988. With permission.)

cial purge and trap systems are available and the technique is easily automated.[30,31]

b. Theoretical Considerations

Theoretical considerations of the P & T method have been addressed in detail by Pankow and associates.[32-34] Several factors affect P & T efficiencies. Water-miscible VOCs are not efficiently extracted by P & T. Water temperature, ionic strength, and volume of purge gas also affect extraction efficiencies.[35] These factors are important in all headspace methods and can be exploited to maximize extraction efficiencies. The kinetics of purging many priority VOCs have been studied and purging rate constants can be used, as an alternative to GC retention times, for the selection of appropriate internal or surrogate standards.[36]

c. Practical Aspects

Purge and trap extraction conditions must be closely controlled to ensure good reproducibility and high extraction efficiencies. Environmental Protection Agency methods require strict adherence to the extraction conditions that are considered to be typical for P & T. In USEPA methods, the set purge time is 11 min, and the purge gas flow is 40 ml/min. Desorption of the analytes from the trap must be carefully performed so that GC resolution is not compromised. Typical des-

orption conditions include ballistic heating to 180°C and a desorption period of 4 min.[3]

Several P & T parameters are not tightly controlled. For example, the volume of water sampled can range from 5 to 25 ml. Larger samples can improve detection limits; however, larger samples require longer purge times. Increased purge times can result in the undesirable effect of depositing increased amounts of water onto the traps with the analytes. Longer purge times can also cause breakthrough of the analytes from the adsorbent trap. Increased purge flow rates can cause similar problems. Despite these concerns, successful P & T methods have been developed that employ 100 ml sample volumes and 20 to 35 min purge times.[37]

The flow rates of gas used for desorption vary and are dependent on the type of GC column used, the thickness of the GC stationary phase, and whether cryofocusing is used. For packed column GC, desorption flow rates of 15 to 60 ml/min may be used; for capillary column GC (usually columns are 0.53 mm i.d.), desorption flow rates range from 4 to 15 ml/min. The GC column can be kept at either ambient or subambient temperatures during sample desorption. A cryogenic trap (approximately −150°C), may be used to focus the analytes into a tight band before introduction onto a GC column; this is especially important when using capillary GC.

One practical consideration in P & T is the elimination of sample contamination. Contaminants primarily arise from impurities in the purge gases and contamination of the sample by laboratory background solvent vapors. Decomposition of trap materials (for example, Tenax decomposes to produce benzene and alkyl benzenes) may produce interferents and increase the detection limits of certain analytes.[37] The use of tubing made from materials other than polytetrafluoroethylene (PTFE), non-PTFE thread sealants, or flow controllers with rubber parts should be avoided because of the possibility that contaminants will be added to the gas stream, which may interfere with the analysis. The determination of CH_2Cl_2 is an extreme example of the problems that can be associated with measuring VOCs. When attempting to measure CH_2Cl_2, only stainless steel tubing may be used in P & T and no CH_2Cl_2 may be opened in the room in which the analysis is being performed. Even using the same laboratory coat that was worn when working previously with CH_2Cl_2 can outgas sufficient amounts of the solvent to interfere with its determination at trace concentrations.[3]

A major problem with P & T is that water from the sample may be introduced into the trap, the lines connecting the trap and the GC column, and into the gas chromatograph itself. This causes problems with analyte adsorption onto the traps and causes loss of chromatographic resolution. In fact, under conventional P & T conditions (discussed above) approximately 0.017 μl of liquid water are removed from the purge vessel per milliliter of purge gas used.[33] For this reason, newer P & T systems incorporate some form of water removal in their designs. Another difficulty with P & T is interfacing this system with a MS detector. Purge and trap typically requires higher purge flows than those compatible with the MS vacuum systems. In some USEPA methods, a jet separator is used to interface P & T with the MS. This is undesirable because analytes are lost with the gas that is removed from the system, resulting in decreased signal. Thus, methods of directly interfacing P & T with MS are gaining acceptance.

d. Improvements

Recent improvements to P & T include modifications of the cryofocusing used to preserve chromatographic resolution and methods for preventing water from being introduced onto the chromatographic column. Whole column cryotrapping (WCC), with and without ice traps, has been used to directly trap purged VOCs onto a 0.32 or 0.53 mm i.d. chromatographic column at −90°C.[33] The major advantage of this system is its simplicity. No adsorbent traps are required; thus, fewer background interferences are observed and analysis times are shorter because no

desorption of analytes from adsorbent traps is necessary. Whole column cryotrapping worked well when < 20 ml of purge gas was used. When > 20 ml of purge gas was used, sufficient water was introduced onto the GC column to interfere with the quantitation of compounds that elute at temperatures near the boiling point of water. Water contamination also caused peak splitting and variations in response factors and retention times.

Strategies for preventing water from reaching the analytical column include the use of different adsorbents and driers. A trap made of Carbopack-B/Carbosieve adsorbent eliminated water interferences and provided better detection limits (in some cases, an order of magnitude improvement) than those of USEPA Method 502.[38] Nafion drying tubes have been used to remove water directly after the purge step[39,40] and have also been used to remove water from air samples analyzed for VOCs;[41] however, some analyte loss was also observed. A short column packed with glass beads at −10°C has been used to trap water before the analytes were collected on the chromatographic column at −90°C.[34] During the final stage of the sample purge, the glass bead trap was warmed to ambient temperature to allow any analytes that may have collected to be transferred to the chromatographic column. This did not result in significant water introduction onto the column; desiccation efficiency was reported to be 90% and < 40 µl of water collected on the chromatographic column. Performance of this technique was superior to WCC as demonstrated by lower relative standard deviations in peak areas and less variations in retention times. Another water control strategy is applied in a new instrumental design. This system uses a turbulent vortex to remove 98% of trapped water (Cyclone system) and condenses the water vapor in a controlled zone to prevent it from entering the GC column.[42]

e. Applications

Purge and trap has been used to analyze many VOCs. Table 2 lists the USEPA methods for drinking water analyses that use the P & T technique and the ranges of method detection limits. Table 3 lists the specific analytes associated with each method. Table 3 also contains a master list of analytes monitored in EPA drinking water analysis methods and the detection limits that should be easily obtained for these analytes. In addition to the analytes of Table 2, other analytes that have been extracted by P & T from drinking water include chloroform, bromodichloromethane, dibromochloromethane, and bromoform at detection limits of 0.01 to 0.05 ppt.[43] Volatile sulfides (H_2S, COS, CH_3SH, CS_2, CH_3SCH_3, $CH_3CH_2CH_2SH$, and CH_3SSCH) have been measured by P & T in fresh waters at detection limits of 0.02 to 0.10 ppt with precision better than 10%.[4] P & T has been used to detect contamination of potable water supplies by solvent mixtures (i.e., gasoline, kerosene, white spirit); recoveries ranged from 84 to 100% for standards of 10 to 5000 ppb.[44] Methyl-*tert*-butyl ether and 1,2-dihaloethanes were determined at 4 ppt by P & T;[45] calibration curves were linear up to 300 ppb and the relative standard deviations of standards containing 18 ppt 1,2-dihaloethanes and 6 ppt methyl-*tert*-butyl ether analyzed over a 2-year period were approximately 3%. Benzenes and naphthalenes, at concentrations of 0.1 ppb, were determined by P & T onto Tenax-GC and cryotrapping.[46] These good detection limits were achieved using a 5-ml sample.

Purge and trap is a relatively simple, well-established method for quantitative extraction of VOCs from drinking water that will continue to be important in environmental monitoring applications. It requires little sample preparation and provides good reproducibilities and detection limits. Typical detection limits range from 0.1 to 0.01 ppb with precisions of 1 to 10%.[47] Purge and trap will continue to improve and will be coupled to novel combinations of detectors, for example, dual detector systems (i.e., photoionization detector in series with an electrolytic conductivity detector) and the ion trap.[48] Field use of P & T, which allowed 10-min determinations of dichloromethane, 1,1-dichloroethane, chloroform, benzene, toluene, dibro-

TABLE 2
USEPA Methods Using the P & T Technique

USEPA method	Detection method[a]	MDL (ppb)[b]	Ref.
502.1, Halogenated VOCs	Packed / electrolytic conductivity	< 0.001 –0.05	3
502.2, VOCs	Capillary / PID + halogen specific	0.01 –3	3
503.1, VOCs, aromatic and unsaturated	Packed / PID	0.002 –0.04	3
524.1, VOCs	Packed / MS	0.01 –2	3
524.2, VOCs	Capillary / MS	0.02 –0.35	3

[a] GC column type / detector type; PID = photoionization detector; MS = mass spectrometer.
[b] MDL = method detection limits; MDL are dependent on both the nature of the analytes and the specific detectors used.

mochloromethane, and tetrachloroethylene at detection limits of 0.5 to 10 ppb in water samples has been reported.[49]

2. Continuous, On-Line Dynamic Headspace

An on-line dynamic headspace analyzer has been used to determine VOCs in drinking water at 15 min intervals.[56] The detection limits reported for this system, approximately 2 ppb for tetrachloroethene, chloroform, fluorobenzene, and toluene, were comparable to those obtained by P & T and the analyses were performed in only 25% of the time required for the P & T analyses. This technique reported superior retention time stability ($\pm$0.02 min/week) to that of P & T ($\pm$0.3 min per few analyses).

3. Closed Loop Stripping (CLS)

Closed loop stripping is a commonly used dynamic headspace method for the determination of VOCs.[57,58] As with headspace and P & T techniques, CLS relies on the partitioning of analytes between the dissolved phase and the vapor phase. Factors such as temperature and ionic strength, which affect analyte solubility in water will affect CLS extraction efficiencies. This technique has been summarized and compared to other methods of analysis for VOCs by Melton.[59] An advantage of CLS over other headspace techniques is that CLS can accommodate large (up to 4 l) water samples.

The first step in CLS extraction is to equilibrate the sample (usually 250 to 1000 ml) at an appropriate temperature (approximately 40°C). Gas is then purged through the sample to extract the analytes, which are collected on a small (1.5 to 5 mg), activated carbon trap. Air that remains in the system after sample loading is used as the purge gas and is continuously recycled, at approximately 100 ml/min, through the sample in a closed circuit. After an extraction period of approximately 2 h, the activated carbon trap is removed and the VOCs are recovered with a small amount (15 μl) of carbon disulfide or CH_2Cl_2. Detection limits for CLS are 1 to 10 ppt and reproducibility of the technique is $\pm$10%.[59]

The advantages of CLS include ease of performance, low levels of contamination, and the technique's inherent sensitivity arising from the continuous purging of the sample. The low levels of contamination can be attributed to the small amounts of solvent required for the extraction of the traps, the small amount of trap material used, and the small volume of gas employed. However, CLS is limited to the analysis of clean samples such as drinking water; samples with high concentrations of VOCs, such as plant effluents, will overload the charcoal traps. Also,

TABLE 3
List of Contaminants and Method Detection Limits (MDL) for Current EPA Methods

Analyte	CAS	MDL (ppt)	USEPA Method	Ref.
Acenaphthene	83-32-9	2000	550, 550.1*	5
Acenaphthylene	208-96-7	100	525.1,* 550, 550.1	3, 5
Acetone	67-64-1	280	524.2	177
Acifluorfen	50594-66-6	100	515.1,* 515.2, 555	3, 177
Acrylonitrile	107-13-1	220	524.2	177
Alachlor	5972-60-8	200	505,* 507, 525.1	3
Aldicarb	116-06-3	1000	531.1	3
Aldicarb sulfone	1646-88-4	2000	531.1	3
Aldicarb sulfoxide	1646-87-3	2000	531.1	3
Aldrin	309-00-2	80	505, 508,* 525.1	3
Allyl chloride	107-05-1	130	524.2	177
Ametryn	834-12-8	2000	507	3
Anthracene	120-2-7	40	525.1,* 550, 550.1	3, 5
Aroclor 1016	12674-11-2	80	505,* 508, 525.1	3
Aroclor 1221	11104-28-2	15000	505,* 508, 525.1	3
Aroclor 1232	11141-16-5	500	505,* 508, 525.1	3
Aroclor 1242	53469-21-9	300	505,* 508, 525.1	3
Aroclor 1248	12672-29-6	100	505,* 508, 525.1	3
Aroclor 1254	11097-69-1	100	505,* 508, 525.1	3
Aroclor 1260	11096-82-5	200	505,* 508, 525.1	3
Aroclor (general screen)	—	500	508A,* 525.1	3
Atraton	1610-17-9	600	507	3
Atrazine	1912-24-9	100	505, 507,* 525.1*	3
Baygon	114-26-1	1000	531.1	3
Bentazon	25057-89-9	200	515.1,* 515.2, 555	3, 177
Benzo[*a*]anthracene	56-55-3	2	525.1, 550,* 550.1	3, 5
Benzene	71-43-2	10	502.2,* 503.1, 524.1, 524.2	3, 177
Benzidine	92-87-5	5300	553	177
Benzo[*b*]fluoranthene	205-82-3	3	525.1, 550,* 550.1	3
Benzo[*k*]fluoranthene	207-08-9	2	525.1, 550,* 550.1	3
Benzo[g,h,i]perylene	191-24-2	10	525.1, 550,* 550.1	3
Benzo[*a*]pyrene	50-32-8	20	525.1, 550, 550.1*	3
Benzoylprop ethyl	33878-50-1	6300	553	177
Bis (2-ethylhexyl)adipate	103-23-1	12000	506	5
Bis (2-ethylhexyl)phthalate	117-81-7	2000	506	5
Bromacil	314-40-9	2000	507	3
Bromobenzene	108-86-1	2	502.1, 502.2, 503.1,* 524.1, 524.2	3, 177
Bromochloroacetic acid	5589-96-3	100	552	5
Bromochloroacetonitrile	83463-62-1	10	551	5
Bromochloromethane	74-97-5	10	502.1, 502.2,* 524.1, 524.2	3, 177
Bromodichloromethane	75-24-4	6	502.1, 502.2, 524.1, 524.2, 551*	3, 5, 177
Bromoform	75-25-2	10	502.1,* 502.2, 524.1, 524.2, 551	3, 5, 177
Bromomethane	74-83-9	20	502.1, 502.2,* 524.1, 524.2	3, 177
Butachlor	23184-66-9	400	507	3
2-Butanone	78-93-3	480	524.1	3
Butylate	2008-41-5	200	507	3
n-Butylbenzene	104-51-8	20	502.2,* 503.1, 524.2	3, 177
sec-Butylbenzene	135-98-8	20	502.2,* 503.1, 524.2	3, 177
tert-Butylbenzene	98-06-6	6	502.2, 503.1,* 524.2	3, 177
Butylbenzylphthalate	85-68-7	300	525.1	3
Carbaryl	63-25-2	2000	531.1	3

TABLE 3 (continued)
List of Contaminants and Method Detection Limits (MDL) for Current EPA Methods

Analyte	CAS	MDL (ppt)	USEPA Method	Ref.
Carbofuran	1563-66-2	2000	531.1	3
Carbon disulfide	75-15-0	93	524.1	3
Carbon tetrachloride	56-23-5	3	502.1,* 502.2, 524.1, 524.2	3, 177
Carboxin	5234-68-5	600	507	3
Caffeine	58-08-2	4400	553	177
Carbaryl	63-25-2	5700	553	177
Chloral hydrate	75-87-6	30	551	5
Chloramben	133-90-4	90	515.1,* 555	3, 177
Chlordane (technical)	57-74-9	100	505,* 508	3
α-Chlordane	5103-71-9	2	505, 508,* 525.1	3, 5
γ-Chlordane	5103-74-2	2	505, 508,* 525.1	3, 5
Chlorneb	2675-77-6	500	508	3
Chloroacetonitrile	107-14-2	120	524.1	3
Chlorobenzene	108-90-7	4	502.1, 502.2, 503.1,* 524.1, 524.2	3, 177
Chlorobenzilate	501-15-6	5000	508	3
2-Chlorobiphenyl	2051-60-7	100	525.1	3
1-Chlorobutane	109-69-3	180	524.2	177
Chloroethane	75-00-3	8	502.1	3
Chloroform	67-66-3	2	502.1, 502.2, 524.1, 524.2, 551 *	3, 177
Chloromethane	74-87-3	10	502.1,* 502.2, 524.1, 524.2	3, 177
o-Chlorophenyl thiourea	5344-82-1	—	553	177
Chloropicrin	76-06-2	10	551	5
Chlorothalonil	2921-88-2	20	508	3
2-Chlorotoluene	95-49-8	8	502.1, 502.2, 503.1,* 524.1, 524.2	3, 177
4-Chlorotoluene	106-43-4	20	502.1, 502.2,* 503.1, 524.1, 524.2	3, 177
Chlorpropham	101-21-3	500	507	3
Chrysene	218-01-9	40	525.1,* 550, 550.1	3, 5
Cycloate	1134-23-2	200	507	3
Dalapon	75-99-0	320	515.1, 552.1 *	3, 177
Dacthal	1831-32-1	130	515.2	177
2,4-D	94-75-7	200	515.1,* 515.2, 555	3, 177
2,4-DB	94-82-6	800	515.1, 515.2,* 555	3, 177
DCPA	1897-45-6	20	508	3
4,4′-DDD	72-54-8	3	508	3
4,4′-DDE	72-55-9	10	508	3
4,4′-DDT	50-29-3	60	508	3
Diazinon	333-41-5	200	507	3
Dibenz[a,h]anthracene	53-70-3	20	525.1, 550,* 550.1	3, 5
Dibromoacetic acid	631-64-1	20	552	5
Dibromoacetonitrile	3252-43-5	30	551	5
Dibromochloromethane	124-48-1	8	502.1, 502.2,* 524.1, 524.2	3, 177
1,2-Dibromo-3-chloro-propane	96-12-8	9	502.2, 504, 524.1, 524.2, 551 *	3, 5, 177
Dibromomethane	74-95-3	400	502.1, 502.2, 524.1,* 524.2	3
1,2-Dibromoethane	106-93-4	0.6	502.1, 502.2, 504, 524.1, 524.2, 551 *	3, 5,177
Di-*n*-butylphthalate	84-72-2	300	506, 525.1 *	3,5
Dicamba	1918-00-9	80	515.1,* 515.2, 555	3, 177

TABLE 3 (continued)
List of Contaminants and Method Detection Limits (MDL) for Current EPA Methods

Analyte	CAS	MDL (ppt)	USEPA Method	Ref.
Dichloroacetic acid	79-43-6	20	552,* 552.1	5, 177
Dichloroacetonitrile	3018-12-0	20	551	5
1,2-Dichlorobenzene	95-50-1	20	502.1, 502.2, 503.1,* 524.1, 524.2	3, 177
1,3-Dichlorobenzene	541-73-1	6	502.1, 502.2, 503.1,* 524.1, 524.2	3, 177
1,4-Dichlorobenzene	106-46-7	6	502.1, 502.2, 503.1,* 524.1, 524.2	3, 177
3,3'-Dichlorobenzidine	91-94-1	1400	553	177
3,5-Dichlorobenzoic acid	51-36-5	60	515.1,* 515.2, 555	3, 177
2,3-Dichlorobiphenyl	84-72-2	100	525.1	3
trans-1,4-Dichloro-2-butene	110-57-6	360	524.2	177
Dichlorodifluoromethane	75-71-8	100	502.1, 502.2, 524.1, 524.2*	3, 177
1,1-Dichloroethane	75-34-3	3	502.1,* 502.2, 524.1, 524.2	3, 177
1,2-Dichloroethane	107-06-2	2	502.1,* 502.2, 524.1, 524.2	3, 177
1,1-Dichloroethene	75-35-4	3	502.1,* 502.2, 524.1, 524.2	3, 177
cis-1,2-Dichloroethene	156-59-4	2	502.1,* 502.2, 524.1, 524.2	3, 177
trans-1,2-Dichloroethene	156-60-5	2	502.1,* 502.2, 524.1, 524.2	3, 177
2,4-Dichlorophenol	120-83-2	300	552	5
1,2-Dichloropropane	78-87-5	40	502.1, 502.2, 524.1, 524.2*	3, 177
1,3-Dichloropropane	142-28-9	40	502.1, 502.2, 524.1, 524.2*	3, 177
2,2-Dichloropropane	590-20-7	350	502.1, 502.2, 524.1, 524.2*	3, 177
1,1-Dichloropropene	563-58-6	20	502.1, 502.2,* 524.1, 524.2	3, 177
cis-1,3-Dichloropropene	10061-01-5	—	502.1, 502.2, 524.1, 524.2	3, 177
trans-1,3-Dichloropropene	10061-02-6	—	502.1, 502.2, 524.1, 524.2	3, 177
1,1-Dichloropropanone	513-88-2	1000	524.2	177
1,1-Dichloro-2-propanone	513-88-2	5	551	5
Dichlorprop	120-36-5	130	515.1, 515.2,* 555	3, 177
Dichlorvos	62-73-7	2000	507	3
Dieldrin	60-57-1	10	505,* 508	3
Diethyl ether	60-29-7	280	524.2	177
Di(2-ethylhexyl)adipate	103-23-1	600	525.1	3
Di(2-ethylhexyl)phthalate	117-81-7	600	525.1	3
Diethylphthalate	84-66-2	800	506, 525.1*	3, 5
3,3'-Dimethoxybenzidine	119-90-4	5700	553	177
3,3'-Dimethylbenzidine	612-82-8	3000	553	177
Dimethylphthalate	131-11-3	40	506, 525.1*	3, 5
Dinoseb	88-85-7	200	515.1,* 515.2, 555	3, 177
Di-*n*-octylphthalate	117-81-7	6000	506	5
Diphenamid	957-51-7	600	507	3
Diquat	85-00-7	400	549.1	177

