National Human Exposure Assessment Survey (NHEXAS)

Arizona Study

Quality Systems and Implementation Plan for Human Exposure Assessment

The University of Arizona
Tucson, Arizona 85721

Cooperative Agreement CR 821560

Standard Operating Procedure **EPA-Compendium**

Title: Compendium of Methods for Analysis of Metals, VOCs, and Pesticides in Water

Source: The University of Arizona

U.S. Environmental Protection Agency
Office of Research and Development
Human Exposure & Atmospheric Sciences Division
Human Exposure Research Branch

Notice: *The U.S. Environmental Protection Agency (EPA), through its Office of Research and Development (ORD), partially funded and collaborated in the research described here. This protocol is part of the Quality Systems Implementation Plan (QSIP) that was reviewed by the EPA and approved for use in this demonstration/scoping study. Mention of trade names or commercial products does not constitute endorsement or recommendation by EPA for use.*

COMPENDIUM OF METHODS FOR ANALYSIS OF METALS AND VOCs IN WATER

TABLE OF CONTENTS

METHOD 524.2. MEASUREMENT OF PURGEABLE ORGANIC COMPOUNDS IN WATER BY CAPILLARY COLUMN GAS CHROMATOGRAPHY/MASS SPECTROMETRY

Revision 4.0

August 1992

A. Alford-Stevens, J. W. Eichelberger, and W. L. Budde
Method 524, Revision 1.0 (1983)

R. W. Slater, Jr.
Revision 2.0 (1986)

J. W. Eichelberger, and W. L. Budde
Revision 3.0 (1989)

J. W. Eichelberger, J. W. Munch, and T. A.Bellar
Revision 4.0 (1992)

ENVIRONMENTAL MONITORING SYSTEMS LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
U.S. ENVIRONMENTAL PROTECTION AGENCY
CINCINNATI, OHIO 45268

METHOD 524.2

MEASUREMENT OF PURGEABLE ORGANIC COMPOUNDS IN WATER BY CAPILLARY COLUMN GAS CHROMATOGRAPHY/MASS SPECTROMETRY

1. SCOPE AND APPLICATION

1.1 This is a general purpose method for the identification and simultaneous measurement of purgeable volatile organic compounds in surface water, ground water, and drinking water in any stage of treatment (1,2). The method is applicable to a wide range of organic compounds, including the four trihalomethane disinfection by-products, that have sufficiently high volatility and low water solubility to be removed from water samples with purge and trap procedures. The following compounds can be determined by this method.

Compound	Chemical Abstract Service Registry Number
Acetone*	67-64-1
Acrylonitrile*	107-13-1
Allyl chloride*	107-05-1
Benzene	71-43-2
Bromobenzene	108-86-1
Bromochloromethane	74-97-5
Bromodichloromethane	75-27-4
Bromoform	75-25-2
Bromomethane	74-83-9
2-Butanone*	78-93-3
n-Butylbenzene	104-51-8
sec-Butylbenzene	135-98-8
tert-Butylbenzene	98-06-6
Carbon disulfide*	75-15-0
Carbon tetrachloride	56-23-5
Chloroacetonitrile*	107-14-2
Chlorobenzene	108-90-7
1-Chlorobutane*	109-69-3
Chloroethane	75-00-3
Chloroform	67-66-3
Chloromethane	74-87-3
2-Chlorotoluene	95-49-8
4-Chlorotoluene	106-43-4
Dibromochloromethane	124-48-1
1,2-Dibromo-3-chloropropane	96-12-8
1,2-Dibromoethane	106-93-4
Dibromomethane	74-95-3
1,2-Dichlorobenzene	95-50-1
1,3-Dichlorobenzene	541-73-1
1,4-Dichlorobenzene	106-46-7
trans-1,4-Dichloro-2-butene*	110-57-6
Dichlorodifluoromethane	75-71-8

1,1-Dichloroethane	75-34-3
1,2-Dichloroethane	107-06-2
1,1-Dichloroethene	75-35-4
cis-1,2-Dichloroethene	156-59-4
trans-1,2-Dichloroethene	156-60-5
1,2-Dichloropropane	78-87-5
1,3-Dichloropropane	142-28-9
2,2-Dichloropropane	590-20-7
1,1-Dichloropropene	563-58-6
1,1-Dichloropropanone*	513-88-2
cis-1,3-Dichloropropene	10061-01-5
trans-1,3-Dichloropropene	10061-02-6
Diethyl ether*	60-29-7
Ethylbenzene	100-41-4
Ethyl methacrylate*	97-63-2
Hexachlorobutadiene	87-68-3
Hexachloroethane*	67-72-1
2-Hexanone*	591-78-6
Isopropylbenzene	98-82-8
4-Isopropyltoluene	99-87-6
Methacrylonitrile*	126-98-7
Methylacrylate*	96-33-3
Methylene chloride	75-09-2
Methyl iodide*	74-88-4
Methylmethacrylate*	80-62-6
4-Methyl-2-pentanone*	108-10-1
Methyl-t-butyl ether*	1634-04-4
Naphthalene	91-20-3
Nitrobenzene*	98-95-3
2-Nitropropane*	79-46-9
Pentachloroethane*	76-01-7
Propionitrile*	107-12-0
n-Propylbenzene	103-65-1
Styrene	100-42-5
1,1,1,2-Tetrachloroethane	630-20-6
1,1,2,2-Tetrachloroethane	79-34-5
Tetrachloroethene	127-18-4
Tetrahydrofuran*	109-99-9
Toluene	108-88-3
1,2,3-Trichlorobenzene	87-61-6
1,2,4-Trichlorobenzene	120-82-1
1,1,1-Trichloroethane	71-55-6
1,1,2-Trichloroethane	79-00-5
Trichloroethene	79-01-6
Trichlorofluoromethane	75-69-4
1,2,3-Trichloropropane	96-18-4
1,2,4-Trimethylbenzene	95-63-6
1,3,5-Trimethylbenzene	108-67-8
Vinyl chloride	75-01-4
o-Xylene	95-47-6
m-Xylene	108-38-3
p-Xylene	106-42-3

* New Compound in Revision 4.0

1.2 Method detection limits (MDLs) (3) are compound, instrument and especially matrix dependent and vary from approximately 0.02 to 1.6 µg/L. The applicable concentration range of this method is primarily column and matrix dependent, and is approximately 0.02 to 200 µg/L when a wide-bore thick-film capillary column is used. Narrow-bore thin-film columns may have a capacity which limits the range to about 0.02 to 20 µg/L. Volatile water soluble, polar compounds which have relatively low purging efficiencies can be determined using this method. Such compounds may be more susceptible to matrix effects, and the quality of the data may be adversely influenced.

1.3 Analytes that are not separated chromatographically, but which have different mass spectra and noninterfering quantitation ions (Table 1), can be identified and measured in the same calibration mixture or water sample as long as their concentrations are somewhat similar (Sect. 11.6.2). Analytes that have very similar mass spectra cannot be individually identified and measured in the same calibration mixture or water sample unless they have different retention times (Sect. 11.6.3). Coeluting compounds with very similar mass spectra, typically many structural isomers, must be reported as an isomeric group or pair. Two of the three isomeric xylenes and two of the three dichlorobenzenes are examples of structural isomers that may not be resolved on the capillary column, and if not, must be reported as isomeric pairs. The more water soluble compounds (> 2% solubility) and compounds with boiling points above 200°C are purged from the water matrix with lower efficiencies. These analytes may be more susceptible to matrix effects.

2. SUMMARY OF METHOD

2.1 Volatile organic compounds and surrogates with low water solubility are extracted (purged) from the sample matrix by bubbling an inert gas through the aqueous sample. Purged sample components are trapped in a tube containing suitable sorbent materials. When purging is complete, the sorbent tube is heated and backflushed with helium to desorb the trapped sample components into a capillary gas chromatography (GC) column interfaced to a mass spectrometer (MS). The column is temperature programmed to facilitate the separation of the method analytes which are then detected with the MS. Compounds eluting from the GC column are identified by comparing their measured mass spectra and retention times to reference spectra and retention times in a data base. Reference spectra and retention times for analytes are obtained by the measurement of calibration standards under the same conditions used for samples. The concentration of each identified component is measured by relating the MS response of the quantitation ion produced by that compound to the MS response of the quantitation ion produced by a compound that is used as an internal standard. Surrogate analytes, whose concentrations are known in every sample, are measured with the same internal standard calibration procedure.

3. DEFINITIONS

3.1 INTERNAL STANDARD (IS) -- A pure analyte(s) added to a sample, extract, or standard solution in known amount(s) and used to measure

the relative responses of other method analytes and surrogates that are components of the same sample or solution. The internal standard must be an analyte that is not a sample component.

3.2 SURROGATE ANALYTE (SA) -- A pure analyte(s), which is extremely unlikely to be found in any sample, and which is added to a sample aliquot in known amount(s) before extraction or other processing and is measured with the same procedures used to measure other sample components. The purpose of the SA is to monitor method performance with each sample.

3.3 LABORATORY DUPLICATES (LD1 and LD2) -- Two aliquots of the same sample taken in the laboratory and analyzed separately with identical procedures. Analyses of LD1 and LD2 indicates precision associated with laboratory procedures, but not with sample collection, preservation, or storage procedures.

3.4 FIELD DUPLICATES (FD1 and FD2) -- Two separate samples collected at the same time and place under identical circumstances and treated exactly the same throughout field and laboratory procedures. Analyses of FD1 and FD2 give a measure of the precision associated with sample collection, preservation and storage, as well as with laboratory procedures.

3.5 LABORATORY REAGENT BLANK (LRB) -- An aliquot of reagent water or other blank matrix that is treated exactly as a sample including exposure to all glassware, equipment, solvents, reagents, internal standards, and surrogates that are used with other samples. The LRB is used to determine if method analytes or other interferences are present in the laboratory environment, the reagents, or the apparatus.

3.6 FIELD REAGENT BLANK (FRB) -- An aliquot of reagent water or other blank matrix that is placed in a sample container in the laboratory and treated as a sample in all respects, including shipment to the sampling site, exposure to sampling site conditions, storage, preservation, and all analytical procedures. The purpose of the FRB is to determine if method analytes or other interferences are present in the field environment.

3.7 LABORATORY PERFORMANCE CHECK SOLUTION (LPC) -- A solution of one or more compounds (analytes, surrogates, internal standard, or other test compounds) used to evaluate the performance of the instrument system with respect to a defined set of method criteria.

3.8 LABORATORY FORTIFIED BLANK (LFB) -- An aliquot of reagent water or other blank matrix to which known quantities of the method analytes are added in the laboratory. The LFB is analyzed exactly like a sample, and its purpose is to determine whether the methodology is in control, and whether the laboratory is capable of making accurate and precise measurements.

3.9 LABORATORY FORTIFIED SAMPLE MATRIX (LFM) -- An aliquot of an environmental sample to which known quantities of the method analytes are

added in the laboratory. The LFM is analyzed exactly like a sample, and its purpose is to determine whether the sample matrix contributes bias to the analytical results. The background concentrations of the analytes in the sample matrix must be determined in a separate aliquot and the measured values in the LFM corrected for background concentrations.

3.10 STOCK STANDARD SOLUTION (SSS) -- A concentrated solution containing one or more method analytes prepared in the laboratory using assayed reference materials or purchased from a reputable commercial source.

3.11 PRIMARY DILUTION STANDARD SOLUTION (PDS) -- A solution of several analytes prepared in the laboratory from stock standard solutions and diluted as needed to prepare calibration solutions and other needed analyte solutions.

3.12 CALIBRATION STANDARD (CAL) -- A solution prepared from the primary dilution standard solution or stock standard solutions and the internal standards and surrogate analytes. The CAL solutions are used to calibrate the instrument response with respect to analyte concentration.

3.13 QUALITY CONTROL SAMPLE (QCS) -- A solution of method analytes of known concentrations which is used to fortify an aliquot of LRB or sample matrix. The QCS is obtained from a source external to the laboratory and different from the source of calibration standards. It is used to check laboratory performance with externally prepared test materials.

4. INTERFERENCES

4.1 During analysis, major contaminant sources are volatile materials in the laboratory and impurities in the inert purging gas and in the sorbent trap. The use of Teflon tubing, Teflon thread sealants, or flow controllers with rubber components in the purging device should be avoided since such materials out-gas organic compounds which will be concentrated in the trap during the purge operation. Analyses of laboratory reagent blanks provide information about the presence of contaminants. When potential interfering peaks are noted in laboratory reagent blanks, the analyst should change the purge gas source and regenerate the molecular sieve purge gas filter. Subtracting blank values from sample results is not permitted.

4.2 Interfering contamination may occur when a sample containing low concentrations of volatile organic compounds is analyzed immediately after a sample containing relatively high concentrations of volatile organic compounds. A preventive technique is between-sample rinsing of the purging apparatus and sample syringes with two portions of reagent water. After analysis of a sample containing high concentrations of volatile organic compounds, one or more laboratory reagent blanks should be analyzed to check for cross-contamination.

4.3 Special precautions must be taken to determine methylene chloride. The analytical and sample storage area should be isolated from all

atmospheric sources of methylene chloride, otherwise random background levels will result. Since methylene chloride will permeate Teflon tubing, all GC carrier gas lines and purge gas plumbing should be constructed of stainless steel or copper tubing. Laboratory worker's clothing should be cleaned frequently since clothing previously exposed to methylene chloride fumes during common liquid/liquid extraction procedures can contribute to sample contamination.

4.4 Traces of ketones, methylene chloride, and some other organic solvents can be present even in the highest purity methanol. This is another potential source of contamination, and should be assessed before standards are prepared in the methanol.

5. SAFETY

5.1 The toxicity or carcinogenicity of chemicals used in this method has not been precisely defined; each chemical should be treated as a potential health hazard, and exposure to these chemicals should be minimized. Each laboratory is responsible for maintaining awareness of OSHA regulations regarding safe handling of chemicals used in this method. Additional references to laboratory safety are available (4-6) for the information of the analyst.

5.2 The following method analytes have been tentatively classified as known or suspected human or mammalian carcinogens: benzene, carbon tetrachloride, 1,4-dichlorobenzene, 1,2-dichlorethane, hexachlorobutadiene, 1,1,2,2-tetrachloroethane, 1,1,2-trichloroethane, chloroform, 1,2-dibromoethane,tetrachloroethene, trichloroethene, and vinyl chloride. Pure standard materials and stock standard solutions of these compounds should be handled in a hood. A NIOSH/MESA approved toxic gas respirator should be worn when the analyst handles high concentrations of these toxic compounds.

6. EQUIPMENT AND SUPPLIES

6.1 SAMPLE CONTAINERS -- 40-mL to 120-mL screw cap vials each equipped with a Teflon faced silicone septum. Prior to use, wash vials and septa with detergent and rinse with tap and distilled water. Allow the vials and septa to air dry at room temperature, place in a 105°C oven for 1 hr, then remove and allow to cool in an area known to be free of organics.

6.2 PURGE AND TRAP SYSTEM -- The purge and trap system consists of three separate pieces of equipment: purging device, trap, and desorber. Systems are commercially available from several sources that meet all of the following specifications.