TABLE 3 (continued)
List of Contaminants and Method Detection Limits (MDL) for Current EPA Methods

Analyte	CAS	MDL (ppt)	USEPA Method	Ref.
Disulfoton	298-04-4	300	507	3
Disulfoton sulfone	2497-06-5	4000	507	3
Disulfoton sulfoxide	2497-07-6	400	507	3
Diuron	330-54-1	4400	553	177
Endosulfan I	959-98-8	20	508	3
Endosulfan II	33213-65-9	20	508	3
Endosulfan sulfate	1031-07-8	20	508	3
Endothall	145-73-3	1800	548.1	177
Endrin	72-20-8	20	505, 508,* 525.1	3
Endrin aldehyde	7421-93-4	30	508	3
Ethoprop	13194-48-4	20	507	3
Ethylbenzene	100-41-4	2	502.1, 503.1,* 524.1, 524.2	3, 177
Ethylene thiourea	96-45-7	—	553	177
Ethyl methacrylate	97-63-2	28	524.2	177
Etridiazole	2593-15-9	30	508	3
Fenamiphos	22224-92-6	1000	507	3
Fenarimol	60168-88-9	400	507	3
Fluoranthene	206-44-0	9	550,* 550.1*	3
Fluorene	86-73-7	100	525.1, 550, 550.1*	3
Fluridone	59756-60-4	4000	507	3
Glyphosate	1071-83-6	6000-8000	547	5
α-Hexachlorocyclohexane	319-84-6	30	508	3
β-Hexachlorocyclohexane	319-85-7	10	508	3
δ-Hexachlorocyclohexane	319-86-8	10	508	3
γ-Hexachlorocyclohexane	58-89-9	20	505, 508,* 525.1	3
Heptachlor	76-44-8	3	505,* 508, 525.1	3
Heptachlor epoxide	1024-57-3	4	505,* 508, 525.1	3
Hexachlorobenzene	118-74-1	2	505,* 508, 525.1	3
2,2',3,3',4,4',6-Heptachlorobiphenyl	52663-71-5	100	525.1	3
2,2',4,4',5,6'-Hexachlorobiphenyl	60145-22-4	100	525.1	3
Hexachlorobutadiene	87-68-3	20	502.2, 503.1,* 524.2	3, 177
Hexachlorocyclopentadiene	77-74-4	30	505, 525.1*	3
Hexachloroethane	67-72-1	57	524.2	177
2-Hexanone	98-82-8	39	524.2	177
Hexazinone	51235-04-2	800	507	3
3-Hydroxycarbofuran	16655-82-6	2000	531.1	3
5-Hydroxydicamba	7600-50-2	40	515.1,* 515.2, 555	3, 177
Indeno[1,2,3,c,d]pyrene	193-39-5	10	525.1, 550,* 550.1	3, 5
Isopropylbenzene	98-82-8	5	502.2, 503.1,* 524.2	3, 177
4-Isopropyltoluene	99-87-6	9	502.2, 503.1,* 524.2	3, 177
Lindane	58-89-9	3	505	3
Linuron	330-55-2	15000	553	177
MCPA	—	800	555	177
MPCP	—	1700	555	177
Merphos	150-50-5	300	507	3
Methacrylonitrile	126-98-7	120	524.2	177
Methiocarb	2032-65-7	4000	531.1	3
Methomyl	16752-77-5	500	531.1	3
Methoxychlor	72-43-5	50	505, 508,* 525.1	3
Methylacrylate	96-33-3	450	524.2	177
Methyl-*t*-butyl ether	1634-04-4	90	524.2	177
Methyl parpoxon	950-35-6	3000	507	3

TABLE 3 (continued)
List of Contaminants and Method Detection Limits (MDL) for Current EPA Methods

Analyte	CAS	MDL (ppt)	USEPA Method	Ref.
Methylene chloride	75-09-2	30	502.1, 502.2, 524.1, 524.2*	3, 177
Methyliodide	77-88-4	19	524.2	177
Methylmethacrylate	80-62-6	430	524.2	177
4-Methyl-2-pentanone	108-10-1	170	524.2	177
Metolachlor	51218-45-2	800	507	3
Metribuzin	21087-64-9	200	507	3
Mevinphos	7786-34-7	5000	507	3
MGK 264	113-48-4	500	507	3
Molinate	2212-67-1	200	507	3
Monobromoacetic acid	79-08-3	7	552,* 552.1	5, 177
Monochloroacetic acid	79-11-8	50	552,* 552.1	5, 177
Monuron	150-68-5	9100	553	177
Naphthalene	91-20-3	40	502.2, 503.1,* 524.2,* 550, 550.1	3, 5, 177
Napropamide	15299-99-7	300	507	3
Nitrobenzene	98-95-3	1200	524.2	177
4-Nitrophenol	100-02-7	100	515.1, 555	3, 177
2-Nitropropane	79-46-9	160	524.2	177
cis-Nonachlor	—	30	505	3
trans-Nonachlor	39765-80-5	10	505,* 525.1	3
Norflurazon	27314-13-2	500	507	3
2,2',3,3',4,5',6,6'-Octachloro-biphenyl	40186-71-8	200	525.1	3
Oxamyl	23135-22-0	2000	531.1	3
Paraquat	1910-42-5	800	549.1	177
Pentachlorophenol	87-86-5	80	515.1,* 515.2, 525.1 555	3, 177
Pebulate	1114-71-2	100	507	3
2,2',3',4,6-Pentachloro-biphenyl	60233-25-2	100	525.1	3
Pentachloroethane	76-01-7	140	524.2	177
cis-Permethrin	52645-53-1	500	508	3
trans-Permethrin	52645-53-1	500	508	3
Phenanthrene	85-01-8	10	525.1,* 550, 550.1	3, 5
Picloram	1918-02-1	100	515.1,* 515.2, 555	3, 177
Prometon	1610-18-0	300	507	3
Prometryn	7287-19-6	200	507	3
Pronamide	23950-58-5	800	507	3
Propachlor	1918-16-7	500	508	3
Propazine	139-40-2	100	507	3
Propionitrile	107-12-0	140	524.2	177
Propylbenzene	103-65-1	9	502.2, 503.1,* 524.2	3, 177
Pyrene	129-00-0	100	525.1, 550, 550.1*	3, 5
Rotenone	83-79-4	7500	553	177
Siduron	1982-49-6	6300	553	177
Simazine	122-34-9	80	505, 507,* 525.1	3
Simetryn	1014-70-6	300	507	3
Stirofos	22248-79-9	800	507	3
Styrene	100-42-5	8	502.2, 503.1,* 524.1, 524.2	3, 177
2,4,5-T	93-76-5	80	515.1,* 515.2, 555	3, 177
2,4,5-TP	93-72-1	60	515.1, 515.2,* 555	3, 177

TABLE 3 (continued)
List of Contaminants and Method Detection Limits (MDL) for Current EPA Methods

Analyte	CAS	MDL (ppt)	USEPA Method	Ref.
Tebuthiuron	34014-18-1	1000	507	3
Terbacil	5902-51-2	5000	507	3
Terbufos	13071-79-9	500	507	3
Terbutryn	886-50-0	300	507	3
2,3,7,8-Tetrachloro-dibenzo-*p*-dioxin	1746-01-6	0.02	513	5
1,1,1,2-Tetrachloroethane	630-20-6	30	502.1, 502.2,* 524.1, 524.2	3, 177
1,1,2,2-Tetrachloroethane	79-34-5	10	502.1,* 502.2, 524.1, 524.2	3, 177
Tetrachloroethene	127-18-4	1	502.1,* 502.2, 503.1, 524.1, 524.2	3, 177
Tetrachloroethylene	127-18-4	4	551	5
2,2',4,4'-Tetrachloro-biphenyl	2437-79-8	100	525.1	3
Tetrahydrofuran	109-99-9	1600	524.2	177
Toluene	108-88-3	10	502.2,* 503.1, 524.1, 524.2	3, 177
Toxaphene (technical)	8001-35-2	1000	505,* 508, 525.1	3
Triademefon	43121-43-3	600	507	3
Trichloroacetic acid	76-03-9	70	552, 552.1 *	5,177
Trichloroacetonitrile	545-06-2	90	551	5
1,2,3-Trichlorobenzene	87-61-6	30	502.1,* 503.1, 524.2	3, 177
1,2,4-Trichlorobenzene	120-82-1	20	502.2,* 503.1, 524.2	3, 177
2,4,5-Trichlorobiphenyl	15862-07-4	60	525.1	3
1,1,1-Trichloroethane	71-55-6	3	502.1,* 502.2, 524.1, 524.2, 551	3, 5, 177
1,1,2-Trichloroethane	79-00-5	7	502.1,* 502.2, 524.1, 524.2	3, 177
Trichloroethene	79-01-6	0.1	502.1,* 502.2, 503.1, 524.1, 524.2	3, 177
Trichloroethylene	79-01-6	2	551	5
Trichlorofluoromethane	75-69-4	80	502.1, 502.2, 524.1, 524.2	3, 177
2,4,6-Trichlorophenol	88-06-2	20	552	5
1,2,3-Trichloropropane	96-18-4	300	502.1, 502.2, 524.1, 524.2 *	3, 177
1,1,1-Trichloro-2-propanone	918-00-3	10	551	5
Tricyclazole	41814-78-2	1000	507	3
Trifluralin	1582-09-8	20	508	3
1,2,4-Trimethylbenzene	94-63-6	6	502.2, 503.1,* 524.2	3, 177
1,3,5-Trimethylbenzene	108-67-8	3	502.2, 503.1,* 524.2	3, 177
Vernolate	1929-77-7	100	507	3
Vinyl chloride	75-01-4	10	502.1,* 502.2, 524.1, 524.2	3, 177
m-Xylene	108-38-3	4	502.1, 503.1,* 524.1, 524.2	3, 177
o-Xylene	95-47-6	4	502.1, 503.1,* 524.1, 524.2	3, 177
p-Xylene	106-42-3	2	502.1, 503.1,* 524.1, 524.2	3, 177

Note: MDL represents concentrations that should be detected easily by a competent laboratory.
* Indicates method with the lowest detection limit; this is the detection limit cited.

recoveries for highly volatile compounds are not good because these compounds tend to break through the traps during extraction. Another limitation of CLS is that compounds that elute from the GC column during the time in which the solvent peak elutes cannot be detected.

One major use of CLS has been to determine compounds, such as geosmin and 2-methylisoborneol (produced by microbiological sources and certain blue-green algae), which cause taste and odor problems when present at concentrations as low as 10 to 30 ppt in water supplies.[60] By using CLS and by adjusting the ionic strength of the sample with Na_2SO_4, quantitative recoveries and detection limits of 0.8 ppt were achieved for geosmin, 2-methylisoborneol, 2-isopropyl-3-methoxypyrazine, 2-isobutyl-3-methoxypyrazine, and 2,3,6-trichloroanisole.[61] The sensitivity and detection limits of this method were reported to be much improved over those for P & T analyses.

Improvements to CLS include the use of thermal desorption instead of solvent extraction of the analytes from the traps and the use of large (> 1 l) samples. Thermal desorption CLS with GC-MS was used to detect halogenated methanes and ethanes and toluene in sewage treatment plant effluents at concentrations ranging from 0.1 to 10 ppb.[62] The major advantages of using thermal desorption are that it allows the detection of analytes that would be obscured by a solvent peak, and that all of the sample extract is introduced into the detector, thus enhancing sensitivity. Recently, CLS of 4 l groundwater samples with solvent extraction of the trap and GC-MS was used to detect tri- and tetrachloroethene at concentrations of 40 and 20 ppt, respectively.[63] These concentrations were approximately a factor of 10 or better than the detection limits reported for recent analyses of the same groundwater using P & T.

4. Static Headspace

Although not as commonly used as P & T, static headspace is a rapid, simple method for extracting and concentrating VOCs from aqueous solutions. Drozd and Novak[50] and Vitenberg[51] have explained the theoretical aspects of this technique. Headspace exploits the equilibrium partitioning of VOCs between thermostated aqueous samples in a sealed container and its enclosed headspace. Like P & T, factors that affect the equilibrium achieved (analyte solubility, temperature, ionic strength, etc.) will also affect extraction efficiencies. For example, elevated temperatures and the addition of salts to a water sample will increase the concentration of analyte in the headspace. The headspace is sampled with a gas-tight syringe and directly injected into a packed or capillary column. Up to 1 ml of gas may be injected on a packed column; up to 20 µl may be directly injected on a capillary column without the loss of column resolution. (Cryofocusing of the analytes can be used with capillary columns if larger injections are necessary.) Reproducibility of this technique ranges from about 10 to 20% and 0.1 to 1 ppb detection limits can be achieved.[25]

Headspace analysis is a good method for performing rapid analysis of VOCs in water. Recently, the headspace method has been used to determine benzene, toluene, ethyl benzene, and the three xylene isomers (all gasoline components) in groundwater.[6] Groundwater samples of 40 ml were collected and returned to the laboratory. Later, 10 ml of water were removed, leaving a 10-ml headspace. After equilibration, 200 to 500 µl of the headspace were sampled and injected on a megabore GC column attached to a photoionization detector followed by a flame ionization detector (FID). The useful working range for this technique was 1 to 15,000 ppb and relative standard deviations of 2 to 8% were reported for the concentration range of 440 to 2200 ppb. Headspace analysis has also been used to determine carbon tetrachloride at > 0.05 ppb and chloroform, trichloroethylene, and tetrachloroethylene at > 0.2 ppb by GC-electron capture detector (ECD) using dibromomethane as an internal standard.[52] Headspace analysis can be easily automated; a headspace sampler with a 3-ml sample loop and cryogenic trapping at −80°C

has been used with a 30 m × 0.32 mm capillary column to determine various VOC at parts per trillion concentrations in water.[53] Semiautomatic headspace injection onto a packed column has been used to determine halogenated hydrocarbons at 1 to 200 ppb in 2 ml drinking water samples.[54] Recently, headspace analysis has been used to monitor selected VOC, including benzene, toluene, cyclohexane, chloroform, and dichloromethane, at low parts per billion concentrations in 30 ml samples of bottled water.[55]

The major advantage of the static headspace method over P & T is its simplicity. Unlike P & T, headspace analysis is rapid, requires no expensive glassware or sample preparation, affords the opportunity to perform repeat analyses on the same sample, and does not require the use of adsorbents. Static headspace also avoids carryover problems associated with the use of traps and is unaffected by foaming problems caused by the presence of surfactants. However, detection limits for static headspace are often worse than for P & T. Nevertheless, headspace analysis is emerging as an important field monitoring technique, especially for monitoring water sources near contaminated sites and sites of industrial or commercial operations.

5. Emerging Techniques

Several novel techniques were introduced recently for the extraction of VOCs from water. The development of new techniques complements existing technologies and responds to the need for rugged, sensitive field monitoring methods.

a. Spray Extraction

Spray extraction of VOCs has been developed to circumvent bubble formation problems associated with the P & T extraction of solutions containing high concentrations of surfactants.[64] A spray nozzle generates small droplets of solution in an extraction chamber. The large surface area of the droplets allows quick equilibration of the analytes between the dissolved and gas phases and the gas phase analytes are concentrated on Tenax TA and thermally desorbed into a GC-MS. This technique was used to detect benzene, toluene, *t*-butylbenzene, tetrachloroethene, *p*-dichlorobenzene, and naphthalene at 10 to 30 ppb, using a sampling time of 2 min and 900 ml water. When water was cycled only once through this system, extraction efficiencies for the above analytes were 10 to 15% better than those of the conventional P & T method; cycling water through the system several times will further improve extractions. In addition to handling samples with high surfactant concentrations, this technique may be valuable at field sites where VOCs could be extracted on-site and collected on Tenax traps, which could then be shipped to the laboratory for analysis.

b. Solid Phase Microextraction

Uncoated fibers and fibers coated with poly(dimethylsiloxane), liquid crystal polyacrylate, or polyimide have been developed to measure VOCs (and SVOCs) in water by a novel technique called solid-phase microextraction.[65-67] Figure 2 shows the solid-phase microextraction device. The 0.05 to 1 mm i.d. fibers are placed into an aqueous sample and equilibrium is established as the water is stirred and the analyte is extracted into the fiber. Typical extraction times range from 2 to 15 min. After equilibrium has been achieved, the fiber is introduced into the injection port of a gas chromatograph, where the analytes are thermally desorbed and subsequently analyzed. The amount of analyte adsorbed by the fiber is linearly related to its concentration in solution and is a function of its distribution constants, the volume of the stationary phase, and the amount of stirring in the solution.

Methyl silicon-coated fibers were used to determine substituted benzene compounds in groundwater.[65] The calibration curves for solid-phase microextraction were linear from 15 to 3000 ppb and detection limits ranged from 1 to 3 ppb with relative standard devia-

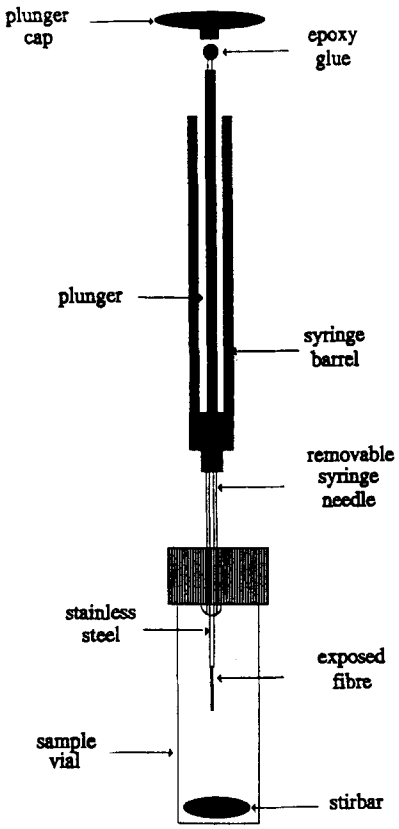

FIGURE 2. Solid-phase microextraction device. (Courtesy of J. Pawliszyn.)

tions ranging from 3 to 20%, depending on the analyte and its concentration. This suggests that this technique, when coupled with ECD, may offer detection limits comparable to those of USEPA Method 624 (P & T), with a three- to sevenfold time savings. Solid-phase microextraction fibers have recently become available commercially (Supelco, Inc.). This inexpensive method, while requiring more development and application work, has great potential for becoming an important field monitoring technique for both VOCs and SVOCs.

c. Single Hollow Fiber Membranes

Another technique that has the potential to be applied in the field is the use of a single hollow fiber membrane to extract VOCs from water.[68,69] A single hollow fiber membrane (8 cm in length and 100 to 400 μm i.d.), is made with silicone or polypropylene and is encased in a 1.5-mm i.d. glass capillary. Water is pumped through the single hollow fiber membrane while helium flows around the exterior of the fiber. The VOCs partition across the membrane and into the helium flow and are cryotrapped prior to GC analysis. Detection limits of $\leqslant 32$ ppb were achieved for the determination of 1,1,1-trichloroethane, trichloroethene, and tetrachloroethene standards in water. For these experiments, the flow rate of water through the fiber was 10 μl/min and the sampling time was 1 min. Calibration curves for this technique were linear for concentrations up to 500 ppb. Memory effects at high analyte concentrations are presently a problem with this technique.

d. Membrane Introduction Mass Spectrometry (MIMS)

On-line analysis of VOCs in water has been accomplished by using a direct insertion, hollow fiber, silicone membrane probe to sample analytes directly from a water sample without any preconcentration.[70-72] The sample flows through a 10-mm membrane loop having a volume of 2 μl and a surface area of 16 mm^2. The analytes permeate the membrane and are directly introduced into an ion trap mass spectrometer. One application of MIMS was the study, in real time, of disinfection by-products in water.[71] Membrane introduction mass spectrometry has achieved detection limits of 0.5 to 10 ppb for many USEPA Method 624 analytes; the detection limits for many analytes (most were 2 ppb or less) were comparable to those obtained when using P & T.[72] The great advantage of this technique is its simplicity; it provides an inexpensive, rapid, and sensitive method for continuous monitoring of environmental contaminants in real time. The main disadvantage of this technique is that the analytes are not subject to chromatographic separation before analysis. In response to this limitation, membrane permeate and trap GC-MS has been developed.[73] In this technique, a membrane is used to

extract analytes from water. The analytes are collected on a Tenax trap and thermally desorbed into a GC column. While this method is not a real time monitoring technique (monitoring time is limited to the time required for the chromatographic analysis), this technique does allow eight to ten samplings of a process stream during an 8-h day. Both MIMS and membrane permeate and trap GC-MS have the ability to sample volatile, polar compounds that are not easily analyzed by P & T. Membrane permeate and trap GC-MS can detect volatile, polar compounds such as 2-propanol, 2-methyl-1-propanol, and 1,4-dioxane at < 100 ppb. Both techniques have the potential for monitoring accidental releases of contaminants into the aquatic environment.

B. Semivolatile Organic Compounds

Methods for the extraction of SVOCs from drinking water rely on the partitioning of analytes from the aqueous phase to either a liquid or a solid organic phase. Liquid-liquid extraction is the most commonly used technique for SVOCs; however, solid-phase extraction (SPE) is gaining popularity because it is less labor intensive and consumes less solvent.

1. Liquid-Liquid Extraction

Liquid-liquid extraction is the most common method for the extraction of SVOCs from water. In liquid-liquid extraction, hydrophobic analytes in water are extracted into an immiscible organic phase. To facilitate extraction, the water and the solvent are typically placed in an separatory funnel, shaker flask, or bottle which is shaken or continuously rotated to increase the surface area of the solvent that is in contact with the water. After extraction, the organic phase is separated from the water and is often dried with Na_2SO_4. The volume of the extract is then reduced, sample cleanup may be performed, and the sample is analyzed.

The partitioning of an analyte between the aqueous and organic phases is a function of its distribution coefficient (D), where D is defined as the ratio of concentrations of the analyte in the organic (C_o) and aqueous (C_a) phases ($D = C_o/C_a$).[74] For a specific analyte, larger values of D mean that a greater proportion of the analyte will be found in the organic solvent (more efficient extraction). By considering the definition of concentration, a useful equation for the fraction of analyte extracted can be derived:

$$n_o/n_{tot} = 1/(1 + V_w/DV_o)$$

where n_{tot} and n_o are total moles of analyte and moles of analyte in the organic phase, respectively, V_w is the drinking water sample volume extracted, and V_o is the organic solvent volume.

Factors that affect the partitioning equilibria may be adjusted to improve extraction efficiencies. The ratio of the volume of the solvent to the volume of the aqueous sample is important; larger ratios favor partitioning of the analyte into the organic phase. Serial solvent extraction is the best approach for obtaining quantitative recoveries of analytes. For example, because of equilibrium considerations, 1 l of water would be more efficiently extracted with two small 60 ml aliquots of CH_2Cl_2 than with a single 120 ml aliquot of CH_2Cl_2. The addition of salts, such as NaCl, to the aqueous phase can improve extraction efficiencies by increasing the ionic strength of the sample, which has the effect of increasing the distribution coefficient.

Table 4 lists USEPA methods for drinking water analyses that use liquid-liquid extraction and illustrates commonly used solvents and typical solvent to sample ratios. Although CH_2Cl_2 is the solvent of choice for most USEPA analyses, its continued use is discouraged because of its potential health hazards. Freon (FC-133) was evaluated as a safer, alternative extraction solvent.[75] While Freon was not as efficient a solvent as CH_2Cl_2 for all compounds, its extraction efficiency was comparable when 100 to 300 ppt of nonpolar organics were extracted and concentrated 1000-fold. However, for envi-

TABLE 4
Liquid-Liquid Extraction Methods Used by USEPA for Drinking Water Analyses

Method	Analytes	Comments	Ref.
504	1,2-Dibromoethane, 1,2-dibromo-3-chloropropane	2 ml hexane to 35 ml sample; 6 g NaCl added before extraction; GC-ECD, 0.01 ppb detection limits	3
505	Organohalide pesticides, PCB	2 ml hexane to 35 ml sample; 6 g NaCl added before extraction; GC-ECD, 0.003 to 15 ppb detection limits	3
506	Phthalate and adipate esters	60 ml methylene chloride (2X) and 40 ml hexane to 1 L sample; 50 g NaCl added before extraction; GC-PID, 0.84 to 11.8 ppb detection limits	5
507	Nitrogen and phosphorus pesticides	60 ml methylene chloride (2X) to 1 l sample; pH to 7 with phosphate buffer and 100 g NaCl added before extraction; GC-NPD, 0.075 to 5 ppb detection limits	3
508	Chlorinated pesticides	60 ml methylene chloride (2X) to 1 l sample; pH to 7 with phosphate buffer and 100 g NaCl added before extraction; GC-ECD, 0.0015 to 5 ppb detection limits	3
508A	PCB screening	60 ml methylene chloride (2X) to 1 l sample; GC-ECD, detects PCB > 0.5 ppb	3
513	2,3,7,8-Tetrachlorodibenzo-*p*-dioxin	60 ml methylene chloride (3X) to l l sample; GC-MS, detection limits matrix dependent, 20 to 2000 ppq	5
515.1	Chlorinated acids	250 g NaCl added to l l sample; pH adjusted to 12 and sample washed with 60 ml methylene chloride (2X); pH to 2; sample extracted with 120 ml ethyl ether; acids derivatized to methylesters with diazomethane; GC-ECD, 0.02 to 1.3 ppb detection limits	3
550	PAH	60 ml methylene chloride (2X) to 1 l sample; HPLC-UV and fluorescence, 0.002 to 3.3 ppb detection limits	5
551	Chlorinated disinfection by-products Chlorinated solvents	2 ml methyl-*t*-butyl ether to 35 ml sample; GC-ECD, 0.002 to 0.092 ppb detection limits	5
552	Haloacetic acids	pH to 11.5; wash the 100 ml sample with 30 ml methyl-*t*-butylether; pH to < 0.5; extract with 15 ml (2X) methyl-*t*-butyl ether; GC-ECD, 0.0074 to 0.32 ppb detection limits	5
553	Benzidines, nitrogen-containing pesticides	pH to 7; add 100 g NaCl; extract with 60 ml (2X) CH_2Cl_2	177

ronmental reasons the use of Freon probably will be phased out. Other recently published methods for the liquid-liquid extraction of analytes at parts per billion and sub-parts per billion concentrations in drinking water include the extraction of halogenated acetic acid with diethylether,[76] the extraction of dihaloacetonitriles with pentane,[77] and the extraction of nitroaromatics and nitramines with toluene and isoamyl acetate.[78]

There are several limitations to liquid-liquid extraction. Polar compounds that can hydrogen bond with water are difficult to remove from aqueous samples. Analytes with COOH and OH groups are difficult to extract; acidification (pH < 2) of the sample prior to extraction is used to force these analytes toward their molecular forms (at high pH, these compounds are present to a greater extent as their anionic forms and would not be efficiently extracted). Trace contaminants are generally present in solvents used for extraction, some at concentrations great enough to interfere with the analysis.[79] This is an excellent reason for optimizing extraction procedures to minimize the amount of solvents required.

Preservatives that are purposely added to solvents may also be a source of analytical artifacts. For example, cyclohexene, which is

often used in CH_2Cl_2, can react with bromide and chloride ions in a sample to form chlorinated and brominated cyclohexene derivatives.[80] Many artifacts formed during liquid-liquid extraction using USEPA Method 625 have been identified by GC-MS, including artifacts formed by oxidation, halogenation, or nitration of phenolic compounds and halogenation and autooxidation of cyclohexenes.[81] This underscores the importance of using solvents of the highest available purity. Another possible problem of liquid-liquid extraction is the formation of emulsions. These can often be broken mechanically by careful use of a stir bar or appropriate tool or by high speed centrifugation. The solvent-water interface can be difficult to detect; copper sulfate has been used to color the aqueous layer to aid in interface detection (USEPA Method 552[5]).

Liquid-liquid extraction of large volumes of water may be accomplished by the use of continuous extractors. Continuous liquid extraction (2 l/h) of 90 l water samples was found to be useful in isolating trace organics for identification and analysis by Ames bioassay.[82] Liquid-liquid extraction using a Goulden extractor with dichloromethane was used to extract 10 to 100 l water samples.[83,84] A total of 35 pesticides, including organochlorines, organophosphates, and triazines, at concentrations of approximately 15 ppb, were extracted as a stream of water making a single pass in a flow-through mechanism. Recoveries for 20 of the 35 pesticides were > 80%; however, this technique was found to be more susceptible to matrix effects than liquid-liquid extraction and some loss of analyte may have been attributed to emulsion formation.

Recently, there has been a trend to reduce the amount of solvents used during sample preparation. The desire to minimize costs of solvent use and disposal, decrease sample preparation time, and minimize amounts of interferents contributed by the solvents has resulted in the development of "microextraction" methods. These methods use considerably less solvent and require less sample than conventional methods. Examples of microextraction include USEPA Methods 504 and 505 (see Table 4), which use 2 ml of hexane to extract analytes from 35 ml of sample, and USEPA Method 551, which uses 2 ml of methyl-*tert*-butyl ether to extract chlorinated solvents and chlorinated disinfection by-products from 35 ml of water. Microextraction (2 ml of methyl-*tert*-butyl ether to 30 ml of water) has been used to extract haloacetic acids and chlorophenols.[85] Organophosphorous pesticides also have been microextracted from water (1 ml of hexane to 500 ml water).[86] The development of microextraction methods will continue. In addition to the reduction in use of toxic organic solvents (which also saves money), less sample will be required to meet required method detection limits as instrumental detection limits are lowered.

2. Solid-Phase Extraction (SPE)

Solid-phase extraction is an emerging technique which requires little solvent and is rapidly replacing liquid-liquid extraction.[87] A review of the use of SPE has been written by Liska et al.[88] In SPE, analytes are adsorbed from an aqueous solution onto a solid support, which is then extracted with a minimal amount of solvent or by thermal desorption. A variety of supports for SPE, including XAD resins and various moieties bonded to silica gel and to silica-impregnated Teflon disks, are available. Solid-phase extraction possesses several characteristics which make it more desirable than traditional liquid-liquid extraction: SPE is easy to use, can be automated, consumes little solvent (minimizing solvent exposure and disposal costs), and is not prone to emulsion problems. In addition, many bonded phases are available to afford selective retention of specific analytes or interferents. Solid-phase extraction using commercially available bonded phase cartridges affords good sensitivity; 100 ml sample volumes can be extracted using 100 mg of packing material and can provide parts per trillion detection limits.[87]

Resin adsorption was one of the earliest SPE techniques to be developed. The use of resins was summarized briefly by Oliver.[25]

Resin has been used for a number of studies. Two grams of 80-100 mesh XAD-4 resin (styrene-divinylbenzene copolymer) were used to extract neutral and anionic analytes from 1 l of water, and allow quantitation at low to sub-parts per billion concentrations.[89] In this application, 30 ml each of diethyl ether (to remove neutral compounds) and HCl saturated ether (to remove anionic compounds) were used to elute the resin. XAD-4 resin, 100-200 mesh, in a 8 cm × 2 mm i.d. column has also been used to collect PAH; sub-parts per billion concentrations of PAH in 3 l water samples were measured by thermal desorption of the cartridge followed by GC-FID.[90] XAD-2 resin, 30 g, in a 30 cm × 1.7 cm i.d. column was used to extract PAH from 1 l water samples;[91] water (30 ml/min) was passed through the column, which was subsequently extracted with tetrahydrofuran and diethylether. Dichloroacetic acid and trichloroacetic acid, both by-products of drinking water disinfection, have been collected using Dowex-1-chloride anion-exchange resin followed by elution with sulfuric acid and extraction into diethylether.[92] A 500-ml sample afforded detection limits of 0.1 ppb with good precision (relative standard deviation of six replicates was approximately 9%). Characterization and determination of organic compounds in drinking water has been performed using Amberlite XAD-2 resin in 16 cm × 4 cm i.d. columns.[93] Drinking water samples of 4000 l were collected at a flow rate of 400 ml/min; the resin was extracted by Soxhlet with 200 ml of acetone/*n*-hexane (50/50 v/v). Phthalate ester plasticizers, PAH (0.1 ppb), and fatty acid methyl esters were the major organic components of the sample. XAD resin was used in an automated preconcentration sampler developed to remove PCDDs and PCDFs (parts per quadrillion) from 30 L water samples.[94] XAD-2 resin, packed in a 18 cm × 2 cm copper tube, has also been used to collect PCDDs and PCDFs (parts of quadrillion) in 200 L samples.[95] Using this system, water could be sampled at flow rates of 140 ml/min; however, only water samples containing 1 to 10 mg (or less) total suspended solids could be collected by this method.

Tenax has been used to sample organic compounds in aqueous solutions.[32] A 0.68-cm^3 Tenax cartridge was used to collect monocyclic and heterocyclic aromatics, PAH and oxo-PAH, pesticides, phthalates, phenols, and alkanes spiked at 20 ppt in 1 l of water. The water sample was passed through the cartridge at 9 ml/min and the cartridge was dried with centrifugation and desiccation for 20 min and thermally desorbed prior to analysis. The limitations of this technique include the inability to process samples of high total organic carbon content and the breakthrough of certain compounds, such as phenols and water-soluble phthalates.

Currently, the most popular and rapidly emerging method of SPE employs commercially available cartridges filled with various phases (see Figure 4 caption) bonded to a silica matrix. Silica-based sorbents are used because silica provides controlled particle size (on the order of 40 μm) and pore size (approximately 60 Å) and large surface area (600 m^2/g);[96] in addition, silica is both mechanically strong and rigid and is chemically stable in a wide variety of solvents. Figure 3 illustrates how a typical SPE analysis is performed. Analytes are extracted as water is passed through a preconditioned cartridge and are adsorbed onto the cartridge as a result of Van der Waals, hydrogen bonding, or electrostatic interactions. Typical extraction times, assuming that particulates are not present and that a 1-g cartridge is used, are 1 to 2 h/l of water. It has been reported that greater extraction efficiencies may be obtained if up to 10% (by volume) of methanol is added to the water being extracted; this ensures that the surface of the modified silica is wetted.[98] The control of flow rate and the maintenance of appropriate vacuum or positive pressure are crucial to reproducible results and good precision. After extraction, the cartridge may be washed to remove interfering compounds and the analytes may be removed with a small amount of solvent. Cartridges are available, with amounts of packing material ranging from 50 mg to 10 g, the smallest cartridge having a capacity of < 2.5 mg and requiring only 125 μl of solvent for analyte elution. The largest cartridge

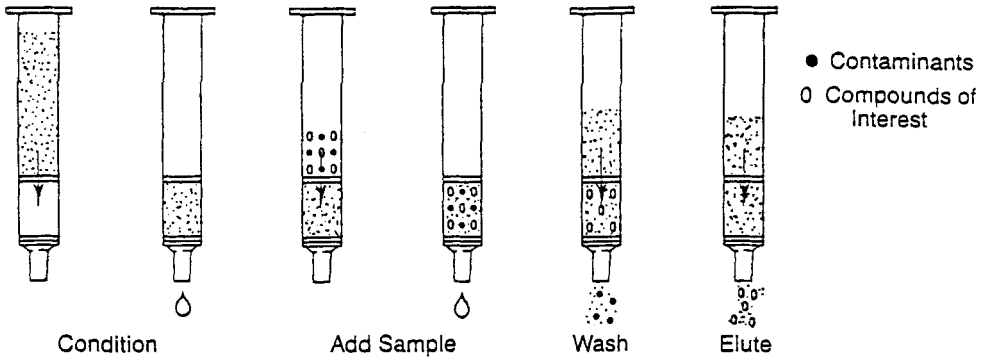

FIGURE 3. Solid-phase extraction. (From *The Supelco Guide to Solid Phase Ectraction*, 2nd ed., Supelco Inc., Bellefonte, PA, 1988. With permission.)

has a capacity of < 0.5 mg and may be eluted with 20 ml of solvent. Solid-phase extraction provides some specificity because many different solid phases are available; the choice of the correct solid phase is critical to obtaining good SPE results. Figure 4 shows a flow chart for the process of selecting the correct solid phase for an application.

Bonded-phase (C_8, C_{18}, or styrenedivinylbenzene) silica has been impregnated into PTFE fibrils to form 47 or 90 mm i.d. disks. Using these disks, water can be extracted rapidly because of the efficient uptake of SVOCs, which is attributed to fast adsorption kinetics. The fast adsorption kinetics are a result of the small particles used (8 μm), close and uniform packing of particles on the disks, and the elimination of channeling associated with cartridges. Using a 47-mm i.d. disk, 1 l of water may be extracted in 10 min, while 1 h is required to extract 1 l of water using a cartridge packed with 1 g of adsorbent.[96] Extraction disks are a relatively new technology; a theoretical discussion of the extraction process and the first data on the extraction of phthalates and pesticides by this method were reported in 1990.[99]

Solid-phase extraction cartridges and disks can provide extractions of comparable efficiencies to liquid-liquid extraction, providing correct procedures and conditions are used. Solid-phase extraction is now recommended for use in several USEPA methods. Table 5 summarizes the use of SPE for analyses of organic compounds in drinking water. A bibliography of the applications of SPE methods for the determination of a variety of analytes has been compiled.[109]

Solid-phase extraction is a valuable technique which will become increasingly important. The development of new phases for analyte extraction is expected. For example, the introduction and use of styrene divinylbenzene disks and acetyl styrene divinylbenzene disks for the extraction of phenols at 98% recovery was recently reported.[199] These phases may extend the range of compounds amenable to SPE. Instruments that currently provide automated SPE sample preparation using commercial SPE cartridges are available. The use of systems that concentrate analytes on pre-columns incorporated into high performance liquid chromatography (HPLC) systems have been studied and may become more commonly used, especially for the analysis of polar compounds.[110,111] Supercritical fluid extraction (SFE) may be developed as an alternate method for eluting analytes from SPE cartridges.[100,101,112] Microcolumns consisting of glass microfiber disks impregnated with modified silica, a new development in SPE extraction technology, have been developed.[113] Microcolumns are reported to have several advantages over the traditional cartridges: their lower bed mass reduces column conditioning requirements, necessitates less solvent for analyte elution, and allows smaller sample sizes. Although the future for SPE in drinking water analysis looks promising, more development work is

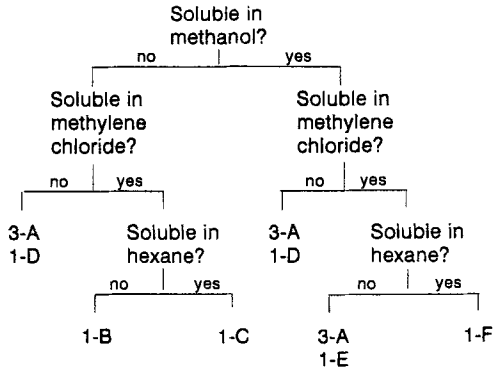

FIGURE 4. Flow chart for selecting SPE phases and solvents for the extraction of hydrophobic organic compounds from drinking water. Numbers on the flow chart correspond to the tube groups listed below; letters correspond to typical elution conditions. (Adapted from "The Supelco Guide to Solid Phase Extraction," 2nd ed., Supelco Inc., Bellefonte, PA, 1988.)