6.2.1 The all glass purging device (Figure 1) should be designed to accept 25-mL samples with a water column at least 5 cm deep. A smaller (5-mL) purging device is recommended if the GC/MS system has adequate sensitivity to obtain the method detection limits required. Gaseous volumes above the sample must be kept to a minimum (< 15 mL) to eliminate dead volume

effects. A glass frit should be installed at the base of the sample chamber so the purge gas passes through the water column as finely divided bubbles with a diameter of < 3 mm at the origin. Needle spargers may be used, however, the purge gas must be introduced at a point about 5 mm from the base of the water column. The use of a moisture control device is recommended to prohibit much of the trapped water vapor from entering the GC/MS and eventually causing instrumental problems.

6.2.2 The trap (Figure 2) must be at least 25 cm long and have an inside diameter of at least 0.105 in. Starting from the inlet, the trap should contain 1.0 cm of methyl silicone coated packing and the following amounts of adsorbents: 1/3 of 2,6-diphenylene oxide polymer, 1/3 of silica gel, and 1/3 of coconut charcoal. If it is not necessary to determine dichlorodifluoromethane, the charcoal can be eliminated and the polymer increased to fill 2/3 of the trap. Before initial use, the trap should be conditioned overnight at 180°C by backflushing with an inert gas flow of at least 20 mL/min. Vent the trap effluent to the room, not to the analytical column. Prior to daily use, the trap should be conditioned for 10 min at 180°C with backflushing. The trap may be vented to the analytical column during daily conditioning; however, the column must be run through the temperature program prior to analysis of samples. The use of alternative sorbents is acceptable, depending on the particular set of target analytes or other problems encountered, but the new trap packing must meet all quality control criteria described in Sect. 9.

6.2.3 The use of the methyl silicone coated packing is recommended, but not mandatory. The packing serves a dual purpose of protecting the Tenax adsorbant from aerosols, and also of insuring that the Tenax is fully enclosed within the heated zone of the trap thus eliminating potential cold spots. Alternatively, silanized glass wool may be used as a spacer at the trap inlet.

6.2.4 The desorber (Figure 2) must be capable of rapidly heating the trap to 180°C either prior to or at the beginning of the flow of desorption gas. The polymer section of the trap should not be heated higher than 200°C or the life expectancy of the trap will decrease. Trap failure is characterized by a pressure drop in excess of 3 lb/in^2 across the trap during purging or by poor bromoform sensitivities. The desorber design illustrated in Fig. 2 meets these criteria.

6.3 GAS CHROMATOGRAPHY/MASS SPECTROMETER/DATA SYSTEM (GC/MS/DS)

6.3.1 The GC must be capable of temperature programming and should be equipped with variable-constant differential flow controllers so that the column flow rate will remain constant throughout desorption and temperature program operation. If the column oven is to be cooled to 10°C or lower, a subambient oven controller will likely be required. If syringe

injections of 4-bromofluorobenzene (BFB) will be used, a split/splitless injection port is required.

6.3.2 Capillary GC Columns. Any gas chromatography column that meets the performance specifications of this method may be used (Sect. 10.2.4.1). Separations of the calibration mixture must be equivalent or better than those described in this method. Four useful columns have been evaluated, and observed compound retention times for these columns are listed in Table 2.

6.3.2.1 Column 1 -- 60 m x 0.75 mm ID VOCOL (Supelco, Inc.) glass wide-bore capillary with a 1.5 μm film thickness.

Column 2 -- 30 m x 0.53 mm ID DB-624 (J&W Scientific, Inc.) fused silica capillary with a 3 μm film thickness.

Column 3 -- 30 m x 0.32 mm ID DB-5 (J&W Scientific, Inc.) fused silica capillary with a 1 μm film thickness.

Column 4 -- 75 m x 0.53 mm id DB-624 (J&W Scientific, Inc.) fused silica capillary with a 3 μm film thickness.

6.3.3 Interfaces between the GC and MS. The interface used depends on the column selected and the gas flow rate.

6.3.3.1 The wide-bore columns 1, 2, and 4 have the capacity to accept the standard gas flows from the trap during thermal desorption, and chromatography can begin with the onset of thermal desorption. Depending on the pumping capacity of the MS, an additional interface between the end of the column and the MS may be required. An open split interface (7) or an all-glass jet separator is an acceptable interface. Any interface can be used if the performance specifications described in this method (Sect. 9 and 10) can be achieved. The end of the transfer line after the interface, or the end of the analytical column if no interface is used, should be placed within a few mm of the MS ion source.

6.3.3.2 When narrow bore column 3 is used, a cryogenic interface placed just in front of the column inlet is suggested. This interface condenses the desorbed sample components in a narrow band on an uncoated fused silica precolumn using liquid nitrogen cooling. When all analytes have been desorbed from the trap, the interface is rapidly heated to transfer them to the analytical column. The end of the analytical column should be placed within a few mm of the MS ion source. A potential problem with this interface is blockage of the interface by frozen

water from the trap. This condition will result in a major loss in sensitivity and chromatographic resolution.

6.3.4 The mass spectrometer must be capable of electron ionization at a nominal electron energy of 70 eV. The spectrometer must be capable of scanning from 35 to 260 amu with a complete scan cycle time (including scan overhead) of 2 sec or less. (Scan cycle time = Total MS data acquisition time in seconds divided by number of scans in the chromatogram.) The spectrometer must produce a mass spectrum that meets all criteria in Table 3 when 25 ng or less of 4-bromofluorobenzene (BFB) is introduced into the GC. An average spectrum across the BFB GC peak may be used to test instrument performance.

6.3.5 An interfaced data system is required to acquire, store, reduce, and output mass spectral data. The computer software should have the capability of processing stored GC/MS data by recognizing a GC peak within any given retention time window, comparing the mass spectra from the GC peak with spectral data in a user-created data base, and generating a list of tentatively identified compounds with their retention times and scan numbers. The software must allow integration of the ion abundance of any specific ion between specified time or scan number limits. The software should also allow calculation of response factors as defined in Sect. 10.2.6 (or construction of a linear or second order regression calibration curve), calculation of response factor statistics (mean and standard deviation), and calculation of concentrations of analytes using either the calibration curve or the equation in Sect. 12.

6.4 SYRINGE AND SYRINGE VALVES

6.4.1 Two 5-mL or 25-mL glass hypodermic syringes with Luer-Lok tip (depending on sample volume used).

6.4.2 Three 2-way syringe valves with Luer ends.

6.4.3 Micro syringes - 10, 100 µL.

6.4.4 Syringes - 0.5, 1.0, and 5-mL, gas tight with shut-off valve.

6.5 MISCELLANEOUS

6.5.1 Standard solution storage containers -- 15-mL bottles with Teflon lined screw caps.

7. REAGENTS AND STANDARDS

7.1 TRAP PACKING MATERIALS

7.1.1 2,6-Diphenylene oxide polymer, 60/80 mesh, chromatographic grade (Tenax GC or equivalent).

7.1.2 Methyl silicone packing (optional) -- OV-1 (3%) on Chromosorb W, 60/80 mesh, or equivalent.

7.1.3 Silica gel -- 35/60 mesh, Davison, grade 15 or equivalent.

7.1.4 Coconut charcoal -- Prepare from Barnebey Cheney, CA-580-26 lot #M-2649 by crushing through 26 mesh screen.

7.2 REAGENTS

7.2.1 Methanol -- Demonstrated to be free of analytes.

7.2.2 Reagent water -- Prepare reagent water by passing tap water through a filter bed containing about 0.5 kg of activated carbon, by using a water purification system, or by boiling distilled water for 15 min followed by a 1-h purge with inert gas while the water temperature is held at 90°C. Store in clean, narrow-mouth bottles with Teflon lined septa and screw caps.

7.2.3 Hydrochloric acid (1+1) -- Carefully add measured volume of conc. HCl to equal volume of reagent water.

7.2.4 Vinyl chloride -- Certified mixtures of vinyl chloride in nitrogen and pure vinyl chloride are available from several sources (for example, Matheson, Ideal Gas Products, and Scott Gases).

7.2.5 Ascorbic acid -- ACS reagent grade, granular.

7.2.6 Sodium thiosulfate -- ACS reagent grade, granular.

7.3 STOCK STANDARD SOLUTIONS -- These solutions may be purchased as certified solutions or prepared from pure standard materials using the following procedures. One of these solutions is required for every analyte of concern, every surrogate, and the internal standard. A useful working concentration is about 1-5 mg/mL.

7.3.1 Place about 9.8 mL of methanol into a 10-mL ground-glass stoppered volumetric flask. Allow the flask to stand, unstoppered, for about 10 min or until all alcohol-wetted surfaces have dried and weigh to the nearest 0.1 mg.

7.3.2 If the analyte is a liquid at room temperature, use a 100-µL syringe and immediately add two or more drops of reference standard to the flask. Be sure that the reference standard falls directly into the alcohol without contacting the neck of the flask. If the analyte is a gas at room temperature, fill a 5-mL valved gas-tight syringe with the standard to the 5.0-mL mark, lower the needle to 5 mm above the methanol meniscus, and slowly inject the standard into the neck area of the flask. The gas will rapidly dissolve in the methanol.

7.3.3 Reweigh, dilute to volume, stopper, then mix by inverting the flask several times. Calculate the concentration in µg/µL from the net gain in weight. When compound purity is certified at 96% or greater, the weight can be used without correction to calculate the concentration of the stock standard.

7.3.4 Store stock standard solutions in 15-mL bottles equipped with Teflon lined screw caps. Methanol solutions of acrylonitrile, methyl iodide, and methyl acrylate are stable for only one week at 4°C. Methanol solutions prepared from other liquid analytes are stable for at least 4 weeks when stored at 4°C. Methanol solutions prepared from gaseous analytes are not stable for more than 1 week when stored at < 0°C; at room temperature, they must be discarded after 1 day.

7.4 PRIMARY DILUTION STANDARDS -- Use stock standard solutions to prepare primary dilution standard solutions that contain all the analytes of concern in methanol or other suitable solvent. The primary dilution standards should be prepared at concentrations that can be easily diluted to prepare aqueous calibration solutions that will bracket the working concentration range. Store the primary dilution standard solutions with minimal headspace and check frequently for signs of deterioration or evaporation, especially just before preparing calibration solutions. Storage times described for stock standard solutions in Sect. 7.3.4 also apply to primary dilution standard solutions.

7.5 FORTIFICATION SOLUTIONS FOR INTERNAL STANDARD AND SURROGATES

7.5.1 A solution containing the internal standard and the surrogate compounds is required to prepare laboratory reagent blanks (also used as a laboratory performance check solution), and to fortify each sample. Prepare a fortification solution containing fluorobenzene (internal standard), 1,2- dichlorobenzene-d_4 (surrogate), and BFB (surrogate) in methanol at concentrations of 5 µg/mL of each (any appropriate concentration is acceptable). A 5-µL aliquot of this solution added to a 25-mL water sample volume gives concentrations of 1 µg/L of each. A 5-µL aliquot of this solution added to a 5-mL water sample volume gives a concentration of 5 µg/L of each. Additional internal standards and surrogate analytes are optional. Additional surrogate compounds should be similar in physical and chemical characteristics to the analytes of concern.

7.6 PREPARATION OF LABORATORY REAGENT BLANK (LRB) -- Fill a 25-mL (or 5-mL) syringe with reagent water and adjust to the mark (no air bubbles). Inject an appropriate volume of the fortification solution containing the internal standard and surrogates through the Luer Lok valve into the reagent water. Transfer the LRB to the purging device. See Sect. 11.1.2.

7.7 PREPARATION OF LABORATORY FORTIFIED BLANK -- Prepare this exactly like a calibration standard (Sect. 7.8). This is a calibration standard that is treated as a sample.

7.8 PREPARATION OF CALIBRATION STANDARDS

7.8.1 The number of calibration solutions (CALs) needed depends on the calibration range desired. A minimum of three CAL solutions is required to calibrate a range of a factor of 20 in concentration. For a factor of 50, use at least four standards, and for a factor of 100 at least five standards. One calibration standard should contain each analyte of concern at a concentration of 2-10 times the method detection limit (Tables 4, 5, and 7) for that compound. The other CAL standards should contain each analyte of concern at concentrations that define the range of the method. Every CAL solution contains the internal standard and the surrogate compounds at the same concentration (5 µg/L suggested for a 5-mL sample; 1 µg/L for a 25-mL sample).

7.8.2 To prepare a calibration standard, add an appropriate volume of a primary dilution standard containing all analytes of concern to an aliquot of acidified (pH 2) reagent water in a volumetric flask. Also add an appropriate volume of internal standard and surrogate compound solution from Sect. 7.5.1. Use a microsyringe and rapidly inject the methanol solutions into the expanded area of the filled volumetric flask. Remove the needle as quickly as possible after injection. Mix by inverting the flask three times only. Discard the contents contained in the neck of the flask. Aqueous standards are not stable in a volumetric flask and should be discarded after 1 hr unless transferred to a sample bottle and sealed immediately.

8. SAMPLE COLLECTION, PRESERVATION, AND STORAGE

8.1 SAMPLE COLLECTION, DECHLORINATION, AND PRESERVATION

8.1.1 Collect all samples in duplicate. If samples, such as finished drinking water or waste water, are suspected to contain residual chlorine, add about 25 mg of ascorbic acid per 40 mL of sample to the sample bottle before filling. If the residual chlorine is likely to be present > 5 mg/L, a determination of the amount of the chlorine may be necessary. Diethyl-p-phenylenediamine (DPD) test kits are commercially available to determine residual chlorine in the field. Add an additional 25 mg of ascorbic acid per each 5 mg/L of residual chlorine. If compounds boiling below 25°C are not to be determined, sodium thiosulfate may be used to reduce the residual chlorine. Fill sample bottles to overflowing, but take care not to flush out the rapidly dissolving ascorbic acid. No air bubbles should pass through the sample as the bottle is filled, or be trapped in the sample when the bottle is sealed. Adjust the pH of the duplicate samples to

< 2 by carefully adding two drops of 1:1 HCl for each 40 mL of sample. Seal the sample bottles, Teflon face down, and shake vigorously for 1 min. Do not mix the ascorbic acid or sodium thiosulfate with the HCl prior to sampling.

8.1.2 When sampling from a water tap, open the tap and allow the system to flush until the water temperature has stabilized (usually about 10 min). Adjust the flow to about 500 mL/min and collect duplicate samples from the flowing stream.

8.1.3 When sampling from an open body of water, such as surface water, waste water, and possible leachate samples, partially fill a 1-quart wide-mouth bottle or 1-L beaker with sample from a representative area. Fill a 60 mL or a 120 mL sample vial with sample from the larger container, and adjust the pH of the sample to about 2 by adding 1+1 HCl dropwise while stirring. Check the pH with narrow range (1.4 to 2.8) pH paper. Record the number of drops of acid necessary to adjust the pH to 2. To collect actual samples, refill the large container with fresh sample and pour sample into sample vials. Follow filling instructions in Sect. 8.1.1. Add the appropriate number of drops of 1+1 HCl to each sample to adjust the pH to about 2. If samples are suspected to contain residual chlorine, add ascorbic acid or sodium thiosulfate according to Sect. 8.1.1.

8.1.4 The samples must be chilled to about 4°C when collected and maintained at that temperature until analysis. Field samples that will not be received at the laboratory on the day of collection must be packaged for shipment with sufficient ice to ensure that they will arrive at the laboratory with a substantial amount of ice remaining in the cooler.

8.1.5 If a sample foams vigorously when HCl is added, discard that sample. Collect a set of duplicate samples but do not acidify them. These samples must be flagged as "not acidified" and must be stored at 4°C or below. These samples must be analyzed within 24 hr of collection time.