Tube group	Tube type	Classification of compound for extraction
1	Octyl bonded silica Octadecyl bonded silica Phenyl bonded silica Cyanopropyl bonded silica	Nonpolar to moderately polar compounds
2	Cyanopropyl bonded silica Silica gel Diol bonded silica Magnesium silicate (Florisil) Aminopropyl bonded silica	polar compounds
3	Cyanopropyl bonded silica Aminopropyl bonded silica Sulfonic acid bonded silicastrong cations, organic bases, strong anions, organic Quaternary amine bonded silicaacids, weak cations Weak cation exchanger	carbohydrates, cations, carbohydrates, weak anions, organic acids

Condition	Typical extraction conditions / solvents
A	Acidic compounds or anionic salts: adjust pH of sample 1–2 pH units higher than pKa of analytes; adjust pH of eluant 1-2 pH units lower than pKa of analytes Basic compounds or cationic salts: adjust pH of sample 1-2 pH units lower than pKa of analytes; adjust pH of eluant 1-2 pH units higher than pKa values Solvents: dilute acids (HCl, acetic, H_3PO_4) and bases (NH_4OH and NaOH) alone or with buffers and water miscible solvents (MeOH, acetonitrile)
B	Solvents: CH_2Cl_2, tetrahydrofuran,
C	Solvents: CH_2Cl_2, tetrahydrofuran, or hexane
D	Add salts, dilute acid, or dilute base to facilitate extraction Solvents: MeOH, acetonitrile, diethylether, tetrahydrofuran; alone or mixed with dilute acid, dilute base, or buffer
E	Add salts, dilute acid, or dilute base to facilitate extraction Solvents: MeOH, acetonitrile, diethylether, tetrahydrofuran, CH_2Cl_2; alone or mixed with dilute acid, base, or buffer
F	Add salts, dilute acid, or dilute base to facilitate extraction

TABLE 5
Applications of Solid Phase Extraction

Analyte	Phase	Size	Extraction solvent	Water vol (L)	Comments	Ref.
Benzidines, nitrogen-containing pesticides (EPA Method 553)	C_{18}	1 g cartridge, 47 mm disk	MeOH	1	Detection limits 2–30 ppb	177
Carbonyl compounds (EPA Method 554)	C_{18}	3 × 500 mg cartridge	EtOH	0.1	Sample adjusted to pH 3 and carbonyls derivatized with 2,4-dinitrophenyl-hydrazine before extraction; detection limits 4–44 ppb	177
Chlorinated acids (EPA Method 515.2)	Polystyrene divinyl-benzene	47 mm disk	10% MeOH in MTBE	0.25	detection limits 0.1–1 ppb	177
Chlorpyrifos, isofenphos, carbaryl iprodione, triadimefon	C_{18}	500 mg cartridge	MeOH	1	Analytes spiked in water; recoveries > 90%	104
Chlorsulfuron, sulfmeturon methyl AC 243,997	C_{18}	1 g cartridge and 1.5 g (2 cartridges in series)	MeOH	0.2–2	Recoveries ranged from 87–100%	103
Diquat, paraquat (EPA Method 549)	C_{18}	500 mg cartridge	Ortho-phosphoric acid and diethylamine in water	0.25 0.80	Detection limits 0.44 ppb diaquat; ppb paraquat	5
Endothall (EPA Method 548.1)	Bio-Rex 5	Manual pack	Acidic MeOH	0.25	Detection limit 2 ppb	177
Haloacetic acids, dalapon (EPA Method 552)	AG-1-X8 resin	Manual pack	Acidic MeOH	0.1	Detection limit 0.1–0.5 ppb	177
Metoxuron, monuron chlortoluron, cyanazin, propazine, vinclozoline	C_{18}	1 g cartridge	Acetonitrile	1	Recoveries ranged from 63–97%	102
Organochlorine pesticides	C_{18}	100 mg cartridge	Ethyl acetate	0.1	Recoveries of 73–83% with standard deviations of 8–11%; extraction efficiencies lower for SPE than by liquid-liquid extraction	108
Organophosphorus pesticides	C_{18}	1 g cartridge	Ethylacetate: isooctane (1:1)	0.5	Methanol not effective elution solvent; addition of 10% (by volume) of MeOH to water improved extraction efficiencies; recoveries for 13 analytes > 90% at 1 ppb	98
PAH, organochlorine pesticides	C_{18}	500 mg cartridge	SFE with CO_2 spiked on	Analytes	Av. recoveries of about 85% by SFE for 10 mg spike cartridge	101

TABLE 5 (continued)
Applications of Solid Phase Extraction

Analyte	Phase	Size	Extraction solvent	Water vol (L)	Comments	Ref.
PAH (EPA Method 550.1)	C_{18}	1 g cartridge, 47 mm disk	CH_2Cl_2	1	Detection limits of 0.004 –2.2 ppb	5
Pesticides	Carbopack B	300 mg cartridge	MeOH and MeOH:CH_2Cl_2 (90:10)	0.5 –2	Carbopack B more effective for trapping polar pesticides; detection limits < 0.1 ppb	105
Phthalates; pesticides	C_8 and C_{18}	47 mm disk, 25 mm disk	MeOH	1	Phthalates extracted best with C_{18} (recoveries 82 –117%); pesticide recoveries 17 –115%; prefiltering or acidifying solution minimized particle clogging of disk	99
Phthalate, adipate esters (EPA Method 506)	C_{18}	1 g cartridge, 47 mm disk	CH_2Cl_2	1	Detection limits 0.8 –11 ppb	5
Semivolatile organics (EPA Method 525.1)	C_{18}	1 g cartridge 47 mm disk	CH_2Cl_2	1	Detection limits 0.001 –15 ppb	3
Sulfonylurea herbicides	C_8 and C_{18}	47 mm disk	Acetonitrile	0.1 –1	Extraction recoveries of 97% for sulfometuron methyl and 93% for chlorsulfuran	100
2,3,7,8-TCDD (EPA Method 513)	C_{18}	47 mm disk	Benzene	1	Detection limit 20 –2000 ppq (matrix dependent)	5
Triazine herbicides	Carbopack B and SCX in tandem	150 mg cartridges	CH2Cl2:acetonitrile (60:40) and 70 mmol KCl in MeOH:water (90:10)	0.1	Quantitative recoveries reported	106
Warfarin	C_{18}	200 mg cartridge	Acetonitrile:0.04 *M* phosphate buffer (1:1)	1	Detection limit 0.02 ppb; recovery 90%	107

needed to optimize SPE performance before current liquid-liquid extraction-based methods are replaced.

3. Direct Aqueous Injection (DAI)

The simplest method for analyzing drinking water involves direct injection onto an HPLC or GC column. The most common DAI methods use HPLC because conventional columns can easily accommodate water. Examples of DAI with HPLC include USEPA Method 531.1 for the determination of *n*-methylcarbamoyloximes and *n*-methylcarbamates[3] and USEPA Method 547 for the determination of glyphosate.[5] To analyze *n*-methylcarbamoyloximes and *n*-methylcarbamates, 400 µl of sample is injected onto a reversed-phase column and the analytes are detected by fluorescence after postcolumn hydrolysis and derivatization with *o*-phthalaldehyde and 2-mercaptoethanol; method detection limits range from 0.5 to 4 ppb. This method was shown to have good recovery and an average precision of approximately 7% (as determined by 8 laboratories) in an interlaboratory validation study.[114] To determine glyphosate, 200 µl of sample is injected onto a cation exchange column. After separation, the glyphosate is oxidized with calcium hypochlorite to produce glycine, which is detected by fluorescence after derivatization with *o*-phthalaldehyde and 2-

mercaptoethanol; the method detection limit ranges from 6 to 9 ppb and is matrix dependent.

Direct aqueous injection may also be performed onto a GC column. This can be difficult because of the physical properties of water.[115] Relative to organic solvents commonly injected into the GC, water has a high boiling point and requires a high temperature in the injector for its vaporization. Water also produces large amounts of vapor – about six times more per unit volume than hexane. Because of its high surface tension, water does not easily wet GC packing materials. Despite these difficulties, the feasibility of the splitless injection of large volumes (200 to 800 μl) of aqueous samples by the overflow technique has been studied.[115] In the overflow technique, most water vapor escapes through the septum purge of the injector, while solutes of higher boiling points are retained in the injector. Using 25 to 35% propanol or 15 to 20% 2-butoxyethanol as co-solvents, 800 μl of an aqueous sample was successfully injected into a 5 mm i.d. injection liner. Fatty acids that eluted at temperatures > 200°C were successfully determined. In another study, aqueous samples with volumes of 50 μl were introduced into a 85°C injection port which was coupled to a GC-FID using a 1-m Nafion drying assembly to remove water and −180°C cryotrap to collect hydrocarbons.[116] Detection limits for the hydrocarbons analyzed (*o*-xylene, ethylbenzene, toluene, benzene, *n*-hexane, *n*-octane, and *n*-heptane) were approximately 2 ppb. In these experiments, the sample size was restricted, not by the capacity of the Nafion dryer, but by the dimensions of the inlet end of the dryer; swelling of the Nafion at the inlet caused temporary blockage of the sweep gas passage when sample size exceeded 50 μl. Detection limits of 0.016 to 0.060 ppb for trihalomethanes were obtained using DAI of 3 μl of an aqueous standard onto a DB-624, 30 m × 0.32 mm, 1.8 μm, column equipped with ECD.[117] These excellent detection limits were attributed to the use of a smaller (100 μl) ECD cell. Trihalomethanes were successfully analyzed by injecting 1 μl of sample onto a 30 m × 0.53 mm, DB-1, fused silica column.[118] By keeping the column at 104°C, the water was rapidly eluted from the column and did not interfere with ECD detection of the analytes. Detection limits for trihalomethanes ranged from 0.1 to 0.5 ppb. The feasibility of DAI and GC-FTIR and GC-ion trap mass spectrometer (ITMS) to monitor water-soluble, low molecular weight alcohols, ketone, nitriles, and esters was assessed.[119] Gas chromatography-Fourier transform infrared spectroscopy detection limits were at low parts per million concentrations and GC-ITMS detection limits were at low parts per billion concentrations for 2 μl injections; thus, GC-FTIR and GC-ITMS may be useful for screening applications.

C. Polar Compounds

The extraction of polar compounds, which are difficult to remove from water, continues to present an analytical challenge. Direct aqueous injection, as discussed in the previous section, presents one solution to this problem. Although inherently not the best technique for the analysis of polar compounds, P & T, using a modification of USEPA Method 524.2 (with a longer GC temperature program and a 75 m × 0.53 mm i.d. DB 625 column) was investigated to determine if several polar compounds could be added to its analyte list.[120] Of 48 compounds tested, only half were suitable for inclusion in Method 524.2. Most of these compounds had detection limits less than parts per billion and temperature fluctuations of > 7°C were found to affect precision for analytes that had purge efficiencies < 50%.

Solid-phase extraction may be used for the extraction of polar compounds. C_{18}-bonded silica has been used to extract triazines and organophosphorus pesticides from water at recoveries of approximately 85%.[121] The development of newer solid phases may facilitate the extraction of polar compounds from water. Styrene divinylbenzene and graphitized carbon black are materials that show promise of being able to extract analytes which are not extracted efficiently by common solid phases. For example, styrene

divinylbenzene has been used in on-line precolumn-LC-diode array detection to determine 50 pesticides in surface water.[122] In this technique, 30 ml of sample is concentrated at a flow rate of 0.5 ml/min on a styrene divinylbenzene copolymer, 10 mm × 2.0 mm i.d., precolumn before being chromatographed on a C_{18} column. For the compounds tested, detection limits ranged from 0.2 to 20 ppb in surface water. Triazine herbicides, at 10 ppt in water, also have been extracted with styrene divinylbenzene copolymers.[123] Chlorotriazines have been extracted by first trapping them in neutral form on PRP-1 and then desorbing and concentrating them at low pH onto a column packed with cation exchange resin.[124] Styrene divinylbenzene disks have been shown to provide excellent recoveries (improved over C_{18} phases) for polar phenoxyacid herbicides and haloacetic acids.[125] Graphitized carbon black has been used to extract various pesticides at method detection limits of 0.1 ppb[105,126] and atrazine and its hydroxylated metabolites.[127]

1. Comparison of Extraction Techniques

Several different extraction methods are available for the analysis of organic compounds. For many analyses, the choice of best extraction technique is not clear; many analytes are extracted equally well by several techniques. For example, in many cases, SPE and liquid-liquid extraction are equally efficient. As previously noted, the use of SPE is growing because of its lower cost, greater throughput, and reduced solvent use. Table 6 compares the attributes of several extraction techniques and may be used as a guideline to method selection. We expect the use of simple, cost efficient techniques, such as headspace analysis, SPE, and MIMS to increase. We also expect to see rapid developments in field portable techniques such as solid-phase microextraction and MIMS. Ultimately, the extraction method of choice for a given application will be one that is best suited to exploit the physical properties of the analytes and will yield the greatest extraction efficiencies in short extraction times.

V. SAMPLE PREPARATION FOR INSTRUMENTAL ANALYSIS

A. Sample Extract Clean Up

Unlike plant and animal tissues that contain many lipids or sediments which are comprised of humic material and sulfur that must be removed before organic analyte determination, drinking water is a relatively clean matrix. Typically, no special sample clean up is required prior to analysis. However, the ultra-trace determination of specific analytes

TABLE 6
Comparison of extraction techniques for organic compounds

Technique	Applicability	Detection limit (MS)	Precision	Expense	Time	Simplicity	Solvent use (ml)
P & T	VOCs, polar VOCs	ppb	1–30%	High	30 min	No	0
CLS	VOCs	ppt	3–20%	High	2 h	No	0
Headspace	VOCs	ppb	2–20%	Low	30 min	Yes	0
Liquid-liquid	SVOCs	ppt	5–50%	High	1 h	Yes	200
SPE	SVOCs, polar OCs	ppt	7–15%	Medium	30 min	Yes	50
SPME	VOCs, SVOCs	ppt	0.6–12%	Low	5 min	Yes	0
MIMS	VOCs, polar VOCs	ppb	NA	High	Real time	Yes	0
Membrane permeate and trap GC/MS	VOCs, polar VOCs	ppb	4–13%	High	1 h	No	0

NA: information not available.

(for example, the polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans) usually requires the removal of compounds that may interfere with their determination.

The optimal situation is to be able to selectively extract the analytes of interest by use of appropriate solvents, solid phases, or extraction conditions (i.e., sample pH and ionic strength). Given the enormous number of organic compounds that are present in trace quantities in the environment, this is often unattainable. Thus, it is important to either remove interferences before analyte extraction or to selectively separate the analytes from interferents after extraction. The key to successful sample clean up is knowing the properties of both analytes and interferences and exploiting their differences.

USEPA Method 552[5] for the analysis of haloacetic acids, which are by-products of chlorine disinfection, provides an illustration of the removal of interferences before analyte extraction. The extraction strategy takes advantage of the strong organic acid characteristics of haloacetic acids. In fact, these organic acids will react with basic sites on glassware and sodium sulfate used in sample preparation; thus, these materials must be acid washed prior to use to prevent losses of analytes due to adsorption. To remove basic and neutral compounds that would interfere with ECD determination of the haloacetic acids, such as chlorinated hydrocarbons and phthalate esters, the pH of the water sample is first adjusted to 11.5 and the sample is extracted with methyl-*t*-butyl ether. The sample is then acidified to pH < 0.5 and the haloacetic acids are extracted with methyl-*t*-butyl ether and then analyzed. This strategy is commonly employed to separate basic and neutral components from acidic compounds.

Interferents and analytes can be separated after extraction. Columns of silica, florisil, alumina, or carbon may be used to separate compounds based on their polarities. An extract, in a relatively nonpolar solvent is introduced onto the column, which is eluted with a series of solvents of increasing polarities. These types of columns have been used to separate PCDDs and PCDFs from polychlorinated biphenyls (PCBs) and other compounds.[128] Carbon is often used to separate planar compounds from the nonplanar; the planar analytes are more strongly retained by the carbon. Graphitized carbon black has also been used to separate base-neutral and acidic pesticides.[129]

Manual packing of clean up columns is laborious; thus, prepackaged extraction cartridges facilitate extract clean up because they require no adsorbent calibration, activation, or deactivation and their use is amenable to automation. The use of SPE cartridges consisting of florisil, alumina, silica, and diol for clean up of samples containing phenols, phthalate esters, PCBs, and organochlorine pesticides has been investigated.[130] Separations of some pesticides from PCB were possible with silica cartridges. Alumina clean up worked reasonably well for phthalate esters. Silica cartridges were used to clean-up extract of phenols that had been derivatized with pentafluorobenzylbromide. Lopez-Avila et al.[130] recently published recovery data for compounds subjected to various clean up methods and reviewed recent applications for sample clean up using SPE cartridges.[130]

The use of the selective properties of SPE materials can be exploited to do in-line clean up or fractionation.[131] An automated system for the collection of wastewater has been described in which sampled water is passed through a series of three columns. First, the water is passed through a C_{18} column, which collects nonpolar compounds. Next, the water is passed through a styrene divinylbenzene copolymer, which collects moderately polar compounds. Finally, the water is passed through an Aminex A5 phase, which collects polar anilines and other bases. Each column is sequentially eluted and its contents are chromatographed on an analytical column. Using this technique, 29 compounds were analyzed at 200 ppb concentrations. While the detection limits for this method are higher than those required for drinking water analyses, this system demonstrates the potential for in-line, automated clean up and shows how the properties of solid phases can be exploited to achieve group separations.

1. Chlorinated Dibenzo-p-dioxins and Dibenzofurans

For the analysis of drinking water for trace organic compounds, the determination of the PCDDs and PCDFs represents the state of the art. Because of the high toxicity of some PCDDs and PCDFs, some regulatory agencies have set drinking water guidelines for PCDDs and PCDFs in the low parts per quadrillion. Considerable controversy still exists about the possible effects of PCDDs and PCDFs on humans, and future guidelines could be set well below parts per quadrillion concentrations. Analyses at such low concentrations are extremely difficult, even for a relatively clean environmental matrix such as drinking water. Even sensitive, specific GC-MS instrumentation cannot adequately perform this determination without an effective sample clean up.

Several studies of PCDDs and PCDFs in drinking water have been reported in the literature.[132-142] For most of these investigations, efforts to achieve ever-lower method detection limits were focused on sampling large volumes of water, followed by extensive sample clean up and GC-MS determination of PCDDs and PCDFs. Liquid-liquid extraction of sample sizes of 4 l,[136] 10 l,[135] and 50 l[132] samples have been reported. In many cases, water samples are first filtered to remove fine particulates, and the particulate filter is extracted by Soxhlet apparatus.[132,137,138] Because the PCDDs and PCDFs are hydrophobic, it is expected that they will be principally associated with the filtered particulates. Solid-phase extraction methods are very attractive for applications such as PCDDs and PCDFs in drinking water, where particulate levels in the sample are low and large sample volumes are required to achieve the necessary method detection limits. The use of XAD-2,[134,139,140,142] reversed-phase C_{18} adsorbent,[137,138] and polyurethane foam (PUF) plugs[141] have all been used for sampling drinking water volumes from 10 to 1500 l. Rappe et al.[141] sampled 1500 l by using PUF and detected 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (2,3,7,8-TCDD) in some samples at concentrations as low as 0.0005 pg/l. However, as sampling volumes become larger, it becomes more difficult to avoid sample contamination or to accurately determine the level of the blank.

Another difficulty with increasingly larger sample sizes is to produce a sample free of chemical interferences for GC-MS determination of the PCDDs and PCDFs. Although the GC-MS technique is highly sensitive and selective, and drinking water samples are "clean" relative to other types of environmental samples, sample clean up is needed because of the large sample sizes extracted and because sub-parts per quadrillion detection limits for the PCDDs and PCDFs are required. For all of the work reported for PCDDs and PCDFs in drinking water, extensive sample clean up is employed. The most common clean up methods employ some combination of silica, sulphuric acid on silica, NaOH or KOH on silica, carbon fibers, and activated alumina. Detailed descriptions of these clean up methods and of complete clean up schemes have been reviewed.[128] Advances in chromatographic procedures, including clean up methods, are largely responsible for our current ability to determine PCDDs and PCDFs in drinking water at sub-parts per quadrillion concentrations.[143] The role of modern GC-MS instrumentation in achieving these detection levels is discussed below.

B. Derivatization

In some situations, it is desirable to derivatize the analytes prior to extraction or instrumental analysis. The advantages of derivatization include enhanced detectability and improved separation efficiencies. Onuska[23] has briefly summarized the types of available derivatization techniques (see Table 7) in a review of the preparation of aquatic samples.

Examples of derivatizations used in drinking water analysis are the reactions of glycine (oxidation product of glyphosate) and of *n*-methylcarbamoyloximes and *n*-methylcarbamates with *o*-phthalaldehyde and 2-mercaptoethanol to form fluorescent deriva-

TABLE 7
Summary of Derivatization Techniques Useful in Environmental Analysis

Derivatization reagent	Uses
Diazomethane	Methylates acidic analytes for GC analysis to neutralize activity of polar functional groups
Trifluoromethyl-, pentafluoropropyl-, heptafluorobutyl anhydrides	Reacts with amines, amides, alcohols, phenols, thiols, enols, glycols, unsaturated compounds and moieties with aromatic rings to form volatile compounds that are easily detected by ECD
Fluoro acyl imidazoles	Acylates hydroxyl groups and primary and secondary amines
Pentafluorobenzyl bromide	Alkylates carboxylic acids, phenols, mercaptans, and sulfonamides for ECD analysis
Silylating reagents	Reacts with hydroxyl, carboxyl, thiol, and primary and secondary amino groups to form volatile derivatives that can be analyzed by GC

tives (USEPA Method 547[5] and USEPA Method 531.1[3]). Pentafluorophenyl hydrazine is used to derivatize endothall prior to SPE and GC-ECD analysis (USEPA Method 548[5]). Diazomethane is used to derivatize halogenated acetic acids[76,77] and chlorophenols[85] prior to GC-ECD analysis. There are many derivatization strategies available; the choice of the best method depends on the properties of the analyte and the analytical technique used for its detection.

C. Use of Internal and Surrogate Standards

An *internal standard* is defined by USEPA as "A pure analyte(s) added to a solution in known amount(s) and used to measure the relative responses of other method analytes that are components of the same solution. The internal standard must be an analyte that is not a sample component."[3] A *surrogate standard* (or surrogate analyte) is "A pure analyte(s), which is extremely unlikely to be found in any sample aliquot in known amount(s) before extraction and is measured with the same procedures used to measure other sample components. The purpose of a surrogate analyte is to monitor method performance with each sample."[3] Although the use of these standards normally would be described in the following section on quality control, they are considered here because of their critical role in assessing the effectiveness of the sample preparation procedures.