8.2 SAMPLE STORAGE

8.2.1 Store samples at ≤ 4°C until analysis. The sample storage area must be free of organic solvent vapors and direct or intense light.

8.2.2 Analyze all samples within 14 days of collection. Samples not analyzed within this period must be discarded and replaced.

8.3 FIELD REAGENT BLANKS (FRB)

8.3.1 Duplicate FRBs must be handled along with each sample set, which is composed of the samples collected from the same

general sample site at approximately the same time. At the laboratory, fill field blank sample bottles with reagent water and sample preservatives, seal, and ship to the sampling site along with empty sample bottles and back to the laboratory with filled sample bottles. Wherever a set of samples is shipped and stored, it is accompanied by appropriate blanks. FRBs must remain hermetically sealed until analysis.

8.3.2 Use the same procedures used for samples to add ascorbic acid and HCl to blanks (Sect. 8.1.1). The same batch of ascorbic acid and HCl should be used for the field reagent blanks in the field.

9. QUALITY CONTROL

9.1 Quality control (QC) requirements are the initial demonstration of laboratory capability followed by regular analyses of laboratory reagent blanks, field reagent blanks, and laboratory fortified blanks. Each laboratory must maintain records to document the quality of the data generated. Additional quality control practices are recommended.

9.2 Initial demonstration of low system background. Before any samples are analyzed, it must be demonstrated that a laboratory reagent blank (LRB) is reasonably free of contamination that would prevent the determination of any analyte of concern. Sources of background contamination are glassware, purge gas, sorbents, and equipment. Background contamination must be reduced to an acceptable level before proceeding with the next section. In general, background from method analytes should be below the method detection limit.

9.3 Initial demonstration of laboratory accuracy and precision. Analyze five to seven replicates of a laboratory fortified blank containing each analyte of concern at a concentration in the range of 0.2-5 µg/L (see appropriate regulations and maximum contaminant levels for guidance on appropriate concentrations).

9.3.1 Prepare each replicate by adding an appropriate aliquot of a quality control sample to reagent water. If a quality control sample containing the method analytes is not available, a primary dilution standard made from a source of reagents different than those used to prepare the calibration standards may be used. Also add the appropriate amounts of internal standard and surrogate compounds. Analyze each replicate according to the procedures described in Sect. 11, and on a schedule that results in the analyses of all replicates over a period of several days.

9.3.2 Calculate the measured concentration of each analyte in each replicate, the mean concentration of each analyte in all replicates, and mean accuracy (as mean percentage of true

value) for each analyte, and the precision (as relative standard deviation, RSD) of the measurements for each analyte. Calculate the MDL of each analyte using the equation described in Sect. 13.2 (3).

9.3.3 For each analyte, the mean accuracy, expressed as a percentage of the true value, should be 80-120% and the RSD should be < 20%. Some analytes, particularly the early eluting gases and late eluting higher molecular weight compounds, are measured with less accuracy and precision than other analytes. The MDLs must be sufficient to detect analytes at the required levels according to the SDWA Regulations. If these criteria are not met for an analyte, take remedial action and repeat the measurements for that analyte to demonstrate acceptable performance before samples are analyzed.

9.3.4 Develop and maintain a system of control charts to plot the precision and accuracy of analyte and surrogate measurements as a function of time. Charting surrogate recoveries is an especially valuable activity because surrogates are present in every sample and the analytical results will form a significant record of data quality.

9.4 Monitor the integrated areas of the quantitation ions of the internal standards and surrogates (Table 1) in all samples, continuing calibration checks, and blanks. These should remain reasonably constant over time. An abrupt change may indicate a matrix effect or an instrument problem. If a cryogenic interface is utilized, it may indicate an inefficient transfer from the trap to the column. These samples must be reanalyzed or a laboratory fortified duplicate sample analyzed to test for matrix effect. A more gradual drift of more than 50% in any area is indicative of a loss in sensitivity, and the problem must be found and corrected.

9.5 LABORATORY REAGENT BLANKS (LRB) -- With each batch of samples processed as a group within a work shift, analyze a LRB to determine the background system contamination. A FRB (Sect. 9.7) may be used in place of a LRB.

9.6 With each batch of samples processed as a group within a work shift, analyze a single laboratory fortified blank (LFB) containing each analyte of concern at a concentration as determined in Sect. 9.3. If more than 20 samples are included in a batch, analyze one LFB for every 20 samples. Use the procedures described in Sect. 9.3.3 to evaluate the accuracy of the measurements, and to estimate whether the MDLs can be obtained. If acceptable accuracy and MDLs cannot be achieved, the problem must be located and corrected before further samples are analyzed. Add these results to the ongoing control charts to document data quality.

9.7 With each set of field samples a field reagent blank (FRB) should be analyzed. The results of these analyses will help define contamina-

tion resulting from field sampling and transportation activities. If the FRB shows unacceptable contamination, a LRB must be measured to define the source of the impurities.

9.8 At least quarterly, replicate LFBs should be analyzed to determine the precision of the laboratory measurements. Add these results to the ongoing control charts to document data quality.

9.9 At least quarterly, analyze a quality control sample (QCS) from an external source. If measured analyte concentrations are not of acceptable accuracy, check the entire analytical procedure to locate and correct the problem source.

9.10 Sample matrix effects have not been observed when this method is used with distilled water, reagent water, drinking water, or ground water. Therefore, analysis of a laboratory fortified sample matrix (LFM) is not required unless the criteria in Section 9.4 are not met. If matrix effects are observed or suspected to be causing low recoveries, analyze a laboratory fortified matrix sample for that matrix. The sample results should be flagged and the LFM results should be reported with them.

9.11 Numerous other quality control measures are incorporated into other parts of this procedure, and serve to alert the analyst to potential problems.

10. CALIBRATION AND STANDARDIZATION

10.1 Demonstration and documentation of acceptable initial calibration is required before any samples are analyzed and is required intermittently throughout sample analysis as dictated by results of continuing calibration checks. After initial calibration is successful, a continuing calibration check is required at the beginning of each 8 hr. period during which analyses are performed. Additional periodic calibration checks are good laboratory practice.

10.2 INITIAL CALIBRATION

10.2.1 Calibrate the mass and abundance scales of the MS with calibration compounds and procedures prescribed by the manufacturer with any modifications necessary to meet the requirements in Sect. 10.2.2.

10.2.2 Introduce into the GC (either by purging a laboratory reagent blank or making a syringe injection) 25 ng or less of BFB and acquire mass spectra for m/z 35-260 at 70 eV (nominal). Use the purging procedure and/or GC conditions given in Sect. 11. If the spectrum does not meet all criteria in Table 3, the MS must be retuned and adjusted to meet all criteria before proceeding with calibration. An average spectrum across the GC peak may be used to evaluate the performance of the system.

10.2.3 Purge a medium CAL solution, (e.g., 10-20 µg/L) using the procedure given in Sect. 11.

10.2.4 Performance criteria for the medium calibration. Examine the stored GC/MS data with the data system software. Figures 3 and 4 shown acceptable total ion chromatograms.

10.2.4.1 GC performance. Good column performance will produce symmetrical peaks with minimum tailing for most compounds. If peaks are unusually broad, or if peaks are running together with little vallies between them, the wrong column has been selected or remedial action is probably necessary (Sect.10.3.6).

10.2.4.2 MS sensitivity. The GC/MS/DS peak identification software should be able to recognize a GC peak in the appropriate retention time window for each of the compounds in calibration solution, and make correct tentative identifications. If fewer than 99% of the compounds are recognized, system maintenance is required. See Sect. 10.3.6.

10.2.5 If all performance criteria are met, purge an aliquot of each of the other CAL solutions using the same GC/MS conditions.

10.2.6 Calculate a response factor (RF) for each analyte and isomer pair for each CAL solution using the internal standard fluorobenzene. Table 1 contains suggested quantitation ions for all compounds. This calculation is supported in acceptable GC/MS data system software (Sect. 6.3.5), and many other software programs. RF is a unitless number, but units used to express quantities of analyte and internal standard must be equivalent.

$$RF = \frac{(A_x)(Q_{is})}{(A_{is})(Q_x)}$$

where: A_x = integrated abundance of the quantitation ion of the analyte.

A_{is} = integrated abundance of the quantitation ion of the internal standard.

Q_x = quantity of analyte purged in nanograms or concentration units.

Q_{is} = quantity of internal standard purged in ng or concentration units.

10.2.6.1 For each analyte and surrogate, calculate the mean RF from analyses of CAL solutions. Calculate the standard deviation (SD) and the relative standard deviation (RSD) from each mean: RSD = 100 (SD/M). If the RSD of any analyte or surrogate mean RF exceeds 20%, either analyze additional aliquots of appropriate CAL solutions to obtain an acceptable RSD of RFs over the entire concentration range, or

take action to improve GC/MS performance Sect. 10.3.6). Surrogate compounds are present at the same concentration on every sample, calibration standard, and all types of blanks.

10.2.7 As an alternative to calculating mean response factors and applying the RSD test, use the GC/MS data system software or other available software to generate a linear or second order regression calibration curve.

10.3 CONTINUING CALIBRATION CHECK -- Verify the MS tune and initial calibration at the beginning of each 8-hr work shift during which analyses are performed using the following procedure.

10.3.1 Introduce into the GC (either by purging a laboratory reagent blank or making a syringe injection) 25 ng or less of BFB and acquire a mass spectrum that includes data for m/z 35-260. If the spectrum does not meet all criteria (Table 3), the MS must be retuned and adjusted to meet all criteria before proceeding with the continuing calibration check.

10.3.2 Purge a medium concentration CAL solution and analyze with the same conditions used during the initial calibration.

10.3.3 Demonstrate acceptable performance for the criteria shown in Sect. 10.2.4.

10.3.4 Determine that the absolute areas of the quantitation ions of the internal standard and surrogates have not decreased by more than 30% from the areas measured in the most recent continuing calibration check, or by more than 50% from the areas measured during initial calibration. If these areas have decreased by more than these amounts, adjustments must be made to restore system sensitivity. These adjustments may require cleaning of the MS ion source, or other maintenance as indicated in Sect. 10.3.6, and recalibration. Control charts are useful aids in documenting system sensitivity changes.

10.3.5 Calculate the RF for each analyte of concern and surrogate compound from the data measured in the continuing calibration check. The RF for each analyte and surrogate must be within 30% of the mean value measured in the initial calibration. Alternatively, if a linear or second order regression is used, the concentration measured using the calibration curve must be within 30% of the true value of the concentration in the medium calibration solution. If these conditions do not exist, remedial action must be taken which may require re-calibration.

10.3.6 Some possible remedial actions. Major maintenance such as cleaning an ion source, cleaning quadrupole rods, etc. require returning to the initial calibration step.

10.3.6.1 Check and adjust GC and/or MS operating conditions; check the MS resolution, and calibrate the mass scale.

10.3.6.2 Clean or replace the splitless injection liner; silanize a new injection liner. This applies only if the injection liner is an integral part of the system.

10.3.6.3 Flush the GC column with solvent according to manufacturer's instructions.

10.3.6.4 Break off a short portion (about 1 meter) of the column from the end near the injector; or replace GC column. This action will cause a slight change in retention times. Analyst may need to redefine retention windows.

10.3.6.5 Prepare fresh CAL solutions, and repeat the initial calibration step.

10.3.6.6 Clean the MS ion source and rods (if a quadrupole).

10.3.6.7 Replace any components that allow analytes to come into contact with hot metal surfaces.

10.3.6.8 Replace the MS electron multiplier, or any other faulty components.

10.3.6.9 Replace the trap, especially when only a few compounds fail the criteria in Sect. 10.3.5 while the majority are determined successfully. Also check for gas leaks in the purge and trap unit as well as the rest of the analytical system.

10.4 Optional calibration for vinyl chloride using a certified gaseous mixture of vinyl chloride in nitrogen can be accomplished by the following steps.

10.4.1 Fill the purging device with 25.0 mL (or 5-mL) of reagent water or aqueous calibration standard.

10.4.2 Start to purge the aqueous mixture. Inject a known volume (between 100 and 2000 µL) of the calibration gas (at room temperature) directly into the purging device with a gas tight syringe. Slowly inject the gaseous sample through a septum seal at the top of the purging device at 2000 µL/min. If the injection of the standard is made through the aqueous

sample inlet port, flush the dead volume with several mL of room air or carrier gas. Inject the gaseous standard before 5 min of the 11-min purge time have elapsed.

10.4.3 Determine the aqueous equivalent concentration of vinyl chloride standard, in µg/L, injected with the equation:

$$S = 0.102\ (C)(V)$$

where S = Aqueous equivalent concentration of vinyl chloride standard in µg/L;
C = Concentration of gaseous standard in mg/L (v/v);
V = Volume of standard injected in mL.

11. PROCEDURE

11.1 SAMPLE INTRODUCTION AND PURGING

11.1.1 This method is designed for a 25-mL sample volume, but a smaller (5 mL) sample volume is recommended if the GC/MS system has adequate sensitivity to achieve the required method detection limits. Adjust the helium purge gas flow rate to 40 mL/min. Attach the trap inlet to the purging device and open the syringe valve on the purging device.

11.1.2 Remove the plungers from two 25-mL (or 5-mL depending on sample size) syringes and attach a closed syringe valve to each. Warm the sample to room temperature, open the sample bottle, and carefully pour the sample into one of the syringe barrels to just short of overflowing. Replace the syringe plunger, invert the syringe, and compress the sample. Open the syringe valve and vent any residual air while adjusting the sample volume to 25.0-mL (or 5-mL). To all samples, blanks, and calibration standards, add 5-µL (or an appropriate volume) of the fortification solution containing the internal standard and the surrogates to the sample through the syringe valve. Close the valve. Fill the second syringe in an identical manner from the same sample bottle. Reserve this second syringe for a reanalysis if necessary.

11.1.3 Attach the sample syringe valve to the syringe valve on the purging device. Be sure that the trap is cooler than 25°C, then open the sample syringe valve and inject the sample into the purging chamber. Close both valves and initiate purging. Purge the sample for 11.0 min at ambient temperature.

11.1.4 Standards and samples must be analyzed in exactly the same manner. Room temperature changes in excess of 10°F may adversely affect the accuracy and precision of the method.

11.2 SAMPLE DESORPTION

11.2.1 Non-cryogenic interface -- After the 11-min purge, place the purge and trap system in the desorb mode and preheat the trap to 180°C without a flow of desorption gas. Then simultaneously start the flow of desorption gas at a flow rate suitable for the column being used (optimum desorb flow rate is 15 mL/min) for about 4 min, begin the GC temperature program, and start data acquisition.

11.2.2 Cryogenic interface -- After the 11-min purge, place the purge and trap system in the desorb mode, make sure the cryogenic interface is a -150°C or lower, and rapidly heat the trap to 180°C while backflushing with an inert gas at 4 mL/min for about 5 min. At the end of the 5 min desorption cycle, rapidly heat the cryogenic trap to 250°C, and simultaneously begin the temperature program of the gas chromatograph, and start data acquisition.

11.2.3 While the trapped components are being introduced into the gas chromatograph (or cryogenic interface), empty the purging device using the sample syringe and wash the chamber with two 25-mL flushes of reagent water. After the purging device has been emptied, leave syringe valve open to allow the purge gas to vent through the sample introduction needle.