Quantitative analysis methods based on the use of internal standards are not novel. Although external standard calibration can give acceptable precision and accuracy for the determination of trace organics in drinking water, it is generally recognized that internal standard calibration is preferable. Almost all modern methods for trace organics that employ GC-MS detection use internal standard calibration. Because of the ability of the MS detector to distinguish between compounds that have differing molecular weights, even if they co-elute from a GC column, internal standards can be used that have the same structure of the analyte. The difference is that the internal standard has been enriched with a heavier, stable isotope of one of the atoms comprising the molecular structure of the analyte. The most common isotope used for the analytes found in drinking water is deuterium. For specialty analyses such as the PCDDs and PCDFs, fully labeled ^{13}C analytes are used as internal standards.

Table 8 shows some of the internal and surrogate standards recommended for use in selected USEPA drinking water methods. In several of the non-GC-MS methods, specific internal or surrogate standards are not recommended; it is left up to the analyst to determine which standards are applicable and

TABLE 8
Use of Standards in Selected EPA Methods

Method	Application	Detection system	Internal standards	Surrogate standards
502.1	Volatile halogenated compounds	GC with Electrolytic conductivity or microcoulometric detector	2-Bromo-1-chloropropane or 1,4-dichlorobutane	None recommended
502.2	Volatile organics	GC with photoionization ECD in series	1-Chloro-2-fluorobenzene and or fluorobenzene and 2-bromo-1-chloropropane	Not specified
507	Nitrogen and phosphorus Pesticides	GC-NPD	Triphenylphosphate	1,3-Dimethyl-2-nitrobenzene
508	Chlorinated pesticides	GC-ECD	Pentachloronitrobenzene[13]	4,4'-Dichlorobiphenyl[37]
513	2,3,7,8-TCDD	GC-high resolution MS	C_{12}-2,3,7,8-TCDD	Cl_4-2,3,7,8-TCDD
515.1	Chlorinated acids	GC-ECD	4,4'-Dibromoocta-fluorobiphenyl	2,4-Dichlorophenylacetic acid
524.1	Purgeable organics	Packed columm GC-MS	Fluorobenzene	D_4-1,2-Dichlorobenzene and 4-bromofluorobenzene
524.2	Purgeable organics	Capillary column GC-MS	Fluorobenzene	D_4-1,2-Dichlorobenzene and 4-bromofluorobenzene
525.1	Organics	Capillary column GC-MS	D_{10}-Acenaphthene D_{10}-Phenanthrene D_{12}-Chrysene	D_{12}-Perylene
531.1	*N*-Methylcarbamoyl-oximes and *N*-Methyl-carbamates	HPLC-fluorescence detector (postcolumn derivatization)	4-Bromo-3,5-dimethylphenyl *N*-methylcarbamate	None recommended
550	Polycyclic aromatic hydrocarbons	HPLC with coupled UV and fluorescence Detectors	Not specified	Not specified
550.1	Polycyclic aromatic hydrocarbons	HPLC with coupled UV and fluorescence Detectors	4,4'-Difluorobiphenyl	Not specified
551	Chlorinated disinfection by-products and chlorinated Solvents	GC-ECD	Not specified	Not specified
552	Haloacetic acids	GC-ECD	Possibly 1,2,3-trichloro-propane	Not specified

known to *not* be present in the samples analyzed. With GC-MS detection, isotopically labeled analogues of the analytes (not found in measureable concentrations in nature) can be used, regardless of the source of drinking water to be assayed.

Surrogate standards are always added before the sample extraction step. The efficiency of recovery of the surrogate is an important indicator of the efficiency of the entire analytical process. When low recovery of a surrogate is observed, it can be generally assumed that recoveries of analytes were also low. The internal standard(s) is often added to the sample just before the instrumental analysis step. In this case we are attempting to determine accurately the various analyte response factors, rather than monitor the effectiveness of the extraction and sample preparation procedures. For the determination of 2,3,7,8-TCDD using USEPA Method 513 (see Table 8), both the surrogate and internal standards are added before sample extraction. In this case, using the isotopically enriched $^{13}C_{12}$-2,3,7,8-TCDD internal standard response factor will also automatically

correct the concentration of the native 2,3,7,8-TCDD for losses during sample preparation. Thus, the use of isotopically enriched analytes as internal standards and surrogate standards when GC-MS detection is employed has some advantages over conventional external standard determinations. The importance of using stable isotope labeled compounds with GC-MS detection of environmental contaminants was discussed previously by Haile.[144]

VI. THE DETERMINATION OF TRACE ORGANICS BY GAS CHROMATOGRAPHY-MASS SPECTROSCOPY

A. Comparison of Instrumental Detection Systems

Once the sampling and sample preparation stages of analysis are completed, several choices of instrumentation systems are available for the determination of trace organic analytes. These systems all have the following characteristics: chromatographic separation of analytes followed by selective and sensitive detection. Although numerous combinations of chromatography and detection systems have been employed, most can be classified by four categories:

1. GC followed by mass spectrometer detection (GC-MS)
2. GC followed by other selective GC detector
3. HPLC followed by UV or fluorescence detection
4. HPLC followed by mass spectrometer detection (HPLC-MS)

Most new developments in detection systems are in HPLC-MS; these are described in the following section. High performance liquid chromatography followed by other selective detectors such as UV/fluorescence is used for a few specific applications, but GC is preferable to HPLC where feasible because of its relative ease of use and much greater resolving power. In Table 8, only 3 of 14 methods listed require HPLC separation. Analytes that are highly water soluble and therefore difficult to extract are candidates for selection of HPLC over GC. In the case of USEPA Methods 550 and 550.1, HPLC is preferred because the fluorescence detector is so sensitive for PAH detection. However, even for this application the use of GC-MS detection is becoming more attractive, because ^{13}C-isotopically enriched PAH standards recently have become commercially available.

Several of the sensitive and selective detectors used for the determination of trace organics in drinking water samples are listed in Table 8. One advantage of GC over HPLC is the wide variety of sensitive, specific detectors available. New developments in HPLC detectors have been reviewed by Fielden,[145] and the characteristics and application of modern GC detectors are described in a recent book.[146] In the majority of applications, MS detection is preferred. Not only are mass spectrometers highly sensitive, but they are very selective. Although other GC detectors have these characteristics, the MS detector's selectivity can be adjusted for virtually any analyte eluted from a GC (or HPLC) column. This "tunable selectivity" sets the MS detector apart from other GC and HPLC detectors. Also, the MS detector is better suited for identification of unknown compounds in the sample extract at trace concentrations. Although other detection systems are better at identifying compounds than the MS detector, no other detector can perform these identifications at the low concentrations required when analyzing extracts of drinking water samples. Notwithstanding the benefits of GC-MS analysis, the development of the diode array detector has greatly increased the flexibility and application of HPLC for trace organic analyte determinations.

B. Choice of Mass Spectrometer System

Many different type of MS systems have been applied to the determination of trace organics in environmental samples. For

drinking water analysis, low resolution quadrupole systems (LRMS) are by far the most commonly used systems. For ultra-trace determination of analytes such as the PCDDs and PCDFs, high resolution mass spectrometer systems (HRMS) are generally used. In a few cases, the use of triple quadrupole tandem mass spectrometry (MS-MS) systems have been reported. Detailed descriptions of the different systems is beyond the scope of this review, but such descriptions have been recently reported elsewhere.[147-148]

The choice of which MS system should be used for a specific application depends on a number of factors, including cost, availability of instrumentation, staff expertise, sample complexity, and detection limits required. For the analysis of extracts from drinking water samples, LRMS systems are adequate for most analytes. Exceptions are the PCDDs and PCDFs, where some regulations require detection limits sufficient to determine these analytes at sub-parts per quadrillion concentrations. For such specialty analyses, HRMS or MS-MS systems are generally employed. LRMS systems can still reach the required detection limits if sample volumes are greatly increased, but HRMS or MS-MS systems are still preferred for their greater specificity. A detailed description of the use of GC-MS systems for the determination of the PCDDs and PCDFs is given elsewhere.[149]

A relatively new type of mass spectrometer, ITMS, has been recently used for the determination of priority pollutants in drinking water.[37,70,93] There is considerable interest in the ITMS because of its simple (therefore rugged) design, relatively low cost, and because future versions of the ITMS may possess both MS-MS and HRMS capabilities. The availability of inexpensive LRMS systems, or low-cost HRMS systems (ITMS) could make conventional GC detectors obsolete except for rapid screening applications.

C. Choice of Gas Chromatography Columns

Modern GC instrumentation has advanced to the stage at which excellent performance and computerized operation can be expected for almost any commercial system. Exceptions may occur in small, portable systems, in which features and capabilities are reduced to save space and weight. Characteristics of modern GC instrumentation were described by Tashiro and Clement.[150] Regardless of the specific type of GC employed, the most important GC component with regard to the quality of the analysis is the analytical GC column. Although several USEPA methods still call for the use of packed GC columns, the authors believe that packed columns are obsolete for the determination of trace organics in drinking water. All of the more recent GC-based USEPA methods for trace organics in drinking water do require the use of capillary columns, and most employ LRMS detection systems. Accordingly, only the use of capillary columns is discussed here.

The evolution of the fused silica capillary column and its application to the determination of priority pollutants in water have been described by others.[151-152] Fused silica capillary columns are preferred because of their excellent performance and because the high flexibility of the columns make them easy to work with (i.e., they are easy to install in GC-MS systems). Choosing which column can be used for a specific application seems confusing, because there are many manufacturers, and each has many different columns from which to choose. However, only a few different GC liquid phases are used for the determination of organics in drinking water. Table 9 lists the various columns recommended for use in different USEPA drinking water methods, and gives the approximately equivalent columns from a few of the leading suppliers. This information was pieced together from recommendations given in various USEPA methods for organics in drinking water, and from the sales literature of a few of the leading suppliers of these columns. Of the many fused silica capillary columns listed in Table 9, only three have substantially different liquid phases. The DB-5, Rtx-5, HP-5, PTE-5, and SPB-5 columns are coated with nonpolar liquid phases composed of approximately 5% diphenyl/95% dimethyl polysilox-

TABLE 9
Common Commercial Fused Silica Capillary Columns used for Drinking Water Analysis

Compound class	EPA method	Approximately equivalent commercial columns			
		Hewlett-Packard	J and W	Restek	Supelco
VOC	502.2	HP-502.2	DB-624	Rtx-502.2 Rtx-Volatiles	VOCOL
Organohalide pesticides and commercial PCB products	505	HP-5	DB-1	Rtx-5	SPB-1
Nitrogen and phosphorus pesticides	507	HP-5MS	DB-5	Rtx-5	PTE-5
Chlorinated pesticides	508	HP-5	DB-5	Rtx-5	PTE-5
PCDDs and PCDFs	1613	—	DB-Dioxin	Rtx-2330 Rtx-5	SP-2331 PTE-5
Purgeable organic compounds	524.2	HP-624	DB-624	Rtx-502.2 Rtx-Volatiles	VOCOL
Semivolatile (base / neutral) organic compounds	525.1	HP-5	DB-5 DB-5.625	Rtx-5	PTE-5

ane. The slightly polar columns used for volatiles analysis (VOCOL, DB-624, Rtx-502.2, Rtx-Volatiles, HP-502.2, HP-624) have similar liquid phases, with a greater proportion of diphenyl (20%). The columns employed for the determination of the PCDDs and PCDFs have very polar phenyl/cyanopropyl liquid phases. Only two or three of the columns in Table 9 are needed to successfully analyze drinking water for the wide range of purgeable and extractable organic compounds that are amenable to GC analysis.

D. Gas Chromatography-Mass Spectrometry Characterization Analysis

Many potential drinking water contaminants have been well studied. An example is chlorine disinfection by-products. Regulators in many countries have developed maximum allowable concentrations of such known contaminants of drinking water, and analytical methods have been developed to accurately determine the concentrations of these target compounds. However, it is always possible that new drinking water contaminants will appear, and a monitoring program designed to protect drinking water quality must include an occasional *characterization analysis*. In a characterization analysis, the objective is to identify as many compounds as possible in the sample extract. For this application, GC-MS is almost universally employed. Other instrumental techniques are effective at organic compound identification, but not at the low parts per billion concentrations amenable to identification by GC-MS.

The importance of characterization analysis was demonstrated by Chen and coworkers,[81] who identified 33 artifacts formed during the preparation of water samples. In another study, the mass spectra of triazine herbicides were studied to provide the basic information required for the trace level determination of these compounds in water by GC-MS.[123] Reference mass spectra of mixed haloacetic acids expected to be found in chlorinated drinking water were determined by Ireland et al.[153] Gas chromatography-mass spectrometry can also be used to determine mycobacteria in water by detection of organic compounds characteristic of specific bacteria. For example, 2-docosanol was monitored for the rapid GC-MS detection of *Mycobacterium xenopi* in drinking water.[154]

Identifications for characterization analyses are performed by detailed interpretation of the masses and relative abundances of peaks found in individual mass spectra. The mass spectra of tens of thousands of organic compounds determined previously are available in computerized data files, which can be rapidly compared to the mass spectra of unknown compounds detected in the analysis of

drinking water extracts. Sophisticated computer programs have been developed to perform this computerized library search, and to select the library compounds whose mass spectra most closely match the mass spectrum of the unknown compound. A close match of the mass spectrum of the unknown compound and the mass spectrum of a compound in the computerized reference database indicates that the unknown has the same or a very similar structure as the reference compound. If the GC retention times of the unknown and reference compounds are also the same, then the identification is considered positive. If a good computerized match is not found, then the unknown structure must be deduced by manual examination of the individual mass fragments in the unknown mass spectrum. Manual interpretation of mass spectra is a difficult task that requires a great deal of training and experience. The accuracy of mass spectral interpretation, whether manual or computerized, is difficult to determine. Recently, a classification system has been developed to help achieve consistency in reporting characterization data.[155] The basic techniques of computerized[156] and manual[157] interpretation of mass spectra have been described.

E. Gas Chromatography-Mass Spectrometry Target Compound Determination

The use of GC-MS for the trace determination of organics in environmental samples is a well-established technique. Although the instrumentation and computer operating software are continually being improved, few fundamental changes in the basic technique have taken place in the past few years. As reported earlier, developments in ITMS technology could allow greatly improved performance in relatively low-cost systems in the near future. Any improvements to GC columns or instrumentation would, of course, also benefit GC-MS. Combinations of techniques to produce total automated analyses are also possible.

Regardless of the potential advances in the GC-MS technique, to maximize the benefit of using GC-MS for the determination of trace organics in drinking water requires an understanding of the basic types of data generated by GC-MS. The four principal data types are mass spectra; total ion chromatogram (TIC), or reconstructed gas chromatogram (RGC); mass chromatogram (MC); and selected ion monitoring (SIM) data. Books have been written about the formation and interpretation of the mass spectrum;[147,148,156,157] it is beyond the scope of this review to present detailed coverage. However, to understand target compound analysis of organics in drinking water it is important to know the basics of how a mass spectrum is produced.

Compounds that are eluted from a GC capillary column enter the ion source of the mass spectrometer where ionization of molecules occurs by their interaction with an electron beam at reduced pressures (about 10^{-6} torr or lower). This process, called electron ionization, is very inefficient; $< 1\%$ of molecules are ionized. The ionized molecules contain a distribution of excess energy, so that some actually undergo decomposition in the ion source. A mixture of many different ion fragments is rapidly formed; the specific ion fragments formed depend on the experimental conditions and the structure of the molecule. The real purpose of the mass spectrometer is to record the relative abundance of the ions formed according to ionic mass (because some ions may be doubly charged, it is actually the mass-to-charge ratio, or m/z, that is recorded). The plot of m/z vs. relative abundance is the mass spectrum. Modern GC-MS systems operate by repetitively scanning the GC eluent, and storing the resulting mass spectra on computer disk. On average, mass spectra are obtained and stored at better than 1/s. By adding the total ion abundance of each mass spectrum and plotting it against time, the TIC (or RGC) is produced. In appearance, the TIC resembles the chromatogram that would have been produced by analysis using a GC-FID.

Figure 5 (top trace) is the TIC from analysis of a standard mixture of SVOCs as determined by GC-LRMS. Quantitation of each

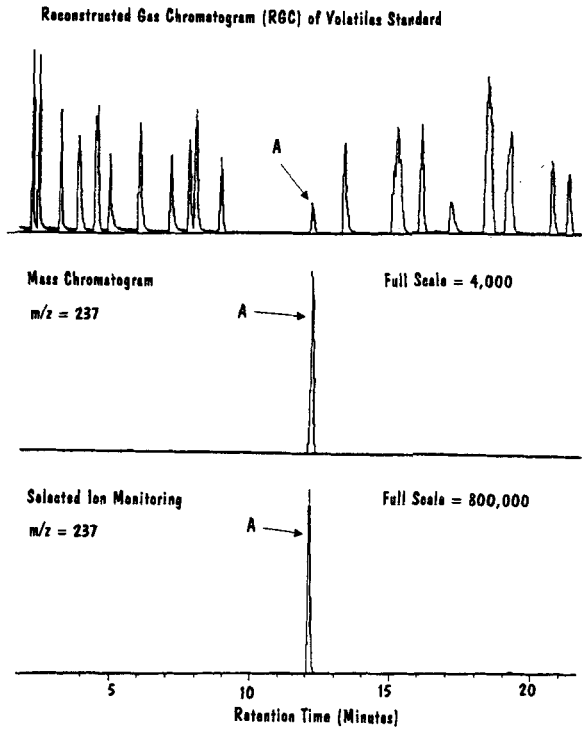

FIGURE 5. Gas chromatography-mass spectrometry analysis of a standard mixture of SVOCs. The upper trace is the TIC (or RGC) plot; the middle trace is a MC of m/z 237, which is a major ion in the mass spectrum of hexachlorocyclopentadiene; the bottom trace is from the SIM analysis of the same SVOC mixture but only monitoring m/z 237. Note that the SIM trace is idendical in appearance to the MC trace, but the full-scale abundance of the SIM trace is 200 times greater.

of the GC peaks detected in samples can be performed by comparing areas or peak heights with those of standards (external or internal). A much more effective method of quantitation of specific target compounds is by plotting only selected ion masses that are found in the target analyte, instead of the total ion abundances. Such plots are the MCs. In Figure 5, the middle trace is a MC of m/z 237, which is a principal mass fragment of the parent compound (hexachlorocyclopentadiene). As only one compound in the TIC contains this m/z in its mass spectrum, only one peak appears in the MC. Although the parent compound is one of the smallest peaks in the TIC, it is selectively detected in the MC. Even if a much larger sample component co-eluted with hexachlorocyclopentadiene, this compound could be accurately quantified, *as long as m / z 237 was not present in the mass spectrum of the co-eluting compound.* The chances are good that at least one m/z in the mass spectrum of a target compound is not found in the mass spectra of other closely eluting compounds.

To achieve the lowest possible detection limits with GC-MS, SIM is employed. In appearance and application, SIM resembles MC. However, for SIM, the ionic masses to be monitored are chosen before GC-MS analysis. By only choosing a few selected masses instead of all the masses in a mass spectrum of a target compound, the abundances of the ions selected can be increased by about 100 times. The increased signal for the ions monitored is obtained because no detector time is wasted on monitoring any of the other ions produced. Figure 5 (bottom trace) shows the SIM analysis of the SVOC standard mix, where only m/z 237 was monitored. This trace appears identical to the MC trace, but the full-scale abundance of the MC trace is only 4000, compared to the full-scale abundance of 800,000 for the SIM trace. The disadvantage of SIM is that monitoring only one ion mass for a target compound increases the possibility of a false positive identification. In practice, at least two characteristic ion masses are generally monitored: one is the quantitation ion and the others are employed for confirmation of identity. While the acquisition of complete mass spectra and use of MCs for target compound determinations are adequate for determination of organics in drinking water at concentrations of about 0.1 ppb or greater (1.0 l sample size), the determination of organics at lower concentrations generally requires the use of SIM.

VII. COMPOUND DETERMINATION BY LIQUID CHROMATOGRAPHY/ MASS SPECTROMETRY

Gas chromatography-mass spectrometry is the most commonly used method of analysis for organic compounds. However, only approximately 20% of all organic compounds can be analyzed by this method.[158] Non-

volatile, thermally labile, or polar (nonderivatized) compounds are not amenable to this technique. Thus, there has been much recent interest in the development of LC-MS for the characterization, confirmation, and quantitation of analytes in drinking water that cannot be analyzed by GC-MS.[159] Although LC-MS is currently not a routine analytical method, it shows great potential for use. For this reason, we have included this discussion of LC-MS.

The main consideration in LC-MS is the selection of an appropriate interface for the desired application. Several LC-MS interfaces are commercially available and are discussed in reviews by Niessen et al.[160] and Voyksner.[161] Currently, the most popular LC-MS interfaces are particle beam, thermospray, and electrospray. The particle beam interface provides electron ionization spectra and thus, is useful for analyte characterization. A particle beam interface is able to accommodate LC flow rates of 0.2 to 0.8 ml/min, which are compatible with those required by commercially available 2.1 mm i.d. and 4.6 mm i.d. LC columns. Both thermospray and electrospray interfaces produce spectra which show chemical ionization characteristics and less fragmentation than particle beam. These techniques are most useful for the confirmation and quantitation of analytes. While the thermospray interface can accommodate LC flow rates of 1 to 2 ml/min, electrospray poses additional chromatographic challenges because it is compatible with flow rates of approximately 1 μl/min; this requires the use of microcolumns or the splitting of LC effluent from conventional LC columns.