11.3 GAS CHROMATOGRAPHY/MASS SPECTROMETRY -- Acquire and store data over the nominal mass range 35-260 with a total cycle time (including scan overhead time) of 2 sec or less. If water, methanol, or carbon dioxide cause a background problem, start at 47 or 48 m/z. If ketones are to be determined, data must be acquired starting at m/z 43. Cycle time must be adjusted to measure five or more spectra during the elution of each GC peak. Suggested temperature programs are provided below. Alternative temperature programs can be used.

11.3.1 Single ramp linear temperature program for wide bore column 1 and 2 with a jet separator. Adjust the helium carrier gas flow rate to within the capacity of the separator, or about 15 mL/min. The column temperature is reduced 10°C and held for 5 min from the beginning of desorption, then programmed to 160°C at 6°C/min, and held until all components have eluted.

11.3.2 Multi-ramp temperature program for wide bore column 2 with the open split interface. Adjust the helium carrier gas flow rate to about 4.6 mL/min. The column temperature is reduced to 10°C and held for 6 min from the beginning of desorption, then heated to 70°C at 10°/min, heated to 120°C at 5°/min, heated to 180° at 8°/min, and held at 180° until all compounds have eluted.

11.3.3 Single ramp linear temperature program for narrow bore column 3 with a cryogenic interface. Adjust the helium carrier gas flow rate to about 4 mL/min. The column temperature is reduced to 10°C and held for 5 min from the beginning of vaporization from the cryogenic trap, programmed at 6°/min for 10 min, then 15°/min for 5 min to 145°C, and held until all components have eluted.

11.3.4 Multi-ramp temperature program for wide bore column 4 with the open split interface. Adjust the helium carrier gas flow rate to about 7.0 mL/min. The column temperature is - 10°C and held for 6 min. from beginning of desorption, then heated to 100°C at 10°C/min, heated to 200°C at 5°C/min and held at 200°C for 8 min or until all compounds of interest had eluted.

11.4 TRAP RECONDITIONING -- After desorbing the sample for 4 min, recondition the trap by returning the purge and trap system to the purge mode. Wait 15 sec, then close the syringe valve on the purging device to begin gas flow through the trap. Maintain the trap temperature at 180°C. Maintain the moisture control module, if utilized, at 90°C to remove residual water. After approximately 7 min, turn off the trap heater and open the syringe valve to stop the gas flow through the trap. When the trap is cool, the next sample can be analyzed.

11.5 TERMINATION OF DATA ACQUISITION -- When all the sample components have eluted from the GC, terminate MS data acquisition. Use appropriate data output software to display full range mass spectra and appropriate plots of ion abundance as a function of time. If any ion abundance exceeds the system working range, dilute the sample aliquot in the second syringe with reagent water and analyze the diluted aliquot.

11.6 IDENTIFICATION OF ANALYTES -- Identify a sample component by comparison of its mass spectrum (after background subtraction) to a reference spectrum in the user-created data base. The GC retention time of the sample component should be within three standard deviations of the mean retention time of the compound in the calibration mixture.

11.6.1 In general, all ions that are present above 10% relative abundance in the mass spectrum of the standard should be present in the mass spectrum of the sample component and should agree within absolute 20%. For example, if an ion has a relative abundance of 30% in the standard spectrum, its abundance in the sample spectrum should be in the range of 10 to 50%. Some ions, particularly the molecular ion, are of special importance, and should be evaluated even if they are below 10% relative abundance.

11.6.2 Identification requires expert judgment when sample components are not resolved chromatographically and produce mass spectra containing ions contributed by more than one analyte.

When GC peaks obviously represent more than one sample component (i.e., broadened peak with shoulder(s) or valley between two or more maxima), appropriate analyte spectra and background spectra can be selected by examining plots of characteristic ions for tentatively identified components. When analytes coelute (i.e., only one GC peak is apparent), the identification criteria can be met but each analyte spectrum will contain extraneous ions contributed by the coeluting compound. Because purgeable organic compounds are relatively small molecules and produce comparatively simple mass spectra, this is not a significant problem for most method analytes.

11.6.3 Structural isomers that produce very similar mass spectra can be explicitly identified only if they have sufficiently different GC retention times. Acceptable resolution is achieved if the height of the valley between two peaks is less than 25% of the average height of the two peaks. Otherwise, structural isomers are identified as isomeric pairs. Two of the three isomeric xylenes and two of the three dichlorobenzenes are examples of structural isomers that may not be resolved on the capillary columns. If unresolved, these groups of isomers must be reported as isomeric pairs.

11.6.4 Methylene chloride, acetone, carbon disulfide, and other background components appear in variable quantities in laboratory and field reagent blanks, and generally cannot be accurately measured. Subtraction of the concentration in the blank from the concentration in the sample is not acceptable because the concentration of the background in the blank is highly variable.

12. DATA ANALYSIS AND CALCULATIONS

12.1 Complete chromatographic resolution is not necessary for accurate and precise measurements of analyte concentrations if unique ions with adequate intensities are available for quantitation.

12.1.1 Calculate analyte and surrogate concentrations.

$$C_x = \frac{(A_x)(Q_{is})\ 1000}{(A_{is})\ RF\ V}$$

where:
- C_x = concentration of analyte or surrogate in µg/L in the water sample.
- A_x = integrated abundance of the quantitation ion of the analyte in the sample.
- A_{is} = integrated abundance of the quantitation ion of the internal standard in the sample.
- Q_{is} = total quantity (in micrograms) of internal standard added to the water sample.
- V = original water sample volume in mL.
- RF = mean response factor of analyte from the initial calibration.

12.1.2 Alternatively, use the GC/MS system software or other available proven software to compute the concentrations of the analytes and surrogates from the linear or second order regression curves.

12.1.3 Calculations should utilize all available digits of precision, but final reported concentrations should be rounded to an appropriate number of significant figures (one digit of uncertainty). Experience indicates that three significant figures may be used for concentrations above 99 µg/L, two significant figures for concentrations between 1- 99 µg/L, and one significant figure for lower concentrations.

12.1.4 Calculate the total trihalomethane concentration by summing the four individual trihalomethane concentrations.

13. METHOD PERFORMANCE

13.1 Single laboratory accuracy and precision data were obtained for the method analytes using laboratory fortified blanks with analytes at concentrations between 1 and 5 µg/L. Results were obtained using the four columns specified (Sect. 6.3.2.1) and the open split or jet separator (Sect. 6.3.3.1), or the cryogenic interface (Sect. 6.3.3.2). These data are shown in Tables 4-8.

13.2 With these data, method detection limits were calculated using the formula (3):

$$MDL = S\, t_{(n-1,1-alpha = 0.99)}$$

where:

$t_{(n-1,1-alpha = 0.99)}$ = Student's t value for the 99% confidence level with n-1 degrees of freedom,

n = number of replicates

S = the standard deviation of the replicate analyses.

14. POLLUTION PREVENTION

14.1 No solvents are utilized in this method except the extremely small volumes of methanol needed to make calibration standards. The only other chemicals used in this method are the neat materials in preparing standards and sample preservatives. All are used in extremely small amounts and pose no threat to the environment.

15. WASTE MANAGEMENT

15.1 There are no waste management issues involved with this method. Due to the nature of this method, the discarded samples are chemically less contaminated than when they were collected.

16. REFERENCES

1. A. Alford-Stevens, J.W. Eichelberger, W.L. Budde, "Purgeable Organic Compounds in Water by Gas Chromatography/Mass Spectrometry, Method 524." Environmental Monitoring and Support Laboratory, U.S. Environmental Protection Agency, Cincinnati, Ohio, February 1983.

2. C. Madding, "Volatile Organic Compounds in Water by Purge and Trap Capillary Column GC/MS," Proceedings of the Water Quality Technology Conference, American Water Works Association, Denver, CO, December 1984.

3. J.A. Glaser, D.L. Foerst, G.D. McKee, S.A. Quave, and W.L. Budde, "Trace Analyses for Wastewaters, "Environ. Sci. Technol., 15, 1426, 1981.

4. "Carcinogens-Working with Carcinogens," Department of Health, Education, and Welfare, Public Health Service, Center for Disease Control, National Institute for Occupational Safety and Health, Publication No. 77-206, August 1977.

5. "OSHA Safety and Health Standards, General Industry," (29CFR1910), Occupational Safety and Health Administration, OSHA 2206, (Revised, January 1976).

6. "Safety in Academic Chemistry Laboratories," American Chemical Society Publication, Committee on Chemical Safety, 3rd Edition, 1979.

7. R.F. Arrendale, R.F. Severson, and O.T. Chortyk, "Open Split Interface for Capillary Gas Chromatography/Mass Spectrometry," Anal. Chem. 1984, 56, 1533.

8. J.J. Flesch, P.S. Fair, "The Analysis of Cyanogen Chloride in Drinking Water," Proceedings of Water Quality Technology Conference, American Water Works Association, St. Louis, MO., November 14-16, 1988.

17. TABLES, DIAGRAMS, FLOWCHARTS, AND VALIDATION DATA

TABLE 1. MOLECULAR WEIGHTS AND QUANTITATION IONS FOR METHOD ANALYTES

Compound	MW[a]	Primary Quantitation Ion	Secondary Quantitation Ions
Internal standard			
Fluorobenzene	96	96	77
Surrogates			
4-Bromofluorobenzene	174	95	174,176
1,2-Dichlorobenzene-d4	150	152	115,150
Target Analytes			
Acetone	58	43	58
Acrylonitrile	53	52	53
Allyl chloride	76	76	49
Benzene	78	78	77
Bromobenzene	156	156	77,158
Bromochloromethane	128	128	49,130
Bromodichloromethane	162	83	85,127
Bromoform	250	173	175,252
Bromomethane	94	94	96
2-Butanone	72	43	57,72
n-Butylbenzene	134	91	134
sec-Butylbenzene	134	105	134
tert-Butylbenzene	134	119	91
Carbon disulfide	76	76	--
Carbon tetrachloride	152	117	119
Chloroacetonitrile	75	48	75
Chlorobenzene	112	112	77,114
1-Chlorobutane	92	56	49
Chloroethane	64	64	66
Chloroform	118	83	85
Chloromethane	50	50	52
2-Chlorotoluene	126	91	126
4-Chlorotoluene	126	91	126
Dibromochloromethane	206	129	127
1,2-Dibromo-3-Chloropropane	234	75	155,157
1,2-Dibromoethane	186	107	109,188
Dibromomethane	172	93	95,174
1,2-Dichlorobenzene	146	146	111,148
1,3-Dichlorobenzene	146	146	111,148
1,4-Dichlorobenzene	146	146	111,148

TABLE 1. (continued)

Compound	MW*	Primary Quantitation Ion	Secondary Quantitation Ions
trans-1,4-Dichloro-2-butene	124	53	88,75
Dichlorodifluoromethane	120	85	87
1,1-Dichloroethane	98	63	65,83
1,2-Dichloroethane	98	62	98
1,1-Dichloroethene	96	96	61,63
cis-1,2-Dichloroethene	96	96	61,98
trans-1,2-Dichloroethene	96	96	61,98
1,2-Dichloropropane	112	63	112
1,3-Dichloropropane	112	76	78
2,2-Dichloropropane	112	77	97
1,1-Dichloropropene	110	75	110,77
1,1-Dichloropropanone	126	43	83
cis-1,3-dichloropropene	110	75	110
trans-1,3-dichloropropene	110	75	110
Diethyl ether	74	59	45,73
Ethylbenzene	106	91	106
Ethyl methacrylate	114	69	99
Hexachlorobutadiene	258	225	260
Hexachloroethane	234	117	119,201
2-Hexanone	100	43	58
Isopropylbenzene	120	105	120
4-Isopropyltoluene	134	119	134,91
Methacrylonitrile	67	67	52
Methyl acrylate	86	55	85
Methylene chloride	84	84	86,49
Methyl iodide	142	142	127
Methylmethacrylate	100	69	99
4-Methyl-2-pentanone	100	43	58,85
Methyl-t-butyl ether	88	73	57
Naphthalene	128	128	--
Nitrobenzene	123	51	77
2-Nitropropane	89	46	--
Pentachloroethane	200	117	119,167
Propionitrile	55	54	--
n-Propylbenzene	120	91	120
Styrene	104	104	78
1,1,1,2-Tetrachloroethane	166	131	133,119
1,1,2,2-Tetrachloroethane	166	83	131,85
Tetrachloroethene	164	166	168,129
Tetrahydrofuran	72	71	72,42
Toluene	92	92	91
1,2,3-Trichlorobenzene	180	180	182
1,2,4-Trichlorobenzene	180	180	182
1,1,1-Trichloroethane	132	97	99,61
1,1,2-Trichloroethane	132	83	97,85

TABLE 1. (continued)

Compound	MW[a]	Primary Quantitation Ion	Secondary Quantitation Ions
Trichloroethene	130	95	130,132
Trichlorofluoromethane	136	101	103
1,2,3-Trichloropropane	146	75	77
1,2,4-Trimethylbenzene	120	105	120
1,3,5-Trimethylbenzene	120	105	120
Vinyl Chloride	62	62	64
o-Xylene	106	106	91
m-Xylene	106	106	91
p-Xylene	106	106	91

[a]Monoisotopic molecular weight calculated from the atomic masses of the isotopes with the smallest masses.

TABLE 2. CHROMATOGRAPHIC RETENTION TIMES FOR METHOD ANALYTES ON THREE COLUMNS WITH FOUR SETS OF CONDITIONS[a]

Compound	Retention Time (min:sec) Column 1[b]	Column 2[b]	Column 2[c]	Column 3[d]	Column 4[e]
Internal standard					
Fluorobenzene	8:49	6:27	14:06	8:03	22:00
Surrogates					
4-Bromofluorobenzene	18:38	15:43	23:38		31:21
1,2-Dichlorobenzene-d4	22:16	19:08	27:25		35:51
Target Analytes					
Acetone					16:14
Acrylonitrile					17:49
Allyl chloride					16:58
Benzene	8:14	5:40	13:30	7:25	21:32
Bromobenzene	18:57	15:52	24:00	16:25	31:52
Bromochloromethane	6:44	4:23	12:22	5:38	20:20
Bromodichloromethane	10:35	8:29	15:48	9:20	23:36
Bromoform	17:56	14:53	22:46	15:42	30:32
Bromomethane	2:01	0:58	4:48	1:17	12:26
2-Butanone					19:41
n-Butylbenzene	22:13	19:29	27:32	17:57	35:41
sec-Butylbenzene	20:47	18:05	26:08	17:28	34:04
tert-Butylbenzene	20:17	17:34	25:36	17:19	33:26
Carbon Disulfide					16:30
Carbon Tetrachloride	7:37	5:16	13:10	7:25	21:11
Chloroacetonitrile					23:51
Chlorobenzene	15:46	13:01	20:40	14:20	28:26
1-Chlorobutane					21:00
Chloroethane	2:05	1:01		1:27	
Chloroform	6:24	4:48	12:36	5:33	20:27
Chloromethane	1:38	0:44	3:24	0:58	9:11
2-Chlorotoluene	19:20	16:25	24:32	16:44	32:21
4-Chlorotoluene	19:30	16:43	24:46	16:49	32:38
Cyanogen chloride (8)				1:03	
Dibromochloromethane	14:23	11:51	19:12	12:48	26:57
1,2-Dibromo-3-Chloropropane	24:32	21:05		18:02	38:20
1,2-Dibromoethane	14:44	11:50	19:24	13:36	27:19
Dibromomethane	10:39	7:56	15:26	9:05	23:22
1,2-Dichlorobenzene	22:31	19:10	27:26	17:47	35:55
1,3-Dichlorobenzene	21:13	18:08	26:22	17:28	34:31
1,4-Dichlorobenzene	21:33	18:23	26:36	17:38	34:45
t-1,4-Dichloro-2-butene					31:44
Dichlorodifluoromethane	1:33	0:42	3:08	0:53	7:16
1,1-Dichloroethane	4:51	2:56	10:48	4:02	18:46

TABLE 2. (continued)

Compound	Retention Time (min:sec) Column 1[b]	Column 2[b]	Column 2[c]	Column 3[d]	Column 4[e]
1,2-Dichloroethane	8:24	5:50	13:38	7:00	21:31
1,1-Dichloroethene	2:53	1:34	7:50	2:20	16:01
cis-1,2-Dichloroethene	6:11	3:54	11:56	5:04	19:53
trans-1,2-Dichloroethene	3:59	2:22	9:54	3:32	17:54
1,2-Dichloropropane	10:05	7:40	15:12	8:56	23:08
1,3-Dichloropropane	14:02	11:19	18:42	12:29	26:23
2,2-Dichloropropane	6:01	3:48	11:52	5:19	19:54
1,1-Dichloropropanone					24:52
1,1-Dichloropropene	7:49	5:17	13:06	7:10	21:08
cis-1,3-dichloropropene	11.58		16:42		24:24
trans-1,3-dichloropropene	13.46		17:54		25:33
Diethyl ether					15:31
Ethylbenzene	15:59	13:23	21:00	14:44	28:37
Ethyl Methacrylate					25:35
Hexachlorobutadiene	26:59	23:41	32:04	19:14	42:03
Hexachloroethane					36:45
Hexanone					26:23
Isopropylbenzene	18:04	15:28	23:18	16:25	30:52
4-Isopropyltoluene	21:12	18:31	26:30	17:38	34:27
Methacrylonitrile					20:15
Methylacrylate					20:02
Methylene Chloride	3:36	2:04	9:16	2:40	17:18
Methyl Iodide					16:21
Methylmethacrylate					23:08
4-Methyl-2-pentanone					24:38
Methyl-t-butyl ether					17:56
Naphthalene	27:10	23:31	32:12	19:04	42:29
Nitrobenzene					39:02
2-Nitropropane					23:58
Pentachloroethane					33:33
Propionitrile					19:58
n-Propylbenzene	19:04	16:25	24:20	16:49	32:00
Styrene	17:19	14:36	22:24	15:47	29:57
1,1,1,2-Tetrachloroethane	15:56	13:20	20:52	14:44	28:35
1,1,2,2-Tetrachloroethane	18:43	16:21	24:04	15:47	31:35
Tetrachloroethene	13:44	11:09	18:36	13:12	26:27
Tetrahydrofuran					20:26
Toluene	12:26	10:00	17:24	11:31	25:13
1,2,3-Trichlorobenzene	27:47	24:11	32:58	19:14	43:31
1,2,4-Trichlorobenzene	26:33	23:05	31:30	18:50	41:26
1,1,1-Trichloroethane	7:16	4:50	12:50	6:46	20:51
1,1,2-Trichloroethane	13:25	11:03	18:18	11:59	25:59
Trichloroethene	9:35	7:16	14:48	9:01	22:42
Trichlorofluoromethane	2:16	1:11	6:12	1:46	14:18
1,2,3-Trichloropropane	19:01	16:14	24:08	16:16	31:47
1,2,4-Trimethylbenzene	20:20	17:42	31:30	17:19	33:33

TABLE 2. (continued)

Compound	Retention Time (min:sec) Column 1[b]	Column 2[b]	Column 2[c]	Column 3[d]	Column 4[e]
1,3,5-Trimethylbenzene	19:28	16:54	24:50	16:59	32:26
Vinyl chloride	1:43	0:47	3:56	1:02	10:22
o-Xylene	17:07	14:31	22:16	15:47	29:56
m-Xylene	16:10	13:41	21:22	15:18	28:53
p-Xylene	16:07	13:41	21:18	15:18	28:53

[a]Columns 1-4 are those given in Sect. 6.3.2.1; retention times were measured from the beginning of thermal desorption from the trap (columns 1-2, and 4) or from the beginning of thermal release from the cryogenic interface (column 3).

[b]GC conditions given in Sect. 11.3.1.

[c]GC conditions given in Sect. 11.3.2.

[d]GC conditions given in Sect. 11.3.3.

[e]GC conditions given in Sect. 11.3.4.

TABLE 3. ION ABUNDANCE CRITERIA FOR 4-BROMOFLUOROBENZENE (BFB)

Mass (M/z)	Relative Abundance Criteria
50	15 to 40% of mass 95
75	30 to 80% of mass 95
95	Base Peak, 100% Relative Abundance
96	5 to 9% of mass 95
173	< 2% of mass 174
174	> 50% of mass 95
175	5 to 9% of mass 174
176	> 95% but < 101% of mass 174
177	5 to 9% of mass 176

TABLE 4. ACCURACY AND PRECISION DATA FROM 16-31 DETERMINATIONS OF THE METHOD ANALYTES IN REAGENT WATER USING WIDE BORE CAPILLARY COLUMN 1[a]

Compound	True Conc. Range (µg/L)	Mean Accuracy (% of True Value)	Rel. Std. Dev. (%)	Method Det. Limit[b] (µg/L)
Benzene	0.1-10	97	5.7	0.04
Bromobenzene	0.1-10	100	5.5	0.03
Bromochloromethane	0.5-10	90	6.4	0.04
Bromodichloromethane	0.1-10	95	6.1	0.08
Bromoform	0.5-10	101	6.3	0.12
Bromomethane	0.5-10	95	8.2	0.11
n-Butylbenzene	0.5-10	100	7.6	0.11
sec-Butylbenzene	0.5-10	100	7.6	0.13
tert-Butylbenzene	0.5-10	102	7.3	0.14
Carbon tetrachloride	0.5-10	84	8.8	0.21
Chlorobenzene	0.1-10	98	5.9	0.04
Chloroethane	0.5-10	89	9.0	0.10
Chloroform	0.5-10	90	6.1	0.03
Chloromethane	0.5-10	93	8.9	0.13
2-Chlorotoluene	0.1-10	90	6.2	0.04
4-Chlorotoluene	0.1-10	99	8.3	0.06
Dibromochloromethane	0.1-10	92	7.0	0.05
1,2-Dibromo-3-chloropropane	0.5-10	83	19.9	0.26
1,2-Dibromoethane	0.5-10	102	3.9	0.06
Dibromomethane	0.5-10	100	5.6	0.24
1,2-Dichlorobenzene	0.1-10	93	6.2	0.03
1,3-Dichlorobenzene	0.5-10	99	6.9	0.12
1,4-Dichlorobenzene	0.2-20	103	6.4	0.03
Dichlorodifluoromethane	0.5-10	90	7.7	0.10
1,1-Dichloroethane	0.5-10	96	5.3	0.04
1,2-Dichloroethane	0.1-10	95	5.4	0.06
1,1-Dichloroethene	0.1-10	94	6.7	0.12
cis-1,2 Dichloroethene	0.5-10	101	6.7	0.12
trans-1,2-Dichloroethene	0.1-10	93	5.6	0.06
1,2-Dichloropropane	0.1-10	97	6.1	0.04
1,3-Dichloropropane	0.1-10	96	6.0	0.04
2,2-Dichloropropane	0.5-10	86	16.9	0.35
1,1-Dichloropropene	0.5-10	98	8.9	0.10
cis-1,2-Dichloropropene				
trans-1,2-Dichloropropene				
Ethylbenzene	0.1-10	99	8.6	0.06
Hexachlorobutadiene	0.5-10	100	6.8	0.11
Isopropylbenzene	0.5-10	101	7.6	0.15
4-Isopropyltoluene	0.1-10	99	6.7	0.12
Methylene chloride	0.1-10	95	5.3	0.03
Naphthalene	0.1-100	104	8.2	0.04
n-Propylbenzene	0.1-10	100	5.8	0.04
Styrene	0.1-100	102	7.2	0.04

TABLE 4. (Continued)

Compound	True Conc. Range (µg/L)	Mean Accuracy (% of True Value)	Rel. Std. Dev. (%)	Method Det. Limit[b] (µg/L)
1,1,1,2-Tetrachloroethane	0.5-10	90	6.8	0.05
1,1,2,2-Tetrachloroethane	0.1-10	91	6.3	0.04
Tetrachloroethene	0.5-10	89	6.8	0.14
Toluene	0.5-10	102	8.0	0.11
1,2,3-Trichlorobenzene	0.5-10	109	8.6	0.03
1,2,4-Trichlorobenzene	0.5-10	108	8.3	0.04
1,1,1-Trichloroethane	0.5-10	98	8.1	0.08
1,1,2-Trichloroethane	0.5-10	104	7.3	0.10
Trichloroethene	0.5-10	90	7.3	0.19
Trichlorofluoromethane	0.5-10	89	8.1	0.08
1,2,3-Trichloropropane	0.5-10	108	14.4	0.32
1,2,4-Trimethylbenzene	0.5-10	99	8.1	0.13
1,3,5-Trimethylbenzene	0.5-10	92	7.4	0.05
Vinyl chloride	0.5-10	98	6.7	0.17
o-Xylene	0.1-31	103	7.2	0.11
m-Xylene	0.1-10	97	6.5	0.05
p-Xylene	0.5-10	104	7.7	0.13

[a]Data obtained by using column 1 with a jet separator interface and a quadrupole mass spectrometer (Sect. 11.3.1) with analytes divided among three solutions.

[b]Replicate samples at the lowest concentration listed in column 2 of this table were analyzed. These results were used to calculate MDLs.

TABLE 5. ACCURACY AND PRECISION DATA FROM SEVEN DETERMINATIONS OF METHOD ANALYTES IN REAGENT WATER USING THE CRYOGENIC TRAPPING OPTION AND A NARROW BORE CAPILLARY COLUMN 3[a]

Compound	True Conc. (µg/L)	Mean Accuracy (% of True Value)	Rel. Std. Dev. (%)	Method Dect. Limit (µg/L)
Benzene	0.1	99	6.2	0.03
Bromobenzene	0.5	97	7.4	0.11
Bromochloromethane	0.5	97	5.8	0.07
Bromodichloromethane	0.1	100	4.6	0.03
Bromoform	0.1	99	5.4	0.20
Bromomethane	0.1	99	7.1	0.06
n-Butylbenzene	0.5	94	6.0	0.03
sec-Butylbenzene	0.5	90	7.1	0.12
tert-Butylbenzene	0.5	90	2.5	0.33
Carbon tetrachloride	0.1	92	6.8	0.08
Chlorobenzene	0.1	91	5.8	0.03
Chloroethane	0.1	100	5.8	0.02
Chloroform	0.1	95	3.2	0.02
Chloromethane	0.1	99	4.7	0.05
2-Chlorotoluene	0.1	99	4.6	0.05
4-Chlorotoluene	0.1	96	7.0	0.05
Cyanogen chloride[b]		92	10.6	0.30
Dibromochloromethane	0.1	99	5.6	0.07
1,2-Dibromo-3-chloropropane	0.1	92	10.0	0.05
1,2-Dibromoethane	0.1	97	5.6	0.02
Dibromomethane	0.1	93	6.9	0.03
1,2-Dichlorobenzene	0.1	97	3.5	0.05
1,3-Dichlorobenzene	0.1	99	6.0	0.05
1,4-Dichlorobenzene	0.1	93	5.7	0.04
Dichlorodifluoromethane	0.1	99	8.8	0.11
1,1-Dichloroethane	0.1	98	6.2	0.03
1,2-Dichloroethane	0.1	100	6.3	0.02
1,1-Dichloroethene	0.1	95	9.0	0.05
cis-1,2 Dichloroethene	0.1	100	3.7	0.06
trans-1,2-Dichloroethene	0.1	98	7.2	0.03
1,2-Dichloropropane	0.1	96	6.0	0.02
1,3-Dichloropropane	0.1	99	5.8	0.04
2,2-Dichloropropane	0.1	99	4.9	0.05
1,1-Dichloropropene	0.1	98	7.4	0.02
cis-1,3-Dichloropropene				
trans-1,3-Dichloropropene				
Ethylbenzene	0.1	99	5.2	0.03
Hexachlorobutadiene	0.1	100	6.7	0.04
Isopropylbenzene	0.5	98	6.4	0.10
4-Isopropyltoluene	0.5	87	13.0	0.26
Methylene chloride	0.5	97	13.0	0.09
Naphthalene	0.1	98	7.2	0.04

TABLE 5. (Continued)

Compound	True Conc. (µg/L)	Mean Accuracy (% of True Value)	Rel. Std. Dev. (%)	Method Dect. Limit (µg/L)
n-Propylbenzene	0.1	99	6.6	0.06
Styrene	0.1	96	19.0	0.06
1,1,1,2-Tetrachloroethane	0.1	100	4.7	0.04
1,1,2,2-Tetrachloroethane	0.5	100	12.0	0.20
Tetrachloroethene	0.1	96	5.0	0.05
Toluene	0.1	100	5.9	0.08
1,2,3-Trichlorobenzene	0.1	98	8.9	0.04
1,2,4-Trichlorobenzene	0.1	91	16.0	0.20
1,1,1-Trichloroethane	0.1	100	4.0	0.04
1,1,2-Trichloroethane	0.1	98	4.9	0.03
Trichloroethene	0.1	96	2.0	0.02
Trichlorofluoromethane	0.1	97	4.6	0.07
1,2,3-Trichloropropane	0.1	96	6.5	0.03
1,2,4-Trimethylbenzene	0.1	96	6.5	0.04
1,3,5-Trimethylbenzene	0.1	99	4.2	0.02
Vinyl chloride	0.1	96	0.2	0.04
o-Xylene	0.1	94	7.5	0.06
m-Xylene	0.1	94	4.6	0.03
p-Xylene	0.1	97	6.1	0.06

[a]Data obtained by using column 3 with a cryogenic interface and a quadrupole mass spectrometer (Sect 11.3.3).
[b]Reference 8.