A. Particle Beam Interface

Figure 6 shows a typical particle beam interface. The LC effluent is introduced as an aerosol into the desolvation chamber. Typically, helium is used as the nebulizing gas and LC flow rates of 0.2 to 0.8 ml/min can be accommodated. In the desolvation chamber, which is at near-atmospheric pressure and heated between 30° and 80°C, the aerosol becomes desolvated. The analyte molecules in the desolvated droplets precipitate to form particles. These particles possess sufficient momentum to carry them through the momentum separator and into the source of the mass spectrometer, where they volatilize and are ionized. The gaseous solvents have momenta several orders of magni-

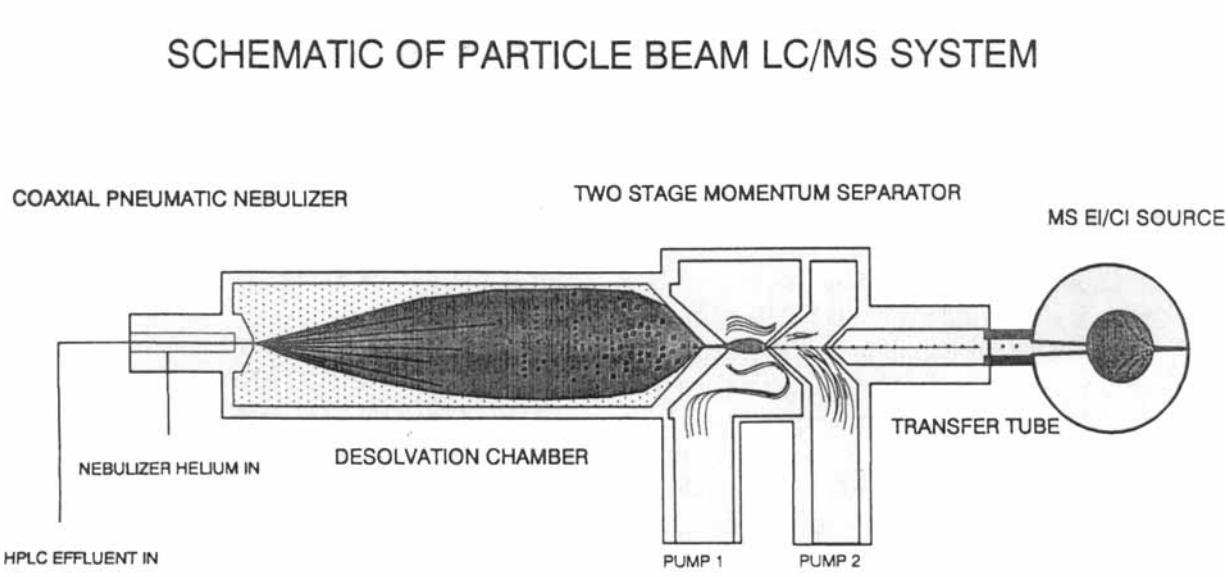

FIGURE 6. Particle beam LC-MS interface. (Courtesy of Hewlett Packard.)

tude lower than the analytes and are removed by the vacuum pumps connected to the momentum separator. A two-stage momentum separator provides an enrichment of 10^4 to 10^5 particles relative to the solvent.[161]

The particle beam interface is most useful for the characterization of organic compounds. Because the LC mobile phase is removed before ionization, this interface provides true electron ionization spectra that can be interpreted and library searched. Particle beam also affords the opportunity to perform chemical ionization with a variety of reagent gases. One limitation of particle beam is that the analytes must be sufficiently volatile to undergo ionization in the vapor phase in the source of the mass spectrometer. This restricts the size of molecules that may be analyzed by this technique. Other limitations of particle beam include possible peak broadening effects,[162] transmission efficiencies across the interface that may be as low as 5 to 20%,[163] and responses of analytes that change as a function of mobile phase composition.[163] "Carrier effects", or increased analyte transmission across the interface caused by the addition of buffers to the LC mobile phase or by co-eluting matrix components, have been documented.[158,164,165] Carrier effects severely restrict quantitative analysis with this interface.[166] Both linear and nonlinear calibration curves have been observed.[167] Detection limits (full scan conditions) for this technique range from approximately 10 to 100 ng; therefore, it is possible to detect parts per billion concentrations of analytes in aqueous matrices.

B. Thermospray Interface

Figure 7 shows a typical thermospray interface. The LC effluent forms a superheated, high velocity aerosol after entering an electrically heated vaporizer. The aerosol droplets enter a heated source and continue to desolvate. Ions are then formed by a chemical ionization process, by ion evaporation (a volatile buffer in the LC mobile phase causes charging of the droplets), or by use of a filament or discharge. Ion evaporation is especially useful because it does not require volatilization of analytes before ionization. After their formation, the ions are extracted through an ion exit cone while neutral molecules are pumped away by the vacuum system.

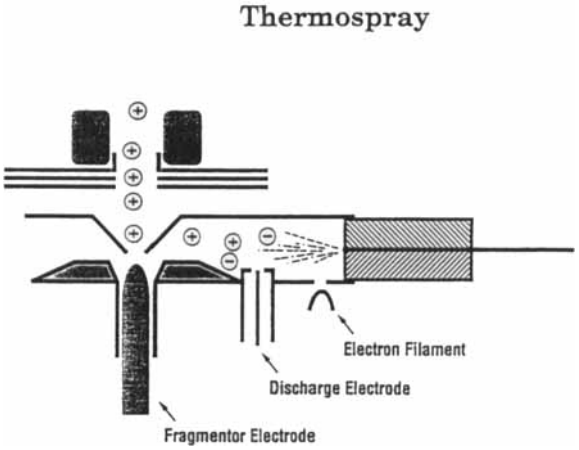

FIGURE 7. Thermospray LC-MS interface. (Courtesy of Hewlett Packard.)

Thermospray is most useful for the confirmation and quantitation of analytes. Work which includes a comparison of particle beam and thermospray has been done by Northington et al.[168] and Voyksner et al.[163] Unlike particle beam, thermospray produces chemical ionization spectra because the LC mobile phase assists ionization, which occurs in the interface region of the mass spectrometer. Molecular ions and adduct ions are usually observed; little fragmentation occurs. The "softer" ionization of the thermospray interface provides sensitive confirmation and quantitation of analytes and often provides molecular weight data. This limits the use of thermospray for analyte characterization. Coupling thermospray with MS-MS can be a useful option to traditional, single quadrupole MS and can provide some structural information about the analytes.[169] Only analytes with basic sites in their structures, such as many pesticides and herbicides, show good thermospray sensitivity — 0.1 to 10 ng of analytes may be detected.[161]

C. Electrospray Interface

Although to the best of our knowledge, no reports of the use of electrospray to analyze drinking water exist, this interface merits discussion because it is becoming increasingly popular for LC-MS analyses.[161] Electrospray has been successfully used for quite some time to analyze pharmaceutical and biological molecules and is expected to be applied to environmental problems in the future. Figure 8 shows an electrospray interface. An electric field between a cylindrical electrode, which is at 2 to 4 kV (V_{cyl} in Figure 8), and a grounded needle through which LC effluent flows, charges the surface of the LC effluent. This causes the formation of a spray of charged drops, which travels through an inert drying gas, and this helps to desolvate the droplets and to remove uncharged particles. The ions then travel through a skimmer and into the mass analyzer. Electrospray produces chemical ionization-type spectra. $[M + H]^+$, $[M-H]^-$, and multiply charged ions are commonly observed. Increased fragmentation of the ions may be obtained by altering the voltages on the skimmer; thus, it is possible to obtain some structural information from electrospray spectra.

One major limitation of electrospray has been the inability to accommodate LC flow rates which are compatible with conventional LC columns. However, the development of the ultrasonic nebulizer has allowed the introduction of effluents with flow rates of 50 to 600 μl/min (compatible with 1 mm i.d. columns) into the mass spectrometer.[170] In addition to electrospray, another atmospheric pressure ionization technique, atmospheric pressure chemical ionization (APCI), can accommodate flow rates of 0.2 to 2 ml/min. Doerge and Bajic[171] detected low nanogram amounts of triazine herbicides under full scan conditions by LC/APCI-MS. Liquid chromatography/atmospheric pressure chemical ionization was more sensitive than particle beam or thermospray. For this reason, LC/APCI-MS may be an excellent method for the determination of pesticides.

The use of LC-MS in drinking water analysis has not been developed well. Table 10 summarizes the use of particle beam and thermospray techniques for the determination of analytes, including aromatic chlorinated sulfonic acids, chlorinated phenoxy acid herbicides, and azo dyes, found in water. It is clear that LC-MS can be useful in environmental analyses, especially for the determination of polar (and water-soluble) com-

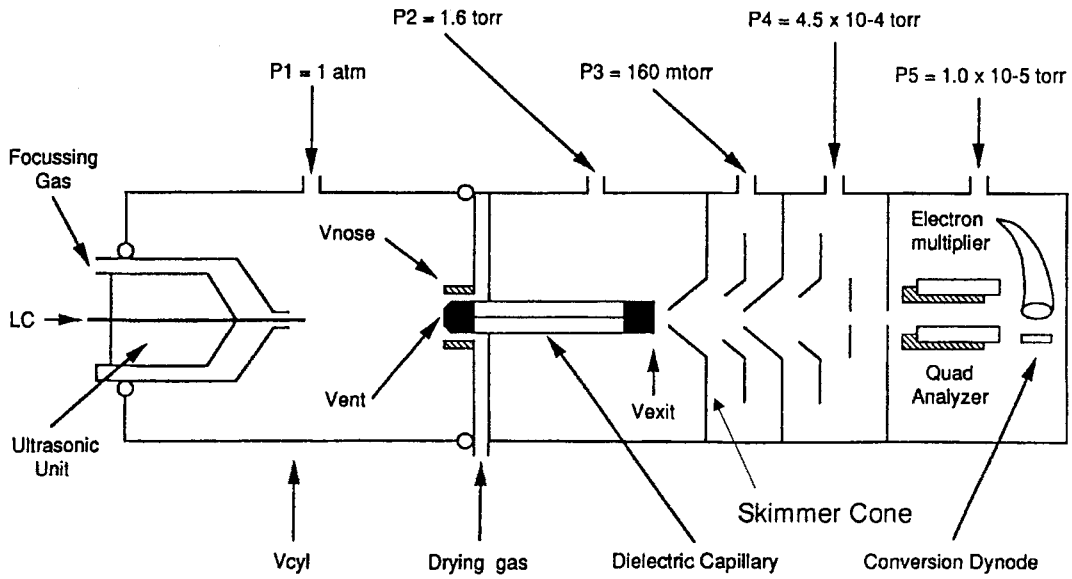

FIGURE 8. Electrospray LC-MS interface. (Courtesy of Analytica of Branford.)

TABLE 10
Summary of LC-MS Analyses Related to Drinking Water

Analyte	Column	Interface	Matrix	Results	Ref.
Alkylphenol polyethoxylates and their acetic acid derivatives	Reversed phase	PB	Drinking water	500 l sample size; semiquantitative analysis; ppt detection limits (full scan)	175
Azo dyes, organophosphorous compounds, *tris*-(2,3-dibromopropyl)phosphate	C_{18}	TS	Drinking water	Sample size matrix and analyte dependent; detection limits low to sub-nanogram per injection, dependent on MS mode used	178
Benzidines, nitrogen-containing pesticides	C_{18}	PB	Drinking water	1 l sample size; detection limits 2–30 ppb	177
Carbamate and phenylurea pesticides	C_{18}	PB	Standard	Evaluation of 2 PB systems and discussion of operating parameters; 10–440 ng of analytes detected (full scan)	173
Chlorophenoxy acids	C_{18}	PB	Spiked water	Methane, electron capture negative ionization used; analytes at 20 ppb water easily detected in 100 ml sample; SIM used	176
126 National Pesticide Survey analytes (U.S.)	C_{18}	PB	Standard	43 analytes detected (full scan) at 100 ng or less; supports possibility of confirming 0.1 ppb concentrations of anayltes in water	172
Nonionic surfactants, plasticizers, plastic additives	Reverse phase	PB	Effluent public treatment works	Identified 32 compounds by LC-MS not detected by semiquantitative analysis; ppb detection limits (full scan)	174
Pesticides	C_{18}	TS	River and simulated Seawater	Confirmed presence of 12 pesticides, including fenamiphos, at 2–20 ppb; TS in both positive and negative ion modes used; sample sizes of 1–4 l	198
Pesticides, amines, organometallics, misc.	C_{18}	PB	Standard	Average detection limits (full scan) 5–50 ng	168
Phthalate esters, polypropylene-oxide pollutants, polypropylene glycol ethers	C_{18}	TS	Drinking water	Obtained mol wt information; performed MS-MS experiments to aide confirmations; 19 l sample size	169

PB = particle beam interface, TS = thermospray interface.

pounds, which are not easily analyzed by GC-MS. Because it produces conventional electron ionization spectra, particle beam offers the potential for the discovery of pollutants not identified by GC-MS. Particle beam MS has been accepted recently by USEPA as a method for the analysis of selected benzidines and nitrogen-containing pesticides using either external standard calibration or isotope dilution (Method 553[177]). Method detection limits range from 2 to 30 ppb. Methods of enhancing particle beam

sensitivity, for example, the use of postcolumn additions of buffers and organic solvents[164,165] and the use of chemical ionization with both positive and negative ion detection, merit further investigation. Under optimized conditions, picogram sensitivities for particle beam are achievable; Tinke et al.[162] have shown that it is possible to detect 40 pg of the pentafluorobenzyl derivative of palmitic acid.

Thermospray offers great potential for the sensitive confirmation and quantitation of target analytes. Thermospray MS has, in fact, been studied by USEPA as a method for monitoring azo dyes, fluorescent brighteners, and organophosphorus pesticides.[178] Detection limits for organophosphorus pesticides are compound dependent and range from 0.2 to 30 ng.

Because of the relative newness of LC-MS compared to GC-MS, much study requires completion before LC-MS becomes an established technique. The ultimate sensitivity of LC-MS depends on the analyte, LC conditions, LC-MS interface selected, and MS conditions. Future LC-MS development will strive to improve the sensitivity of the technique, continue to develop quantitative methods, and will study the coupling of the liquid chromatograph to different MS systems (e.g., high resolution MS, MS-MS, and the ion trap).

D. Comparison of Gas and Liquid Chromatography-Mass Spectrometry

Gas chromatography-mass spectrometry is always preferred over LC-MS for the determination of analytes that are amenable to either technique. The reasons are straightforward: many more theoretical plates per column for GC columns compared to LC columns make the resolving power of GC much better than LC. The reader should note that this has mainly to do with the length of columns used; GC columns for drinking water analyses are typically 30 to 60 m long, while the longest LC columns are about 25 cm. In addition, detection limits for organic analytes by using GC-MS are typically 10 to 100 times lower than those possible via LC-MS.

Regardless of the above limitations, LC-MS has much wider applicability than GC-MS, and its use is expected to grow. Ironically, one of the reasons for limited use of LC-MS for drinking water analysis is because polar or high molecular weight compounds that may be present in drinking water, some of which may be toxic or carcinogenic, have not been studied because they are not readily amenable to GC-MS analysis. Improvements in the LC-MS interface to allow much lower detection limits are essential to increasing the applicability of LC-MS to drinking water analysis.

VIII. IMMUNOCHEMICAL METHODS AND TOXICITY TESTING

Although employed with considerable success for clinical analysis applications for some time, bioanalytical methods are relatively recent tools for environmental applications. A comprehensive review of immunoassay techniques as applied to environmental samples was prepared recently by Sherry.[179] Immunoassay techniques offer speed of analysis, very high specificity, and reduced sample preparation. Although detection limits using these techniques are not yet as low as those that can be reached by employing state-of-the-art conventional analytical techniques, they are sufficient for many routine monitoring and screening applications. For example, a recent method for detecting cyanazine in water had a detection limit of 35 ppt.[180] Results from the enzyme-linked immunoassay (ELISA) method were comparable to the results from GC measurements. The high specificity of these methods may be a disadvantage in many drinking water applications, where the desired result is to quantify dozens of potential contaminants in a single determination, as is possible by using GC-MS methods. However, some analyses, such as the determination of the PCDDs and PCDFs, are so costly that a specific rapid immunoassay-based screening method may be desir-

able. For PCDD and PCDF determinations in drinking water, lower immunoassay detection limits are required. While the low-cost, rapid nature of immunochemical methods are appealing, it does not seem likely their use for drinking water analysis applications will become commonplace without significant additional refinements to the methodology, except perhaps for special applications such as the PCDDs and PCDFs.

The use of toxicity testing methods in drinking water analysis is expected to increase, although to date only a few studies have been reported. Because the effects on biological systems of a complex mixture of chemicals is presently almost impossible to predict, testing methods in which living organisms are directly exposed to the water sample have received much attention. Work in this area has been focused on the testing of environmental waters and industrial effluents rather than drinking water, but some drinking water investigations have been reported. The Ames assay was employed to study the mutagenic activity of drinking water by Lippincott[82] and Onodera[93]. These are not routine testing procedures; the amount of water sampled typically is > 100 l. In another study, the genotoxic potential in drinking water was measured by using a Salmonella/microsome testing system.[181] Suijbert et al. considered this test a good indicator of human exposure to potential carcinogens. It seems likely that toxicity testing methods will be used to supplement rather than to replace conventional analytical methods. If rapid, rugged, sensitive, and inexpensive toxicity testing methods for drinking water are developed, they could be used to screen many samples. Those samples showing significant positive response to the tests employed would then be analyzed by conventional GC-MS or LC-MS-based methods to identify the specific toxic contaminants.

IX. QUALITY CONTROL AND QUALITY ASSURANCE

Quality control (QC) and quality assurance (QA) considerations must be integral parts of any complete analytical method. Apart from the objective of generating data of defined quality, QA/QC measures are key factors in defending analytical data during legal proceedings, which becomes increasingly important as more environmental legislation is passed. Because this review is focussed on the technical aspects of drinking water analysis, bench-level QC procedures are emphasized. An excellent review on analytical quality assurance,[182] and a general discussion of the total quality process in the laboratory[183] have recently been published. It seems likely that laboratory accreditation or similar activities will become increasingly important, especially as the impact of government regulatory activities increases. A critical assessment of the impact of accreditation activities was presented by Staats.[184]

A. Elements of Quality Control for Trace Organics in Drinking Water

The specific bench-level QC activities taken depend on many factors, including cost limitations, the experience of the analyst, detection limits needed, regulatory requirements, detector employed, and the objectives of the analysis (i.e., rapid screening survey vs. accurate, precise data used for litigation). Table 11 is a compilation of many QC elements specified in USEPA GC-MS-based methods for organics in drinking water. Table 11 is not comprehensive, but it contains many of the QC actions that must be taken to ensure data of known quality are generated. For complete QC specifications, the reader is referred to the detailed method documentation of individual methods.[3,5] Of special interest is the many different types of QC samples specified. By incorporating all of these QC samples in a regular analysis program, the analyst can be reasonably sure that if results for the QC samples are all within specifications, then the sample data will fall within the known limits of accuracy and precision for the method used. Readers should note that the authors do not refer to the results of sample analyses as being "correct" so much as that they are of *known quality.*

TABLE 11
Quality Control Elements in EPA Drinking Water Methods

	Description of QC Action	Description of Action / Comments
Sampling and Sample Storage	Holding times specified	Volatiles analysis: samples collected in duplicate and analyzed within 14 d, maximum; organics analysis: samples extracted within 7 d and extracts analyzed within 30 d
	Sample preservation and storage	Stored at 4°C; pH adjusted to 2 at time of sampling; residual chlorine removed
Sample Types and Blanks	Field duplicates	Two samples collected under identical conditions; measures precision associated with analysis
	Field reagent blank	Reagent water placed in sample container and exposed to field conditions; treated as sample
	Laboratory reagent blank	Reagent water treated as sample; measures laboratory and reagent contamination / interferences
	Laboratory fortified blank	Analytes added to reagent water; analyze 1 / sample batch; analyze replicates quarterly; to determine if method is in control, and if measurements accurate and precise at the method detection limit
	Laboratory duplicates	Two sample aliquots analyzed separately; measures precision of laboratory procedures
	Laboratory performance check solution	Solution of analytes, surrogates, internal standards; to evaluate performance of the instrument system
	Quality control sample (QCS)	QCS obtained from external source — is sample matrix with analytes added, used to fortify reagent water or samples; purpose is to check performance with externally prepared reference material
Standards and Calibration	Internal standards (IS)	Use of IS recommended; stable isotope labeled analytes used for GC-MS methods
	Surrogate standards (SS)	Stable isotope labeled compounds used for GC-MS methods; used to monitor method performance within each sample — added to sample before extraction
	Preparation of stock solutions	Detailed preparation instructions for stock solutions specified; minimum storage times specified
	Calibration	Calibration procedures and ranges specified; verify calibration at start of each 8-h work shift
	Control charts	Use of control charts recommended (i.e., chart absolute areas of quantitation ions and surrogates to check consistent MS sensitivity — action taken if absolute areas drop below critical value)
	GC-MS response factors (RF)	RFs for analytes and surrogates must be within 30% of mean value from the initial calibration; relative standard deviation of RFs from analysis of calibration solutions must be < 20%
	Accuracy and precision	Initial accuracy shown by analysis of 5–7 replicates of blank fortified with analytes in 0.2–5 mg / l range; mean accuracy must be > 70–130% of true value, RSD < 20%; plot on control charts

TABLE 11 (continued)
Quality Control Elements in EPA Drinking Water Methods

	Description of QC Action	Description of Action / Comments
GC-MS performance	GC performance criteria	GC criteria includes acceptable peak shapes; separation criteria for selected analytes specified; GC retention time (RT) of analyte must be within 3 standard deviations of mean RT of analyte in calibration mix
	MS tuning criteria	MS tuning criteria specified for mass calibration compound used
	System background	Before samples are analyzed, low GC-MS system background must be demonstrated
	GC-MS identification criteria	Criteria for matching the mass spectrum of a sample peak to a corresponding analyte mass spectrum: all ions of abundance > 10% in mass spectrum of analyte must be present in sample mass spectrum, and relative abundances must agree within 20% absolute

The degree to which results are accurate and precise depends on the ability of the analytical method used to eliminate determinate error.