TABLE 6. ACCURACY AND PRECISION DATA FROM SEVEN DETERMINATIONS OF THE METHOD ANALYTES IN REAGENT WATER USING WIDE BORE CAPILLARY COLUMN 2[a]

Compound	No.[b]	Mean Accuracy (% of True Value, 2 µg/L Conc.)	RSD (%)	Mean Accuracy (% of True Value, 0.2 µg/L Conc.)	RSD (%)
Internal Standard					
Fluorobenzene	1	-	-	-	-
Surrogates					
4-Bromofluorobenzene	2	98	1.8	96	1.3
1,2-Dichlorobenzene-d_4	3	97	3.2	95	1.7
Target Analytes					
Benzene	37	97	4.4	113	1.8
Bromobenzene	38	102	3.0	101	1.9
Bromochloromethane	4	99	5.2	102	2.9
Bromodichloromethane	5	96	1.8	100	1.8
Bromoform	6	89	2.4	90	2.2
Bromomethane	7	55	27.	52	6.7
n-Butylbenzene	39	89	4.8	87	2.3
sec-Butylbenzene	40	102	3.5	100	2.8
tert-Butylbenzene	41	101	4.5	100	2.9
Carbon tetrachloride	8	84	3.2	92	2.6
Chlorobenzene	42	104	3.1	103	1.6
Chloroethane[c]					
Chloroform	9	97	2.0	95	2.1
Chloromethane	10	110	5.0	d	
2-Chlorotoluene	43	91	2.4	108	3.1
4-Chlorotoluene	44	89	2.0	108	4.4
Dibromochloromethane	11	95	2.7	100	3.0
1,2-Dibromo-3-chloropropane[c]					
1,2-Dibromoethane[c]					
Dibromomethane	13	99	2.1	95	2.2
1,2-Dichlorobenzene	45	93	2.7	94	5.1
1,3-Dichlorobenzene	46	100	4.0	87	2.3
1,4-Dichlorobenzene	47	98	4.1	94	2.8
Dichlorodifluoromethane	14	38	25.	d	
1,1-Dichloroethane	15	97	2.3	85	3.6
1,2-Dichloroethane	16	102	3.8	100	2.1
1,1-Dichloroethene	17	90	2.2	87	3.8
cis-1,2-Dichloroethene	18	100	3.4	89	2.9
trans-1,2-Dichloroethene	19	92	2.1	85	2.3

TABLE 6. (Continued)

Compound	No.[b]	Mean Accuracy (% of True Value, 2 µg/L Conc.)	RSD (%)	Mean Accuracy (% of True Value, 0.2 µg/L Conc.)	RSD (%)
1,2-Dichloropropane	20	102	2.2	103	2.9
1,3-Dichloropropane	21	92	3.7	93	3.2
2,2-Dichloropropane[c]					
1,1-Dichloropropene[c]					
cis-1,3-Dichloropropene[c]					
trans-1,3-Dichloropropene	25	96	1.7	99	2.1
Ethylbenzene	48	96	9.1	100	4.0
Hexachlorobutadiene	26	91	5.3	88	2.4
Isopropylbenzene	49	103	3.2	101	2.1
4-Isopropyltoluene	50	95	3.6	95	3.1
Methylene chloride	27	e		e	
Naphthalene	51	93	7.6	78	8.3
n-Propylbenzene	52	102	4.9	97	2.1
Styrene	53	95	4.4	104	3.1
1,1,1,2-Tetrachloroethane	28	99	2.7	95	3.8
1,1,2,2-Tetrachloroethane	29	101	4.6	84	3.6
Tetrachloroethene	30	97	4.5	92	3.3
Toluene	54	105	2.8	126	1.7
1,2,3-Trichlorobenzene	55	90	5.7	78	2.9
1,2,4-Trichlorobenzene	56	92	5.2	83	5.9
1,1,1-Trichloroethane	31	94	3.9	94	2.5
1,1,2-Trichloroethane	32	107	3.4	109	2.8
Trichloroethene	33	99	2.9	106	2.5
Trichlorofluoromethane	34	81	4.6	48	13.
1,2,3-Trichloropropane	35	97	3.9	91	2.8
1,2,4-Trimethylbenzene	57	93	3.1	106	2.2
1,3,5-Trimethylbenzene	58	88	2.4	97	3.2
Vinyl chloride	36	104	3.5	115	14.
o-Xylene	59	97	1.8	98	1.7
m-Xylene	60	f		f	
p-Xylene	61	98	2.3	103	1.4

[a]Data obtained using column 2 with the open split interface and an ion trap mass spectrometer (Sect. 11.3.2) with all method analytes in the same reagent water solution.
[b]Designation in Figures 1 and 2.
[c]Not measured; authentic standards were not available.
[d]Not found at 0.2 µg/L.
[e]Not measured; methylene chloride was in the laboratory reagent blank.
[f]m-xylene coelutes with and cannot be distinguished from its isomer p-xylene, No 61.

TABLE 7. ACCURACY AND PRECISION DATA FROM SEVEN DETERMINATIONS OF METHOD ANALYTES IN REAGENT WATER USING WIDE BORE CAPILLARY COLUMN 4

Compound	True Conc. (µg/L)	Mean Conc. Detected (ug/L)	Rel. Std. Dev. (%)	Method Det. Limit (µg/L)
Acetone	1.0	1.6	5.7%	0.28
Acrylonitrile	1.0	0.81	8.7%	0.22
Allyl chloride	1.0	0.90	4.7%	0.13
2-Butanone	2.0	2.7	5.6%	0.48
Carbon disulfide	0.20	0.19	15%	0.093
Chloroacetonitrile	1.0	0.83	4.7%	0.12
1-Chlorobutane	1.0	0.87	6.6%	0.18
t-1,2-Dichloro-2-butene	1.0	1.3	8.7%	0.36
1,1-Dichloropropanone	5.0	4.2	7.7%	1.0
Diethyl ether	1.0	0.92	9.5%	0.28
Ethyl methacrylate	0.20	0.23	3.9%	0.028
Hexachloroethane	0.20	0.18	10%	0.057
2-Hexanone	1.0	1.1	12%	0.39
Methacrylonitrile	1.0	0.92	4.2%	0.12
Methylacrylate	1.0	1.2	12%	0.45
Methyl iodide	0.20	0.19	3.1%	0.019
Methylmethacrylate	1.0	1.0	13%	0.43
4-Methyl-2-pentanone	0.40	0.56	9.7%	0.17
Methyl-tert-butylether	0.40	0.52	5.6%	0.090
Nitrobenzene	2.0	2.1	18%	1.2
2-Nitropropane	1.0	0.83	6.2%	0.16
Pentachloroethane	0.20	0.23	20%	0.14
Propionitrile	1.0	0.87	5.3%	0.14
Tetrahydrofuran	5.0	3.9	13%	1.6

TABLE 8. ACCURACY AND PRECISION FROM FOUR DETERMINATIONS OF METHOD ANALYTES IN THREE WATER MATRICES FORTIFIED AT 20 µG/L

Compound	REAGENT WATER			RAW WATER			TAP WATER		
	Mean (µg/L)	Dev. (%)	(% of True Value)	Mean (µg/L)	Dev. (%)	(% of True Value)	Mean (µg/L)	Dev. (%)	(% of True Value)
Acetone	19	12%	95%	21	3.7%	105%	22	8.2%	110%
Acrylonitrile	20	4.7%	100%	22	3.4%	110%	21	1.3%	105%
Allyl chloride	20	5.1%	100%	20	2.8%	100%	19	3.5%	95%
2-Butanone	17	11%	85%	19	7.3%	95%	17	5.6%	85%
Carbon disulfide	19	6.4%	95%	18	2.5%	90%	18	3.0%	90%
Chloroacetonitrile	20	4.1%	100%	23	4.7%	115%	23	1.3%	115%
1-Chlorobutane	18	6.4%	90%	19	2.2%	95%	17	2.2%	85%
t-1,2-Dichloro-2-butene	19	4.1%	95%	22	2.9%	110%	21	0.90%	105%
1,1-Dichloropropanone	20	5.6%	100%	22	6.4%	110%	21	7.7%	105%
Diethyl ether	18	6.7%	90%	22	3.4%	110%	22	2.6%	110%
Ethyl methacrylate	20	3.7%	100%	23	2.6%	115%	22	1.8%	110%
Hexachloroethane	20	6.1%	100%	21	2.5%	105%	21	2.0%	105%
2-Hexanone	19	6.3%	95%	21	3.8%	105%	21	4.0%	105%
Methacrylonitrile	20	3.4%	100%	23	2.9%	115%	22	2.0%	110%
Methylacrylate	20	3.7%	100%	22	3.1%	110%	21	2.1%	105%

TABLE 8 (Continued)

Compound	REAGENT WATER			RAW WATER			TAP WATER		
	Mean (µg/L)	Dev. (%)	(% of True Value)	Mean (µg/L)	Dev. (%)	(% of True Value)	Mean (µg/L)	Dev. (%)	(% of True Value)
Methyl iodide	20	4.4%	100%	19	3.8%	95%	19	3.0%	95%
Methylmethacrylate	20	3.7%	100%	23	3.3%	115%	23	2.7%	115%
4-Methyl-2-pentanone	19	8.7%	95%	21	5.5%	105%	22	7.2%	110%
Methyl-tert-butylether	19	3.5%	95%	22	2.5%	110%	22	3.6%	110%
Nitrobenzene	20	5.4%	100%	22	4.8%	110%	21	2.4%	105%
2-Nitropropane	20	6.1%	100%	23	5.1%	115%	22	3.2%	110%
Pentachloroethane	19	5.2%	95%	21	2.6%	105%	22	1.7%	110%
Propionitrile	20	4.5%	100%	23	3.9%	115%	23	2.4%	115%
Tetrahydrofuran	20	2.8%	100%	24	3.2%	120%	21	2.9%	105%

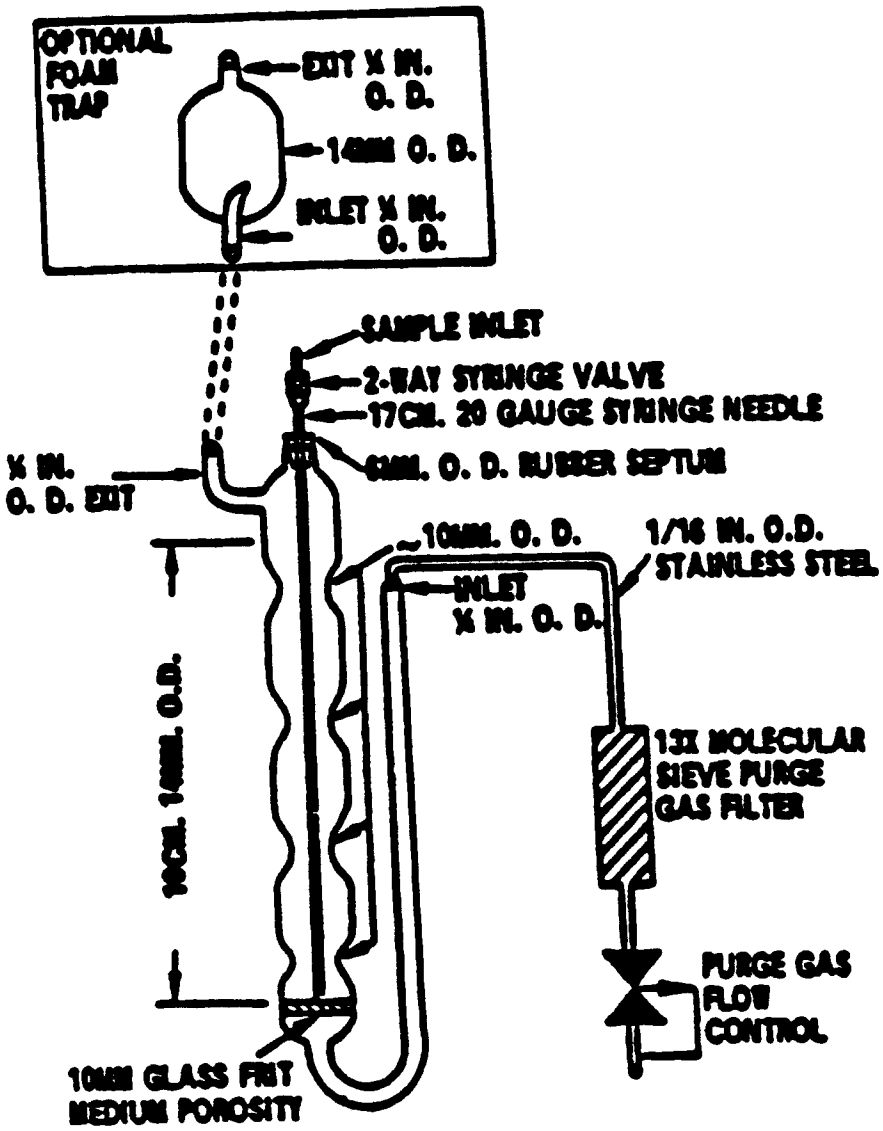


FIGURE 1. PURGING DEVICE

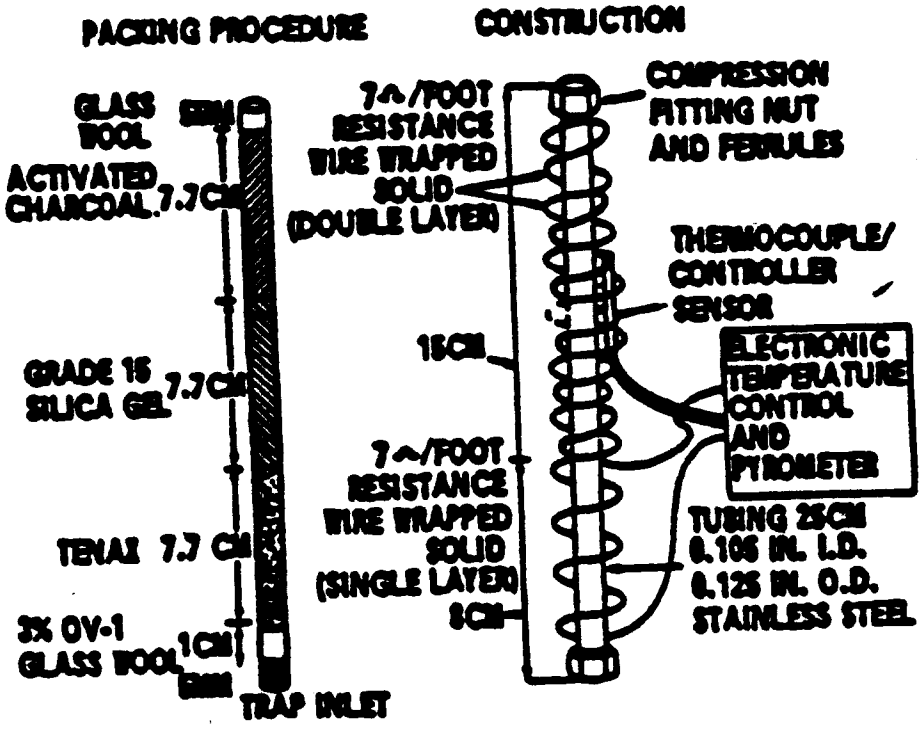


FIGURE 2. TRAP PACKINGS AND CONSTRUCTION TO INCLUDE DESORB CAPABILITY

FIGURE 3. NORMALIZED TOTAL ION CURRENT CHROMATOGRAM FROM A VOLA LE COMPOUND CALIBRATION MIXTURE CONTAINING 25 ng (5 ng/L) OF MOST COMPOUNDS. THE COMPOUND IDENTIFICATION NUMBERS ARE GIVEN IN TABLE 6.