B. Analysis at the Detection Limit

For the determination of trace organics in drinking water, the detection limit concept is much more important than for many other environmental analysis applications because human exposure to toxic compounds in drinking water is direct, and because relatively little is known about long-term, low-level exposure to these chemicals. Therefore, the public is concerned over the detection of any toxic compound in drinking water, even when found near the method detection limit. For some compounds such as the PCDDs and PCDFs, some believe no threshold "safe" concentration exists; of course, we can never measure a "true zero concentration" of anything, so analysts are forced to develop methods to detect increasingly smaller concentrations of some compounds. In principle, one could achieve arbitrarily small detection levels by sampling larger volumes of drinking water. Aside from the practical difficulties of very large sample sizes, the QC measures needed become much more difficult to implement. For example, the measurement of an appropriate blank becomes far more difficult. The relation of the detection limit to the information needs of water quality management were discussed previously,[185] and several papers have studied the statistical treatment of data below the detection limit.[186,187]

How to deal with analyte data determined at or near the detection limit is a continuous problem in the environmental analysis field in general, and especially for drinking water analysis. One of the barriers to achieving consistency in dealing with this issue is that the number of different definitions of detection limits seems to be about the same as the number of analysts. Although a few "standard" detection limit definitions exist, the application of these definitions to the interpretation of real sample data is far from standard. Recently, a move to reexamine the definition of detection limit and related terms was initiated.[188] One of the recommendations of this work is to use the term detection *level* instead of detection *limit*. This new term recognizes to the fact that in environmental analyses the lower limit of analyte detection depends on each individual sample; therefore the "official" method

detection limit could not be used to censor low-level analytical data.

C. Real-Matrix Certified Reference Materials

One of the most serious limitations in the determination of trace organics in drinking water is the scarcity of certified reference materials (CRMs). In a recent paper that described the activities of the Community Bureau of Reference regarding the preparation of new CRMs, no CRMs for water analysis were available.[189] Candidate CRMs for metals in water are under development, but the situation for trace organics is bleak. The situation is similar at the National Institute for Standards and Technology (NIST, formerly National Bureau of Standards). Certified reference materials for hydrophobic organics such as the PCDDs and PCDFs are especially difficult to prepare, and if such CRMs were available, there likely would be some problems regarding their shelf-life. One way around this problem may be to create generator columns that could be used to deliver a fixed concentration of analyte when eluted under standard conditions.[190] Maier[191] discussed the difficulties in proving accuracy without CRMs, and concluded that it could be done, but at a much greater investment in resources than would be needed with the use of CRMs.[191]

D. Results of Collaborative Studies

Only a few collaborative and round-robin studies involving trace organics in drinking water have been reported recently.[136,192,193] In a study of PCDDs and PCDFs spiked into reagent water at concentrations ranging from 25 to 100 ppq, the average percent relative standard deviations (%RSDs) for six participating laboratories ranged from 10 to 60. Laboratories that used LRMS detection found the analysis very difficult, while those laboratories that employed HRMS or MS-MS detection performed much better. By using only advanced HRMS or MS-MS detection, %RSDs of better than 20 for parts per quadrillion-level PCDD and PCDF determination in drinking water should be obtained.

Collaborative studies were reported for the determination of nitrogen- and phosphorus-containing pesticides (USEPA Method 507)[192] and organochlorine pesticides (USEPA Method 508)[193] in drinking water. In both studies, %RSDs of better than 20 were obtained for most analytes detected, and the performance of the methods were comparable in reagent water and finished drinking water samples. However, some compounds (carboxin, disulfoton, metolachlor, pronamide, simazine, α-chlordane, 1,1′-dichloro-2,2′-bis(4-chlorophenyl)ethene 4,4'-DDE, and methoxychlor) exhibited statistically significant matrix effects for the finished drinking water. Kessels has shown the precision that can be obtained for the P & T determination of VOCs.[31] In a single laboratory study, he achieved RSDs better than 5% for 37 of 71 VOCs studied. Only 2 of 71 VOCs exhibited RSDs > 10% for the commercial P & T system he employed.

X. SUMMARY AND FUTURE PROSPECTS

The determination of organic compounds in drinking water will continue to be a very important part of the effort to protect humans from toxic environmental contaminants. Current methods can accurately quantify compounds at sub-parts per billion concentrations with RSDs > 20%. In special cases, determination of contaminants at parts per quadrillion concentrations with similar accuracy and precision is possible.

For the forseeable future, the mature technique of capillary column GC-MS will be the instrumentation of choice for this application. Improvements such as HRMS and MS-MS using the ITMS may make such advanced detection modes affordable for the routine analysis laboratory and thus may push routine detection levels 10 to 100 times below current levels within the next 2 to 5 years. New methods such as permeate trap MS may lead to more rapid determinations and increased automation. Some improve-

ments in GC column technology are expected, but advances in this area are not expected to be dramatic. Application of other chromatographic techniques, such as capillary electrophoresis[194] may provide improved performance for specific applications. The use of LC-MS will increase, as more attention is spent on highly polar organics not easily determined by using GC-MS methods. However, considerable research is required to lower the detection levels achievable, and to make LC-MS more rugged for routine application. The quantitative aspects of LC-MS need attention, as calibration can be very difficult and the precision and accuracy of quantitative data are often poor.

The most important recent advances in the analysis of drinking water for trace organics are in the sample preparation area, and it seems likely this trend will continue for at least the next few years. An exciting possibility is that by combining the techniques of SPE, SFE, and GC-MS, a totally automated analysis system can be developed in which drinking water is passed through an extraction disk which is then put directly into the analysis system with no additional treatment except for the addition of internal standards. Supercritical fluid extraction itself probably will be studied more for use in drinking water applications.[112,196,197]

Research is also needed on the basic chemistry of drinking water samples. Only a few studies have been conducted to determine sample storage times and conditions, and of possible sample changes during storage. Recommended sampling and sample storage conditions for most analytes are then generally extrapolated from these few investigations.

Much reference has been made in this review to USEPA methodologies. This simply reflects the great deal of effort USEPA has spent on drinking water monitoring, and the great influence USEPA methodologies have on other regulatory bodies. However, improvements in analytical technology and in the range of application of drinking water methods over the past decade has resulted in a proliferation of methodologies that have overlapping applicability.[197] We recommend that regulators adopt wherever possible a *performance-based* approach when specifying which analytical methods are allowed in regulations. Thus, the detection levels, precision and accuracy, and other key performance criteria would be specified in regulation, rather than specific methodologies. By using this approach, improvements to methods can be incorporated into standard protocols immediately as they are validated.

Although excellent performance for the determination of trace organics in drinking water can be achieved by using existing methodologies, improvements to the front-end chemistry and new developments in high resolution ITMS operation may substantially improve this performance in the next few years.

ACKNOWLEDGMENT

The authors gratefully acknowledge the assistance of J. Fred Banks, Greg Bartosiewicz, Robert Belardi, William Budde, Joel Cheng, Janusz Pawliszyn, and Don Robinson for their generous assistance in providing figures and information used in this review.

REFERENCES

1. Keith, L.H. *Environmental Sampling and Analysis: A Practical Guide*; Lewis Publishers: Chelsea, MI 1991.
2. *1992 Annual Book of ASTM Standards, Part II, Volume 11.01*; American Society for Testing and Materials: Philadelphia, 1992; pp 169–175.
3. United States Environmental Protection Agency *Methods for the Determination of Organic Compounds in Drinking Water*, EPA-600/4-88/039, PB91-231480; National Technical Information Service: Springfield, VA, 1991.
4. Caron, F.; Kramer, J.R. *Anal. Chem.* **1989**, *61*, 114–118.
5. United States Environmental Protection Agency; *Methods for the Determination of Organic Compounds in Drinking Water, Supplement I*, EPA-600/4-90/020, PB91-146027, National Technical Information Service: Springfield, VA, 1990.
6. Roe, V.D.; Lacy, M.J.; Stuart, J.D.; Robbins, G.A. *Anal. Chem.* **1989**, *61*, 2584–2585.

7. Foreman, W.T.; Zaugg, S.D.; Faires, L.M.; Werner, M.G.; Leiker, T.J.; Rogerson, P.F. *Environ. Sci. Technol.* **1992**, *26*, 1307–1312.
8. Crozier, P.W.; Hall, C.D.; Gurprasad, L.; Matchuk, L. *Stability of Polynuclear Aromatic Hydrocarbons in Chlorinated Drinking Water, Proc. Environ. Res. Technol. Branch, Technol. Transfer Conf.*, Environment Ontario, Toronto, 1992 (published in electronic format).
9. Chen, P.H.; Van Ausdale, W.A.; Roberts, D.F. *Environ. Sci. Technol.* **1991**, *25*, 540–546.
10. Munch, D.J.; Frebis, C.P. *Environ. Sci. Technol.* **1992**, *26*, 921–925.
11. Barth, R.C.; Wimsatt, J.C. *American Water Works Association Proc. 1992 Water Quality Technol. Conf.*, Toronto, November, 1992, pp. 251–271.
12. Neaves, W.M.; Fong, B. *Chlorinated and Nonchlorinated Organics Storage Studies, R. A. C. Project No. 412C*, Ontario Ministry of the Environment: Toronto, 1990.
13. Lopez-Avila, V.; Dodhiwala, N.S.; Milanes, J.; Beckert, W.F. *J. Assoc. Off. Anal. Chem.* **1989**, *72*, 593–602.
14. Sherman, P.L.; Kyne, J.M.; Gable, R.C.; Pustinger, J.V.; Mcmillin, C.R. *Determination of Haloethers in Industrial and Municipal Wastewaters*, PB81-123290, National Technical Information Service: Springfield, VA, 1981.
15. Rhoades, J.W.; Thomas, R.E.; Johnson, D.E.; Tillery, J.B. *Determination of Phthalates in Industrial and Municipal Wastewaters*, PB81-232167, National Technical Information Service: Springfield, VA, 1981.
16. Strupp, D.; Klussmann, U.; Ebing, W. *Fresnius' Z. Anal. Chem.* **1985**, *322*, 747–751.
17. Wong, A.S. *Determination of TCDD in Industrial and Municipal Wastewaters*, PB82-196882, National Technical Information Service: Springfield, VA, 1981.
18. Lee, H.B.; Leishman, P.D.; Todd, S.; Chau, A.S.Y.; *Natural Waters Research Institute Contribution No. 86-219*, Canadian Centre for Inland Waters: Burlington, Ontario, 1987.
19. Ripley, B.D.; Wilkinson, R.J.; Chau, A.S.Y.; *J. Assoc. Off. Anal. Chem.* **1974**, *57*, 1033.
20. Lee, H.B.; Stokker, Y.D.; Arafat, N.; Chau, A.S.Y.; *Natural Waters Research Institute Contribution No. 87-123*, Canadian Centre for Inland Waters: Burlington, Ontario, 1987.
21. Hodgson, D.W.; Thompson, J.F.; Watts, R.R. *J. Assoc. Off. Anal. Chem.* **1982**, *65*, 94–102.
22. Hennion, M.C. *Trends Anal. Chem.* **1991**, *10*, 317–323.
23. Onuska, F.I. *J. High Resol. Chromatogr.* **1989**, *12*, 4–11.
24. Afghan, B.K.; Chau, A.S.Y., Eds., *Analysis of Trace Organics in the Aquatic Environment*; CRC Press: Boca Raton, FL, 1989.
25. Oliver, B.G., in *Analysis of Trace Organics in the Aquatic Environment*; Afghan, B.K.; Chau, A.S.Y., Eds., CRC Press: Boca Raton, FL, 1989; pp 2–29.
26. Thomas, C.L.P., *LC-GC*, **1992**, *10*, 832–840.
27. Hites, R.A. *Environ. Sci. Technol.* **1992**, *7*, 1285–1287.
28. *Fundamentals of Purge and Trap*, Tekmar Publ. Note B121988.
29. Maier, I.; Fieber, M. *J. High Resol. Chromatogr. Chromatogr. Commun.* **1988**, *11*, 566–576.
30. Vickers, A.K. *Am. Lab.* **1991**, 23–27.
31. Kessels, H.; Hoogerwerf, W.; Lips, J. *J. Chromatogr. Sci.* **1992**, *30*, 247–255.
32. Pankow, J.F.; Ligocki, M.P.; Rosen, M.E.; Isabelle, L.M.; Hart, K.M. *Anal. Chem.* **1988**, *60*, 40–47.
33. Pankow, J.F.; Rosen, M.E. *Environ. Sci. Technol.* **1988**, *22*, 398–405.
34. Pankow, J.F. *Environ. Sci. Technol.* **1991**, *25*, 123–126.
35. Driss, M.R.; Bouguerra, M.L. *Int. J. Environ. Anal. Chem.* **1991**, *45*, 193–204.
36. Lin, D.P.; Falkenberg, C.; Payne, D.A.; Thakkar, J.; Tang, C.; Elly, C. *Anal. Chem.* **1993**, *65*, 999–1002.
37. Ontario Ministry of the Environment; Laboratory Services Branch Draft Method, "Determination of Volatile Organics in Drinking Water and Aqueous Samples by Purge and Trap GC/MS," December 1992.
38. Mehran, M.F.; Nickelsen, M.G.; Golkar, N.; Cooper, W.J. *J. High Resol. Chromatogr.* **1990**, *13*, 429–433.
39. Cochran, J.W. *J. High Resol. Chromatogr. Chromatogr. Commun.* **1987**, *10*, 573–575.
40. Cochran, J.W. *J. High Resol. Chromatogr. Chromatogr. Commun.* **1990**, *11*, 663–665.
41. McClenny, W.A.; Pleil, J.D.; Holdren, M.W.; Smith, R.N.; *Anal. Chem.* **1984**, *56*, 2947–2951.
42. Vickers, A.K.; Datta, M. *Am. Lab.* **1993**, 28N–28S.
43. Lépine, L.; Archambault, J.F. *Anal. Chem.* **1992**, *64*, 810–814.
44. Bianchi, A.P.; Varney, M.S.; Phillips, J. *J. Chromatogr.* **1992**, *557*, 429–439.
45. Bianchi, A.; Varney, M.S. *J. High Resol. Chromatogr.* **1989**, *12*, 184–186.
46. Barnung, T.N.; Grahl-Nielsen, O. *J. Chromatogr.* **1989**, *466*, 271–278.
47. Ho, J.S.-Y. *J. Chromatogr. Sci.* **1989**, *27*, 91–98.
48. Eichelberger, J.W.; Bellar, T.A.; Donnelly, J.P.; Budde, W.L.; *J. Chromatogr. Sci.* **1990**, *28*, 460–467.
49. Yan, X.; Carney, K.R.; Overton, E.B. *J. Chromatogr. Sci.* **1992**, *30*, 491–496.
50. Drozd, J.; Novak, J. *J. Chromatogr.* **1979**, *165*, 141–165.
51. Vitenberg, A.G. *J. Chromatogr. Sci.*, **1984**, *22*, 122–124.

52. Herzfeld, D.; van der Gun, K.-D.; Louw, R. *Chemosphere.*, **1989**, *18*, 1425–1430.
53. Gryder-Boutet, D.E.; Kennish, J.M. *J. Am. Water Works Assoc.* **1988**, *80(10)*, 52–55.
54. Freiria-Gandara, J.J.; Alvarez-Devesa, A.; Lorenzo-Ferreira, R. A.; Bermejo-Martinez, F. *Anal. Lett.*, **1990**, *23*, 1938–1958.
55. Page, B.D.; Conacher, H.B.S.; Salminen, J.; Nixon, G.R.; Riedel, G.; Mori, B.; Gagnon, J.; Brousseau, R. *J. Assoc. Off. Anal. Chem.* **1993**, *76*, 26–31.
56. Schnable, J.G.; Dussert, B.; Suffet, I.H.; Hertz, C.D. *J. Chromatogr.* **1990**, *513*, 47–54.
57. Grob, K. *J. Chromatogr.* **1973**, *84*, 255–273.
58. Grob, K. *J. Chromatogr.* **1974**, *90*, 303–313.
59. Melton, R.G.; Coleman, W.E.; Slater, R.W.; Kopfler, F.C.; Allen, W.K.; Aurand, T.A.; Mitchell, D.E.; Voto, S.J.; Lucas, S.V.; Watson, S.C., in *Advances in the Identification and Analysis of Organic Pollutants in Water*, Vol. 2; Keith, L.H., Ed.; Ann Arbor Science: Ann Arbor, MI, 1981; pp 597–674.
60. Krasner, S.W.; Hwang, C.J.; McGuire, M.J., in *Advances in the Identification and Analysis of Organic Pollutants in Water*, Vol. 2; Keith, L.H., Ed.; Ann Arbor Science: Ann Arbor, MI, 1981; pp 689–712.
61. Hwang, C.J.; Krasner, S.W.; McGuire, M.J.; Moylan, M.S.; Dale, M.S. *Environ. Sci. Technol.* **1984**, *18*, 535–539.
62. Graydon, J.W.; Grob, K.; Zuercher, F.; Giger, W. *J. Chromatogr.* **1984**, *285*, 307–318.
63. Buszka, P.M.; Zaugg, S.D.; Werner, M.G. *Bull. Environ. Contam. Toxicol.* **1990**, *45*, 507–515.
64. Baykut, G.; Voigt, A. *Anal. Chem.* **1992**, *64*, 677–681.
65. Arthur, C.L.; Killam, L.M.; Motlagh, S.; Lim M.; Potter, D.W.; Pawliszyn, J. *Environ. Sci. Technol.* **1992**, *26*, 979–983.
66. Arthur, C.L.; Potter, D.W.; Buchholz, K.D.; Motlagh, S.; Pawliszyn, J. *LC-GC*, **1992**, *10*, 656–661.
67. Arthur, C.L.; Killam, L.M.; Buchholz, K.D.; Pawliszyn, J.; Berg, J.R. *Anal. Chem.* **1992**, *64*, 1960–1966.
68. Pratt, K.F.; Pawliszyn, J. *Anal. Chem.* **1992**, *64*, 2101–2106.
69. Pratt, K.F.; Pawliszyn, J. *Anal. Chem.* **1992**, *64*, 2107–2110.
70. Lister, A.K.; Wood, K.V.; Cooks, R.G.; Noon, K.R. *Biomed. Environ. Mass Spectrom.* **1989**, *18*, 1063–1070.
71. Gazda, M.; Dejarme, L.E.; Choudhury, T.K.; Cooks, R.G.; Margerum, D.W. *Environ. Sci. Technol.* **1993**, *27*, 557–561.
72. Cooks, R.G.; Choudhury, T.K.; Dejarme, L.E.; Bauer, S.; Patrick, J. *Ultratrace analysis of organic compounds in water*, in *Proc. 41st ASMS Conf. Mass Spectrometry and Allied Topics*, San Francisco, 1993.
73. Shoemaker, J.A.; Bellar, T.A.; Eichelberger, J.W.; Budde, W.L. *J. Chromatogr. Sci.* **1993**, *31*, 279–284.
74. Ramette, R.W. *Chemical Equilibrium and Analysis*; Addison-Wesley: Reading, MA, 1981, pp 570–591.
75. Ibrahim, E.A.; Suffet, I.H. *J. Chromatogr.* **1988**, *454*, 217–232.
76. Peters, R.J.B.; Erkelens, C.; De Leer, E.W.B.; De Galan, L. *Water Res.* **1991**, *25*, 473–477.
77. Peters, R.J.B.; De Leer, E.W.B.; De Galan, L. *Water Res.* **1990**, *24*, 797–800.
78. Hable, M.; Stern, C.; Asowata, C.; Williams, K. *J. Chromatogr. Sci.* **1991**, *29*, 131–135.
79. Middleditch, B.S. *Analytical Artifacts*; Elsevier: Amsterdam, 1989.
80. Wang, D.T.; Meresz, O.; Taguchi, V.Y.; Jenkins, S.W.D.; Robinson, D.R. *Anal. Lett.* **1988**, *21*, 1749–1756.
81. Chen, P.H.; Van Ausdale, W.A.; Keeran, W.S.; Roberts, D.F. *Chemosphere.* **1993**, *26*, 1743–1749.
82. Lippincott, R.L.; Ibrahim, E.A.; Louis, J.B.; Atherholt, T.B.; Suffet, I.H. *Water Res.* **1990**, *24*, 709–716.
83. Foster, G.D.; Rogerson, P.F. *Int. J. Environ. Anal. Chem.* **1990**, *41*, 105–117.
84. Foster, G.D.; Foreman, W.T.; Gates, P.M. *J. Agric. Food Chem.* **1991**, *39*, 1618–1622.
85. Barth, R.C.; Fair, P.S. *J. Am. Water Works Assoc.* **1992**, *84(11)*, 94–98.
86. Bourgeois, D.; Gaudet, J.; Deveau, P.; Mallet, V.N. *Bull. Environ. Contam. Toxicol.* **1993**, *50*, 433–440.
87. Newman, A. *Environ. Sci. Technol.* **1992**, *26*, 1294–1295.
88. Liska, I.; Krupcik, J.; Leclercq, A. *J. High Resol. Chromatogr.* **1989**, *12*, 577–590.
89. Junk, G.A.; Richard, J.J., in *Advances in the Identification and Analysis of Organic Pollutants in Water*, Vol. 1; Keith, L.H., Ed.; Ann Arbor Science: Ann Arbor, MI, 1981; pp 295–316.
90. Ryan, J.J.; Fitz, J.S., in *Advances in the Identification and Analysis of Organic Pollutants in Water*, Vol. 2; Keith, L.H., Ed.; Ann Arbor Science: Ann Arbor, MI 1981; pp 317–328.
91. Caton, J.E.; Barnes, Z.K.; Kubota, G.; Griest, W.H.; Maskarinec, M.P., in *Advances in the Identification and Analysis of Organic Pollutants in Water*, Vol. 2; Keith, L.H., Ed.; Ann Arbor Science: Ann Arbor, MI 1981; pp 329–344.
92. Hargesheimer, E.E.; Satchwill, T. *Aqua.* **1989**, *38*, 345–351.
93. Onodera, S. *J. Chromatogr.* **1991**, *557*, 413–427.
94. Uza, M.; Hunsinger, R.; Thompson, T.; Clement, R.E. *Chemosphere.* **1990**, *20*, 1349–1354.
95. Ryan, J.J., in *Environmental Carcinogens: Methods of Analysis and Exposure Measurement, Volume 11—Polychlorinated Dioxins and Dibenzofurans*; Rappe, C.; Buser, H.R.; Dodet, B.; O'Neill, I.K.,

Eds; International Agency for Research on Cancer: Lyon, France, 1991; pp 199–203.
96. Bartosiewicz, G.N., Varian Sample Preparation Products, personal communication, 1993.
97. *The Supelco Guide to Solid Phase Extraction, 2nd ed.*, Supelco Inc.: Bellefonte, PA, 1988.
98. Borburgh, H.J.; Hammers, W.M. *Toxicol. Environ. Chem.* **1992**, *35*, 79–86.
99. Hagen, D.F.; Markell, C.G.; Schmitt, G.A.; Blevins, D.D. *Anal. Chim. Acta*. **1990**, *236*, 157–164.
100. Howard, A.L.; Taylor, L.T. *J. Chromatogr. Sci.* **1992**, *30*, 374–382.
101. Ho, J.S.; Tang, P.H. *J. Chromatogr. Sci.* **1992**, *30*, 344–350.
102. De La Vigne, U.; Jänchen, D.E.; Weber, W.H. *J. Chromatogr.* **1991**, *553*, 489–496.
103. Wells, M.J.M.; Michael, J.L. *J. Chromatogr. Sci.* **1987**, *25*, 345–351.
104. Brooks, M.W.; Tessier, D.; Soderstrom, D.; Jenkins, J.; Clark, J.M. *J. Chromatogr. Sci.* **1990**, *28*, 487–489.
105. Di Corcia, A.; Marchetti, M. *Environ. Sci. Technol.* **1992**, *26*, 66–74.
106. Battista, M.; Di Corcia, A.; Marchetti, M. *Anal. Chem.* **1989**, *61*, 935–939.
107. Dalbacke, J.; Dahlquist, I.; Persson, C. *J. Chromatogr.* **1990**, *507*, 381–387.
108. Tan, G.H. *Analyst*. **1992**, *117*, 1129–1132.
109. *Applications Bibliography*, Varian Sample Preparation Products, Harbour City, CA, 1992.
110. Marvin, C.H.; Brindle, I.D.; Hall, C.D.; Chiba, M. *J. Chromatogr.* **1990**, *503*, 167–176.
111. Brouwer, E.R.; Van Iperen, D.J.; Liska, I.; Lingeman, H.; Brinkman, U.A.Th. *Int. J. Environ. Anal. Chem.* **1992**, *47*, 257–266.
112. Tang, P.H.; Ho, J.S.; Eichelberger, J.W. *J. Assoc. Off. Anal. Chem.* **1993**, *76*, 72–82.
113. Hearne, G.M.; Hall, D.O. *Am. Lab.* **1993**, 20H–28M.
114. Edgell, K.W.; Biederman, L.A.; Longbottom, J.E. *J. Assoc. Off. Anal. Chem.* **1991**, *74*, 309–317.
115. Grob, K.; Fröhlich, D. *J. High Resol. Chromatogr.* **1993**, *16*, 224–228.
116. Coutant, R.W.; Keigley, G.W. *Anal. Chem.* **1988**, *60*, 2536–2537.
117. Carmichael, D.; Holmes, W. *J. High Resol. Chromatogr.* **1990**, *13*, 267–269.
118. Temmerman, I.F.M.M.; Quaghebeur, D.J.M. *J. High Resol. Chromatogr.* **1990**, *13*, 379–381.
119. Gurka, D.F.; Pyle, S.M.; Titus, R. *Anal. Chem.* **1992**, *64*, 1749–1754.
120. Munch, J.W.; Eichelberger, J.W. *J. Chromatogr. Sci.* **1992**, *30*, 471–477.
121. Moltó, J.C.; Font, P.G.; Mañes, J. *J. Chromatogr.* **1991**, *555*, 137–145.
122. Liska, I.; Brouwer, E.R.; Ostheimer, A.G.L.; Lingeman, H.; Brinkman, U.A.Th.; Geerdink, R.B.; Mulder, W.H. *Int. J. Environ. Anal. Chem.* **1992**, *47*, 267–291.
123. Bagheri, H.; Vreuls, J.J.; Ghijsen, R.T.; Brinkman, U.A.Th. *Chromatographia*. **1992**, *34*, 5–13.
124. Coquart, V.; Hennion, M.-C. *J. Chromatogr.* **1991**, *585*, 67–73.
125. Yoo, L.J.; Shen, Y.; Fitzsimmons, S.; Rigby, M.; *American Water Works Association Proc. 1992 Water Quality Technol. Conf.*, Toronto, 1992; pp 1335–1358.
126. Di Corcia, A.; Samperi, R.; Marcomini, A.; Stelluto, S. *Anal. Chem.* **1993**, *65*, 907–912.
127. Cai, Z.; Ramanujam, V.M.S.; Monson, S.J.; Gross, M.L. Determination of hydroxyatrazine in water at low-ppt levels by carbon black cartridge extraction and high resolution FAB-MS, in *Proc. 41st ASMS Conf. Mass Spectrometry and Allied Topics*, San Francisco, 1993.
128. Clement, R.E.; Tosine, H.M., in *Analysis of Trace Organics in the Aquatic Environment*; Afghan, B.K.; Chau, A.S.Y., Eds.; CRC Press: Boca Raton, FL, 1989; Chapter 5.
129. Di Corcia, A.; Marchetti, M. *Anal. Chem.* **1991**, *63*, 580–585.
130. Lopez-Avila, V.; Benedicto, J.; Milanes, J. *Evaluation of Sample Extract Cleanup Using Solid-Phase Extraction Cartridges*, EPA/600/4-89/049, PB90-162520, National Technical Information Service: Springfield, VA, 1989.
131. Nielen, M.W.F.; Brinkman, U.A.Th.; Frei, R.W. *Anal. Chem.* **1985**, *57*, 806–810.
132. Miyata, H.; Ohta, S.; Aozasa, O. *Proc. 12th Int. Symp. Chlorinated Dioxins and Related Compounds; Organohalogen Compounds*, Vol. 9; Ecoinforma Press: Bayreuth, Germany, 1992; pp 151–154.
133. Pomazanov, V.; Kuntsevich, A.; Vengerov, Y.; Dmitriyeva, L.; Asadova, L. *Proc. 12th Int. Symp. Chlorinated Dioxins and Related Compounds; Organohalogen Compounds*, Vol. 9; Ecoinforma Press: Bayreuth, Germany, 1992; pp 177–182.
134. Uza, M.; Hunsinger, R.; Thompson, T.; Clement, R.E. *Chemosphere*. **1990**, *20*, 1349–1354.
135. Jobb, B.; Uza, M.; Hunsinger, R.; Roberts, K.; Tosine, H.; Clement, R.; Bobbie, B.; LeBel, G.; Williams, D.; Lau, B. *Chemosphere*. **1990**, *20*, 1553–1558.
136. Tashiro, C.; Clement, R.E.; Davies, S.; Oliver, B.; Munshaw, T.; Fenwick, J.; Chittim, B.; Foster, M.G. *Chemosphere*. **1990**, *20*, 1313–1317.
137. Meyer, C.; O'Keefe, P.; Hilker, D.; Rafferty, L.; Wilson, L.; Connor, S.; Aldous, K. *Chemosphere*. **1989**, *19*, 21–26.
138. O'Keefe, P.; Meyer, C.; Smith, R.; Hilker, D.; Aldous, K.; Wilson, L. *Chemosphere*. **1986**, *15*, 1127–1134.
139. LeBel, G.; Williams, D.T.; Hollebone, B.R.; Shewchuk, C.; Brownlee, L.J.; Tosine, H.; Clement, R.; Suter, S. *Int. J. Environ. Anal. Chem.* **1990**, *38*, 21–29.
140. Hollebone, B.R.; Shewchuk, C.; Brownlee, L.J.; Tosine, H.; Clement, R.; Suter, S.; LeBel, G.;

Williams, D.T. *Int. J. Environ. Anal. Chem.* **1990** *38*, 9–20.
141. Rappe, C.; Kjeller, L.-O.; Kulp, S.E. *Proc. 10th Int. Symp. Chlorinated Dioxins and Related Compounds; Organohalogen Compounds*, Vol. 2; Ecoinforma Press: Bayreuth, Germany, 1990; pp 207–210.
142. LeBel, G.L.; Williams, D.T.; Ryan, J.J.; Lau, B.P.-Y. Evaluation of XAD-2 resin cartridges for concentration/isolation of chlorinated dibenzo-*p*-dioxins and furans from drinking water at the parts-per-quadrillion level, in *Chlorinated Dioxins and Dibenzofurans in Perspective*; Rappe, C.; Choudhary, G.; Keith, L.H., Eds.; Lewis Publishers: Chelsea, MI, 1986; pp 329–341.
143. Clement, R.E. *Anal. Chem.* **1991**, *63*, 1130A–1139A.
144. Haile, C.L. The use of stable isotope labeled compounds in environmental analytical chemistry, in *Synthesis and Applications of Isotopically Labeled Compounds, Proc. Int. Symp.*; Duncan, W.P.; Susan, A.B., Eds.; 1993; pp 359–364.
145. Fielden, P.R. *J. Chromatogr. Sci.* **1992**, *30*, 45–52.
146. Hill, H.H.; McMinn, D.G., Eds.; *Detectors for Capillary Chromatography, Chemical Analysis*, 121; New York: John Wiley & Sons, 1992.
147. Clement, R.E.; Reiner, E.J. Mass spectrometric detectors, in *Detectors for Capillary Chromatography, Chemical Analysis*, 121; Hill, H.H.; McMinn, D.G., Eds.; New York: John Wiley & Sons, 1992, pp 327–353.
148. Reiner, E.J.; Clement, R.E., The mass spectrometer as a gas chromatographic detector, in *Gas Chromatography: Biochemical, Biomedical and Clinical Applications, Chemical Analysis*, 111; Clement, R.E., Ed.; New York: John Wiley & Sons, 1990, pp 87–108.
149. Clement, R.E.; Tosine, H.M. *Mass Spectrom. Rev.* **1988**, *7*, 593–636.
150. Tashiro, C.; Clement, R.E., Characteristics of modern GC instrumentation, in *Gas Chromatography: Biochemical, Biomedical and Clinical Applications, Chemical Analysis*, 111; Clement, R.E., Ed.; New York: John Wiley & Sons, 1990; pp 25–54.
151. Jennings, W. *High Resol. Chromatogr. Chromatogr. Commun.* **1980**, *3*, 601–608.
152. Lautamo, R.M.A.; Decker, D.; Jennings, W.; Mehran, M.F. *Chromatographia*. **1992**, *34*, 331–334.
153. Ireland, J.C.; Moore, L.A.; Pourmoghaddas, H.; Stevens, A.A. *Biomed. Environ. Mass Spectrom.* **1988**, *17*, 483–486.
154. Alugupalli, S.; Larsson, L.; Slosarek, M.; Jaresova, M. *Appl. Environ. Microsc.* **1992**, *58*, 3538–3541.
155. Taguchi, V.Y.; Wang, D.T.; Jenkins, S.W.D.; Kleins, R.J.; Clement, R.E. *Can. J. Appl. Spectrosc.* **1992**, *37*, 145–148.
156. Karasek, F.W.; Clement, R.E.; *Basic Gas Chromatography-Mass Spectrometry: Principles and Techniques*; Elsevier: Amsterdam, 1988.
157. McLafferty, F.W;. *Interpretation of Mass Spectra*, 3rd ed.; University Science Books: Mill Valley, CA, 1980.
158. Brown, M.A.; Stephens, R.D.; Kim, S. *Trends Anal. Chem.* **1991**, *10*, 330–336.
159. Budde, W.L.; Behymer, T.D.; Bellar, T.A.; Ho, J.S. *J. Am. Water Works Assoc.* **1990**, *82(9)*, 60–65.
160. Niessen, W.M.A.; Tjaden, U.R.; Van Der Greef, J. *J. Chromatogr.* **1991**, *554*, 3–26.
161. Voyksner, R.D., *Proc. 7th Int. Congr. Pestic. Chem.*, Hamberg, Germany, 1990, pp 384–395.
162. Tinke, A.P.; Van Der Hoeven, R.A.M.; Niessen, W.M.A.; Tjaden, U.R.; Van Der Greef, J. *J. Chromatogr.* **1991**, *554*, 119–124.
163. Voyskner, R.D.; Smith, C.S.; Knox, P.C. *Biomed. Environ. Mass Spectrom.* **1990**, *19*, 523–534.
164. Bellar, T.A.; Behymer, T.D.; Budde, W.L. *J. Am. Soc. Mass Spectrom.* **1990**, *1*, 92–98.
165. Mattina, M.J.I. *J. Chromatogr.* **1991**, *549*, 237–245.
166. Ho, J.S.; Behymer, T.D.; Budde, W.L.; Bellar, T.A. *J. Am. Soc. Mass Spectrom.* **1992**, *3*, 662–671.
167. Apffel, A.; Perry, M.L. *J. Chromatogr.* **1991**, *554*, 103–118.
168. Northington, D.J.; Hovanec, B.M.; Shelton, M. *Am. Environ. Lab.*, **1990**, October, 34–41.
169. Schröder, H.Fr. *J. Chromatogr.* **1991**, *554*, 251–266.
170. Banks, J.F.; Shen, S.; Whitehouse, C.M. Extending the range of ESI/LC/MS applications using a new electrospray ion source, in *Proc. 41st ASMS Conf. Mass Spectrometry and Allied Topics*; San Francisco, 1993.
171. Doerge, D.R.; Bajic, S. *Rapid Commun. Mass Spectrom.* **1992**, *6*, 663–666.
172. Miles, C.J.; Doerge, D.R.; Bajic, S. *Arch. Environ. Contam. Toxicol.* **1992**, *22*, 247–251.
173. Behymer, T.D.; Bellar, T.A.; Budde, W.L. *Anal. Chem.* **1990**, *62*, 1686–1690.
174. Clark, L.B.; Rosen, R.T.; Hartman, T.G.; Louis, J.B; Rosen, J.D. *Int. J. Environ. Anal. Chem.* **1991**, *45*, 169–178.
175. Clark, L.B.; Rosen, R.T.; Hartman, T.G.; Louis, J.B.; Suffet, I.H.; Lippincott, R.L.; Rosen, J.D. *Int. J. Environ. Anal. Chem.* **1992**, *47*, 167–180.
176. Mattina, M.J.I. *J. Chromatogr.* **1991**, *542*, 385–395.
177. United States Environmental Protection Agency; *Methods for the Determination of Organic Compounds in Drinking Water, Supplement II*, EPA-600/R-92/129, PB91-146027, National Technical Information Service: Springfield, VA, 1992.
178. United States Environmental Protection Agency; *Solvent Extractable Non-Volatile Compounds by High Performance Liquid Chromatography / Thermospray / Mass Spectrometry (HPLC / TSP / MS) or Ultraviolet (UV) Detection*, Draft Method 8321, National Technical Information Service: Springfield, VA, 1990.
179. Sherry, J.P. *Crit. Rev. Anal. Chem.* **1992**, *23*, 217–300.
180. Lawruk, T.S.; Lachman, C.E.; Jourdan, S.W.;

Fleeker, J.R.; Herzog, D.P.; Rubio, F.M. *J. Agric. Food Chem.* **1993**, *41*, 747–752.
181. Suijbert, L.; Kollar, G.; Ollos, G.; Ribari, L. *Bull. Environ. Contam. Toxicol.* **1993**, *51*, 349–355.
182. Mesley, R.J.; Pocklington, W.D.; Walker, R.F. *Analyst.* **1991**, *116*, 975–990.
183. Nadkarni, R.A. *Anal. Chem.* **1991**, *63*, 675A–682A.
184. Staats, G. *Fresenius' J. Anal. Chem.* **1993**, *345*, 739–743.
185. Porter, P.S.; Ward, R.C.; Bell, H.F. *Environ. Sci. Technol.* **1988**, *22*, 856–861.
186. Hornung, R.W.; Reed, L.D. *Appl. Occup. Environ. Hyg.* **1990**, *5*, 46–51.
187. Helsel, D.R. *Environ. Sci. Technol.* **1990**, *24*, 1766–1774.
188. Keith, L. Radian Corporation, Austin, TX, personal communication.
189. Griepink, B.; Maier, E.A.; Quevauviller, P.; Muntau, H. *Fresenius' J. Anal. Chem.* **1991**, *339*, 599–603.
190. Lodge, K.B. *Chemosphere.* **1989**, *18*, 933–940.
191. Maier, E.A. *Anal. Proc.* **1990**, *27*, 269–270.
192. Edgell, K.W.; Jenkins, E.L.; Lopez-Avila, V.; Longbottom, J.E. *J. Assoc. Off. Anal. Chem.* **1991**, *74*, 295–309.
193. Lopez-Avila, V.; Wesselman, R.; Edgell, K. *J. Assoc. Off. Anal. Chem.* **1990**, *73*, 276–286.
194. Dinelli, G.; Vicari, A.; Catizone, P. *J. Agric. Food Chem.* **1993**, *41*, 742–746.
195. Ehntholt, D.J.; Thrun, K.; Eppig, C. *Int. J. Environ. Anal. Chem.* **1983**, *12*, 219–235.
196. Gere, D.R.; Knipe, C.R.; Castelli, P.; Hedrick, J.; Randall Frank, L.G.; Schulenberg-Schell, H.; Orolin, J.; Lee, H.B. *J. Chromatogr. Sci.* **1993**, *31*, 246–258.
197. Hites, R.A.; Budde, W.L. *Environ. Sci. Technol.* **1991**, *25*, 999–1006.
198. Barceló, D.; Durand, G.; Bouvot, V.; Nielen, M. *Environ. Sci. Technol.* **1993**, *27*, 271–277.
199. Schmidt, L.; Sun, J.J.; Fritz, J.S.; Hagen, D.F.; Markell, C.G.; Wisted, E.E. *J. Chromatogr.* **1993**, *641*, 57–61.