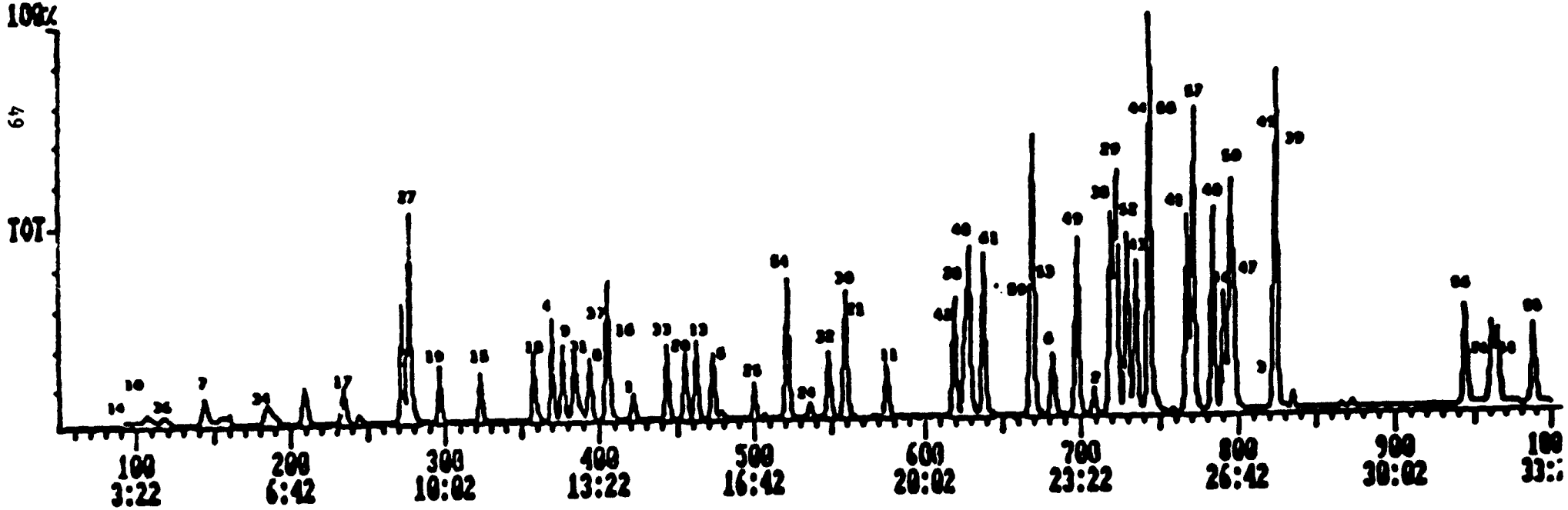
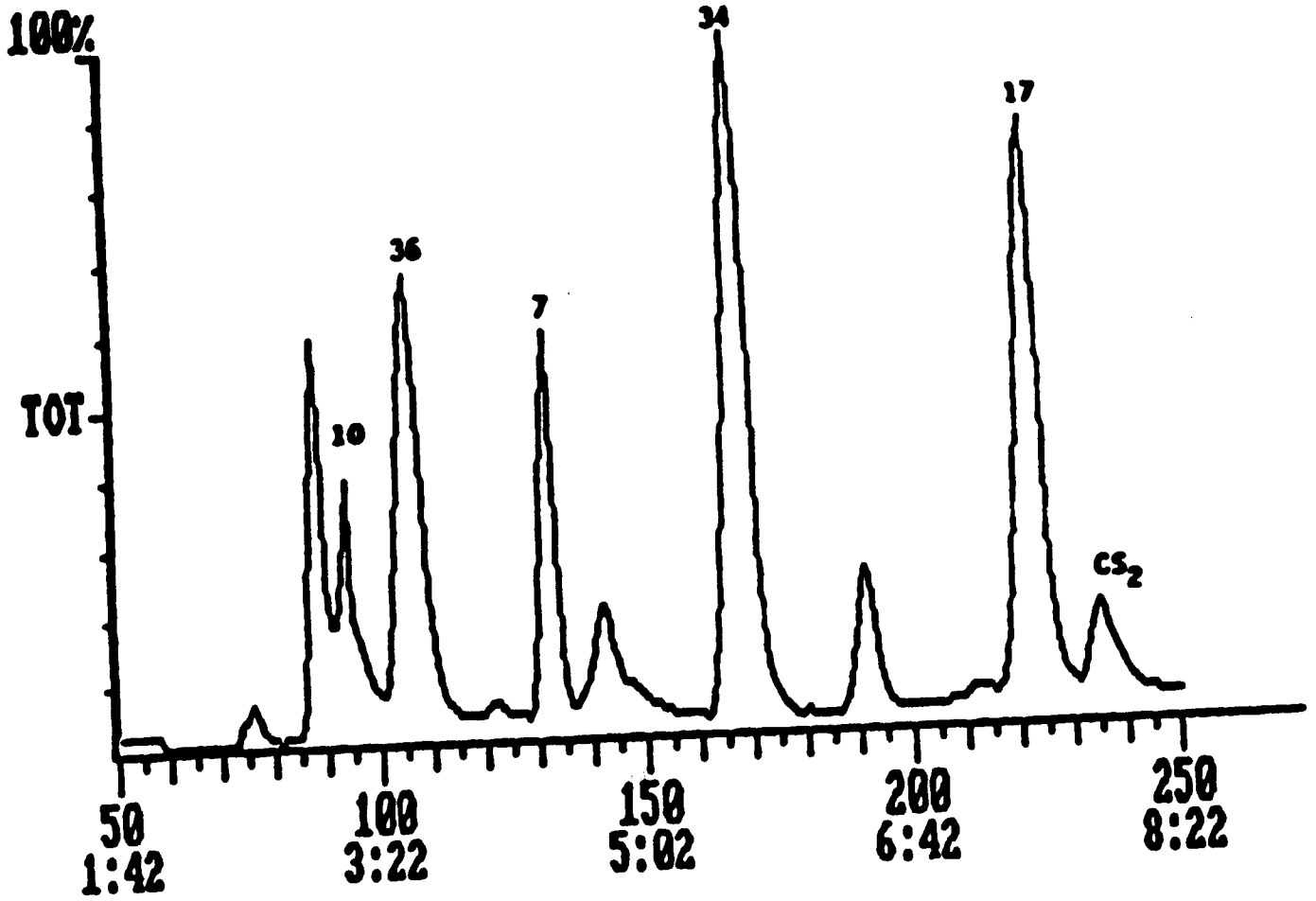


FIGURE 4. AMPLIFIED FIRST EIGHT MINUTES OF A TOTAL ION CURRENT CHROMATOGRAM FROM A VOLATILE COMPOUND CALIBRATION MIXTURE CONTAINING 25 ng (5 µg/L) OF EACH COMPONENT. THE COMPOUND IDENTIFICATION NUMBERS ARE GIVEN IN TABLE 6.



METHOD 200.8

DETERMINATION OF TRACE ELEMENTS IN WATERS AND WASTES BY INDUCTIVELY COUPLED PLASMA - MASS SPECTROMETRY

Stephen E. Long
Technology Applications, Inc.

and

Theodore D. Martin
Inorganic Chemistry Branch
Chemistry Research Division

Revision 4.4
April 1991

ENVIRONMENTAL MONITORING SYSTEMS LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
U.S. ENVIRONMENTAL PROTECTION AGENCY
CINCINNATI, OHIO 45268

METHOD 200.8

DETERMINATION OF TRACE ELEMENTS IN WATERS AND WASTES BY INDUCTIVELY COUPLED PLASMA - MASS SPECTROMETRY

1. SCOPE AND APPLICATION

1.1 This method provides procedures for determination of dissolved elements in ground waters, surface waters and drinking water. It may also be used for determination of total recoverable element concentrations in these waters as well as wastewaters, sludges and solid waste samples.

1.2 Dissolved elements are determined after suitable filtration and acid preservation. Acid digestion procedures are required prior to determination of total recoverable elements. In order to reduce potential interferences, dissolved solids should not exceed 0.2% (w/v) (Sect. 4.1.4).

1.3 This method is applicable to the following elements:

Element		Chemical Abstract Services Registry Numbers (CASRN)
Aluminum	(Al)	7429-90-5
Antimony	(Sb)	7440-36-0
Arsenic	(As)	7440-38-2
Barium	(Ba)	7440-39-3
Beryllium	(Be)	7440-41-7
Cadmium	(Cd)	7440-43-9
Chromium	(Cr)	7440-47-3
Cobalt	(Co)	7440-48-4
Copper	(Cu)	7440-50-8
Lead	(Pb)	7439-92-1
Manganese	(Mn)	7439-96-5
Molybdenum	(Mo)	7439-98-7
Nickel	(Ni)	7440-02-0
Selenium	(Se)	7782-49-2
Silver	(Ag)	7440-22-4
Thallium	(Tl)	7440-28-0
Thorium	(Th)	7440-29-1
Uranium	(U)	7440-61-1
Vanadium	(V)	7440-62-2
Zinc	(Zn)	7440-66-6

Estimated instrument detection limits (IDLs) for these elements are listed in Table 1. These are intended as a guide to instrumental limits typical of a system optimized for multielement determinations and employing commercial instrumentation and pneumatic nebulization sample introduction. However, actual method detection limits (MDLs)

and linear working ranges will be dependent on the sample matrix, instrumentation and selected operating conditions.

1.4 This method is suitable for the determination of silver in aqueous samples containing concentrations up to 0.1 mg/L. For the analysis of wastewater samples containing higher concentrations of silver, succeeding smaller volume, well mixed sample aliquots must be prepared until the analysis solution contains < 0.1 mg/L silver.

1.5 This method should be used by analysts experienced in the use of inductively coupled plasma mass spectrometry (ICP-MS), the interpretation of spectral and matrix interferences and procedures for their correction. A minimum of six months experience with commercial instrumentation is recommended.

2. SUMMARY OF METHOD

2.1 The method describes the multi-element determination of trace elements by ICP-MS[1-3]. Sample material in solution is introduced by pneumatic nebulization into a radiofrequency plasma where energy transfer processes cause desolvation, atomization and ionization. The ions are extracted from the plasma through a differentially pumped vacuum interface and separated on the basis of their mass-to-charge ratio by a quadrupole mass spectrometer having a minimum resolution capability of 1 amu peak width at 5% peak height. The ions transmitted through the quadrupole are registered by a continuous dynode electron multiplier or Faraday detector and the ion information processed by a data handling system. Interferences relating to the technique (Sect. 4) must be recognized and corrected for. Such corrections must include compensation for isobaric elemental interferences and interferences from polyatomic ions derived from the plasma gas, reagents or sample matrix. Instrumental drift as well as suppressions or enhancements of instrument response caused by the sample matrix must be corrected for by the use of internal standardization.

3. DEFINITIONS

3.1 DISSOLVED - Material that will pass through a 0.45 μm membrane filter assembly, prior to sample acidification.

3.2 TOTAL RECOVERABLE - The concentration of analyte determined on an unfiltered sample following treatment with hot dilute mineral acid.

3.3 INSTRUMENT DETECTION LIMIT (IDL) - The concentration equivalent of the analyte signal, which is equal to three times the standard deviation of the blank signal at the selected analytical mass(es).

3.4 METHOD DETECTION LIMIT (MDL) - The minimum concentration of an analyte that can be identified, measured and reported with 99% confidence that the analyte concentration is greater than zero.

3.5 LINEAR DYNAMIC RANGE (LDR) - The concentration range over which the analytical working curve remains linear.

3.6 LABORATORY REAGENT BLANK (LRB) (preparation blank) - An aliquot of reagent water that is treated exactly as a sample including exposure to all labware, equipment, solvents, reagents, and internal standards that are used with other samples. The LRB is used to determine if method analytes or other interferences are present in the laboratory environment, the reagents or apparatus.

3.7 CALIBRATION BLANK - A volume of ASTM type I water acidified with the same acid matrix as is present in the calibration standards.

3.8 INTERNAL STANDARD - 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.

3.9 STOCK STANDARD SOLUTION - A concentrated solution containing one or more analytes prepared in the laboratory using assayed reference compounds or purchased from a reputable commercial source.

3.10 CALIBRATION STANDARD (CAL) - A solution prepared from the stock standard solution(s) which is used to calibrate the instrument response with respect to analyte concentration.

3.11 TUNING SOLUTION - A solution which is used to determine acceptable instrument performance prior to calibration and sample analyses.

3.12 LABORATORY FORTIFIED BLANK (LFB) - An aliquot of reagent water to which known quantities of the method analytes are added in the laboratory. The LFB is analyzed exactly like a sample, and its purpose is to determine whether method performance is within accepted control limits.

3.13 LABORATORY FORTIFIED SAMPLE MATRIX (LFM) - An aliquot of an environmental sample to which known quantities of the method analytes are added in the laboratory. The LFM is analyzed exactly like a sample, and its purpose is to determine whether the sample matrix contributes bias to the analytical results. The background concentrations of the analytes in the sample matrix must be determined in a separate aliquot and the measured values in the LFM corrected for the concentrations found.

3.14 QUALITY CONTROL SAMPLE (QCS) - A solution containing known concentrations of method analytes which is used to fortify an aliquot of LRB matrix. The QCS is obtained from a source external to the laboratory and is used to check laboratory performance.

4. INTERFERENCES

4.1 Several interference sources may cause inaccuracies in the determination of trace elements by ICP-MS. These are:

4.1.1 Isobaric elemental interferences - Are caused by isotopes of different elements which form singly or doubly charged ions of the same nominal mass-to-charge ratio and which cannot be resolved by the mass spectrometer in use. All elements determined by this method have, at a minimum, one isotope free of isobaric elemental interference. Of the analytical isotopes recommended for use with this method (Table 4), only molybdenum-98 (ruthenium) and selenium-82 (krypton) have isobaric elemental interferences. If alternative analytical isotopes having higher natural abundance are selected in order to achieve greater sensitivity, an isobaric interference may occur. All data obtained under such conditions must be corrected by measuring the signal from another isotope of the interfering element and subtracting the appropriate signal ratio from the isotope of interest. A record of this correction process should be included with the report of the data. It should be noted that such corrections will only be as accurate as the accuracy of the isotope ratio used in the elemental equation for data calculations. Relevant isotope ratios and instrument bias factors should be established prior to the application of any corrections.

4.1.2 Abundance sensitivity - Is a property defining the degree to which the wings of a mass peak contribute to adjacent masses. The abundance sensitivity is affected by ion energy and quadrupole operating pressure. Wing overlap interferences may result when a small ion peak is being measured adjacent to a large one. The potential for these interferences should be recognized and the spectrometer resolution adjusted to minimize them.

4.1.3 Isobaric polyatomic ion interferences - Are caused by ions consisting of more than one atom which have the same nominal mass-to-charge ratio as the isotope of interest, and which cannot be resolved by the mass spectrometer in use. These ions are commonly formed in the plasma or interface system from support gases or sample components. Most of the common interferences have been identified[3], and these are listed in Table 2 together with the method elements affected. Such interferences must be recognized, and when they cannot be avoided by the selection of alternative analytical isotopes, appropriate corrections must be made to the data. Equations for the correction of data should be established at the time of the analytical run sequence as the polyatomic ion interferences will be highly dependent on the sample matrix and chosen instrument conditions.

4.1.4 Physical interferences - Are associated with the physical processes which govern the transport of sample into the plasma, sample conversion processes in the plasma, and the transmission of ions through the plasma-mass spectrometer interface. These interferences may result in differences between instrument responses for the sample and the calibration standards. Physical interferences may occur in the transfer of solution to the nebulizer (e.g., viscosity effects), at the point of aerosol formation and transport to the plasma (e.g., surface tension), or during excitation and ionization processes within the plasma itself. High levels of dissolved solids in the sample may contribute deposits of material on the extraction and/or skimmer cones reducing the effective diameter of the orifices and therefore ion transmission. Dissolved solids levels not exceeding 0.2% (w/v) have been recommended[3] to reduce such effects. Internal standardization may be effectively used to compensate for many physical interference effects[4]. Internal standards ideally should have similar analytical behavior to the elements being determined.

4.1.5 Memory interferences - Result when isotopes of elements in a previous sample contribute to the signals measured in a new sample. Memory effects can result from sample deposition on the sampler and skimmer cones, and from the buildup of sample material in the plasma torch and spray chamber. The site where these effects occur is dependent on the element and can be minimized by flushing the system with a rinse blank between samples (Sect. 7.6.3). The possibility of memory interferences should be recognized within an analytical run and suitable rinse times should be used to reduce them. The rinse times necessary for a particular element should be estimated prior to analysis. This may be achieved by aspirating a standard containing elements corresponding to ten times the upper end of the linear range for a normal sample analysis period, followed by analysis of the rinse blank at designated intervals. The length of time required to reduce analyte signals to within a factor of ten of the method detection limit, should be noted. Memory interferences may also be assessed within an analytical run by using a minimum of three replicate integrations for data acquisition. If the integrated signal values drop consecutively, the analyst should be alerted to the possibility of a memory effect, and should examine the analyte concentration in the previous sample to identify if this was high. If a memory interference is suspected, the sample should be reanalyzed after a long rinse period.

5. SAFETY

5.1 The toxicity or carcinogenicity of reagents used in this method have not been fully established. Each chemical should be regarded as a

potential health hazard and exposure to these compounds should be as low as reasonably achievable. Each laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method[5,6]. A reference file of material data handling sheets should also be available to all personnel involved in the chemical analysis.

5.2 Analytical plasma sources emit radiofrequency radiation in addition to intense UV radiation. Suitable precautions should be taken to protect personnel from such hazards.

6. APPARATUS AND EQUIPMENT

6.1 INDUCTIVELY COUPLED PLASMA - MASS SPECTROMETER

6.1.1 Instrument capable of scanning the mass range 5-250 amu with a minimum resolution capability of 1 amu peak width at 5% peak height. Instrument may be fitted with a conventional or extended dynamic range detection system.

6.1.2 Argon gas supply (high-purity grade, 99.99%).

6.1.3 A variable-speed peristaltic pump is required for solution delivery to the nebulizer.

6.1.4 A mass-flow controller on the nebulizer gas supply is required. A water-cooled spray chamber may be of benefit in reducing some types of interferences (e.g., from polyatomic oxide species).

6.1.5 Operating conditions - Because of the diversity of instrument hardware, no detailed instrument operating conditions are provided. The analyst is advised to follow the recommended operating conditions provided by the manufacturer. It is the responsibility of the analyst to verify that the instrument configuration and operating conditions satisfy the analytical requirements and to maintain quality control data verifying instrument performance and analytical results. Instrument operating conditions which were used to generate precision and recovery data for this method (Sect. 13) are included in Table 6.

6.1.6 If an electron multiplier detector is being used, precautions should be taken, where necessary, to prevent exposure to high ion flux. Otherwise changes in instrument response or damage to the multiplier may result. Samples having high concentrations of elements beyond the linear range of the instrument and with isotopes falling within scanning windows should be diluted prior to analysis.

6.2 LABWARE - For the determination of trace levels of elements, contamination and loss are of prime consideration. Potential

contamination sources include improperly cleaned laboratory apparatus and general contamination within the laboratory environment from dust, etc. A clean laboratory work area, designated for trace element sample handling must be used. Sample containers can introduce positive and negative errors in the determination of trace elements by (1) contributing contaminants through surface desorption or leaching, (2) depleting element concentrations through adsorption processes. All reuseable labware (glass, quartz, polyethylene, Teflon, etc.) including the sample container should be cleaned prior to use. Labware may be soaked overnight and thoroughly washed with laboratory-grade detergent and water, rinsed with water, and soaked for four hours in a mixture of dilute nitric and hydrochloric acid (1+2+9), followed by rinsing with water, ASTM type I water and oven drying.

NOTE: Chromic acid must not be used for cleaning glassware.

6.2.1 Glassware - Volumetric flasks, graduated cylinders, funnels and centrifuge tubes.

6.2.2 Assorted calibrated pipettes.

6.2.3 Conical Phillips beakers, 250-mL with 50-mm watch glasses. Griffin beakers, 250-mL with 75-mm watch glasses.

6.2.4 Storage bottles - Narrow mouth bottles, Teflon FEP (fluorinated ethylene propylene) with Tefzel ETFE (ethylene tetrafluorethylene) screw closure, 125-mL and 250-mL capacities.

6.3 SAMPLE PROCESSING EQUIPMENT

6.3.1 Air Displacement Pipetter - Digital pipet system capable of delivering volumes from 10 to 2500 µL with an assortment of high quality disposable pipet tips.

6.3.2 Balance - Analytical, capable of accurately weighing to 0.1 mg.

6.3.3 Hot Plate - (Corning PC100 or equivalent).

6.3.4 Centrifuge - Steel cabinet with guard bowl, electric timer and brake.

6.3.5 Drying Oven - Gravity convection oven with thermostatic control capable of maintaining 105°C ± 5°C.

7. REAGENTS AND CONSUMABLE MATERIALS

7.1 Reagents may contain elemental impurities that might affect the integrity of analytical data. Owing to the high sensitivity of ICP-

MS, high-purity reagents should be used whenever possible. All acids used for this method must be of ultra high-purity grade. Suitable acids are available from a number of manufacturers or may be prepared by sub-boiling distillation. Nitric acid is preferred for ICP-MS in order to minimize polyatomic ion interferences. Several polyatomic ion interferences result when hydrochloric acid is used (Table 2), however, it should be noted that hydrochloric acid is required to maintain stability in solutions containing antimony and silver. When hydrochloric acid is used, corrections for the chloride polyatomic ion interferences must be applied to all data.

7.1.1 Nitric acid, concentrated (sp.gr. 1.41).

7.1.2 Nitric acid (1+1) - Add 500 mL conc. nitric acid to 400 mL of ASTM type I water and dilute to 1 L.

7.1.3 Nitric acid (1+9) - Add 100 mL conc. nitric acid to 400 mL of ASTM type I water and dilute to 1 L.

7.1.4 Hydrochloric acid, concentrated (sp.gr. 1.19).

7.1.5 Hydrochloric acid (1+1) - Add 500 mL conc. hydrochloric acid to 400 mL of ASTM type I water and dilute to 1 L.

7.1.6 Hydrochloric acid (1+4) - Add 200 mL conc. hydrochloric acid to 400 mL of ASTM type I water and dilute to 1 L.

7.1.7 Ammonium hydroxide, concentrated (sp.gr. 0.902).

7.1.8 Tartaric acid (CASRN 87-69-4).

7.2 WATER - For all sample preparation and dilutions, ASTM type I water (ASTM D1193) is required. Suitable water may be prepared by passing distilled water through a mixed bed of anion and cation exchange resins.

7.3 STANDARD STOCK SOLUTIONS - May be purchased from a reputable commercial source or prepared from ultra high-purity grade chemicals or metals (99.99 - 99.999% pure). All salts should be dried for 1 h at 105°C, unless otherwise specified. (CAUTION: Many metal salts are extremely toxic if inhaled or swallowed. Wash hands thoroughly after handling). Stock solutions should be stored in Teflon bottles. The following procedures may be used for preparing standard stock solutions:

NOTE: Some metals, particularly those which form surface oxides require cleaning prior to being weighed. This may be achieved by pickling the surface of the metal in acid. An amount in excess of the desired weight should be pickled repeatedly, rinsed with water, dried and weighed until the desired weight is achieved.

7.3.1 Aluminum solution, stock 1 mL = 1000 μg Al: Pickle aluminum metal in warm (1+1) HCl to an exact weight of 0.100 g. Dissolve in 10 mL conc. HCl and 2 mL conc. nitric acid, heating to effect solution. Continue heating until volume is reduced to 4 mL. Cool and add 4 mL ASTM type I water. Heat until the volume is reduced to 2 mL. Cool and dilute to 100 mL with ASTM type I water.

7.3.2 Antimony solution, stock 1 mL = 1000 μg Sb: Dissolve 0.100 g antimony powder in 2 mL (1+1) nitric acid and 0.5 mL conc. hydrochloric acid, heating to effect solution. Cool, add 20 mL ASTM type I water and 0.15 g tartaric acid. Warm the solution to dissolve the white precipitate. Cool and dilute to 100 mL with ASTM type I water.

7.3.3 Arsenic solution, stock 1 mL = 1000 μg As: Dissolve 0.1320 g As_2O_3 in a mixture of 50 mL ASTM type I water and 1 mL conc. ammonium hydroxide. Heat gently to dissolve. Cool and acidify the solution with 2 mL conc. nitric acid. Dilute to 100 mL with ASTM type I water.

7.3.4 Barium solution, stock 1 mL = 1000 μg Ba: Dissolve 0.1437 g $BaCO_3$ in a solution mixture of 10 mL ASTM type I water and 2 mL conc. nitric acid. Heat and stir to effect solution and degassing. Dilute to 100 mL with ASTM type I water.

7.3.5 Beryllium solution, stock 1 mL = 1000 μg Be: Dissolve 1.965 g $BeSO_4.4H_2O$ (DO NOT DRY) in 50 mL ASTM Type I water. Add 1 mL conc. nitric acid. Dilute to 100 mL with ASTM type I water.

7.3.6 Bismuth solution, stock 1 mL = 1000 μg Bi: Dissolve 0.1115 g Bi_2O_3 in 5 mL conc. nitric acid. Heat to effect solution. Cool and dilute to 100 mL with ASTM type I water.

7.3.7 Cadmium solution, stock 1 mL = 1000 μg Cd: Pickle cadmium metal in (1+9) nitric acid to an exact weight of 0.100 g. Dissolve in 5 mL (1+1) nitric acid, heating to effect solution. Cool and dilute to 100 mL with ASTM type I water.

7.3.8 Chromium solution, stock 1 mL = 1000 μg Cr: Dissolve 0.1923 g CrO_3 in a solution mixture of 10 mL ASTM type I water and 1 mL conc. nitric acid. Dilute to 100 mL with ASTM type I water.

7.3.9 Cobalt solution, stock 1 mL = 1000 μg Co: Pickle cobalt metal in (1+9) nitric acid to an exact weight of 0.100 g. Dissolve in 5 mL (1+1) nitric acid, heating to effect solution. Cool and dilute to 100 mL with ASTM type I water.

7.3.10 Copper solution, stock 1 mL = 1000 μg Cu: Pickle copper metal in (1+9) nitric acid to an exact weight of 0.100 g. Dissolve in 5 mL (1+1) nitric acid, heating to effect solution. Cool and dilute to 100 mL with ASTM type I water.

7.3.11 Indium solution, stock 1 mL = 1000 μg In: Pickle indium metal in (1+1) nitric acid to an exact weight of 0.100 g. Dissolve in 10 mL (1+1) nitric acid, heating to effect solution. Cool and dilute to 100 mL with ASTM type I water.

7.3.12 Lead solution, stock 1 mL = 1000 μg Pb: Dissolve 0.1599 g $PbNO_3$ in 5 mL (1+1) nitric acid. Dilute to 100 mL with ASTM type I water.

7.3.13 Magnesium solution, stock 1 mL = 1000 μg Mg: Dissolve 0.1658 g MgO in 10 mL (1+1) nitric acid, heating to effect solution. Cool and dilute to 100 mL with ASTM type I water.

7.3.14 Manganese solution, stock 1 mL = 1000 μg Mn: Pickle manganese flake in (1+9) nitric acid to an exact weight of 0.100 g. Dissolve in 5 mL (1+1) nitric acid, heating to effect solution. Cool and dilute to 100 mL with ASTM type I water.

7.3.15 Molybdenum solution, stock 1 mL = 1000 μg Mo: Dissolve 0.1500 g MoO_3 in a solution mixture of 10 mL ASTM type I water and 1 mL conc. ammonium hydroxide., heating to effect solution. Cool and dilute to 100 mL with ASTM type I water.

7.3.16 Nickel solution, stock 1 mL = 1000 μg Ni: Dissolve 0.100 g nickel powder in 5 mL conc. nitric acid, heating to effect solution. Cool and dilute to 100 mL with ASTM type I water.

7.3.17 Scandium solution, stock 1 mL = 1000 μg Sc: Dissolve 0.1534 g Sc_2O_3 in 5 mL (1+1) nitric acid, heating to effect solution. Cool and dilute to 100 mL with ASTM type I water.

7.3.18 Selenium solution, stock 1 mL = 1000 μg Se: Dissolve 0.1405 g SeO_2 in 20 mL ASTM type I water. Dilute to 100 mL with ASTM type I water.

7.3.19 Silver solution, stock 1 mL = 1000 μg Ag: Dissolve 0.100 g silver metal in 5 mL (1+1) nitric acid, heating to effect solution. Cool and dilute to 100 mL with ASTM type I water. Store in dark container.

7.3.20 Terbium solution, stock 1 mL = 1000 μg Tb: Dissolve 0.1176 g Tb_4O_7 in 5 mL conc. nitric acid, heating to effect solution. Cool and dilute to 100 mL with ASTM type I water.

7.3.21 Thallium solution, stock 1 mL = 1000 µg Tl: Dissolve 0.1303 g $TlNO_3$ in a solution mixture of 10 mL ASTM type I water and 1 mL conc. nitric acid. Dilute to 100 mL with ASTM type I water.

7.3.22 Thorium solution, stock 1 mL = 1000 µg Th: Dissolve 0.2380 g $Th(NO_3)_4.4H_2O$ (DO NOT DRY) in 20 mL ASTM type I water. Dilute to 100 mL with ASTM type I water.

7.3.23 Uranium solution, stock 1 mL = 1000 µg U: Dissolve 0.2110 g $UO_2(NO_3)_2.6H_2O$ (DO NOT DRY) in 20 mL ASTM type I water and dilute to 100 mL with ASTM type I water.

7.3.24 Vanadium solution, stock 1 mL = 1000 µg V: Pickle vanadium metal in (1+9) nitric acid to an exact weight of 0.100 g. Dissolve in 5 mL (1+1) nitric acid, heating to effect solution. Cool and dilute to 100 mL with ASTM type I water.

7.3.25 Yttrium solution, stock 1 mL = 1000 µg Y: Dissolve 0.1270 g Y_2O_3 in 5 mL (1+1) nitric acid, heating to effect solution. Cool and dilute to 100 mL with ASTM type I water.

7.3.26 Zinc solution, stock 1 mL = 1000 µg Zn: Pickle zinc metal in (1+9) nitric acid to an exact weight of 0.100 g. Dissolve in 5 mL (1+1) nitric acid, heating to effect solution. Cool and dilute to 100 mL with ASTM type I water.

7.4 MULTIELEMENT STOCK STANDARD SOLUTIONS - Care must be taken in the preparation of multielement stock standards that the elements are compatible and stable. Originating element stocks should be checked for the presence of impurities which might influence the accuracy of the standard. Freshly prepared standards should be transferred to acid cleaned, not previously used FEP fluorocarbon bottles for storage and monitored periodically for stability. The following combinations of elements are suggested:

Standard Solution A		Standard Solution B
Aluminum	Manganese	Barium
Antimony	Molybdenum	Silver
Arsenic	Nickel	
Beryllium	Selenium	
Cadmium	Thallium	
Chromium	Thorium	
Cobalt	Uranium	
Copper	Vanadium	
Lead	Zinc	

Multielement stock standard solutions A and B (1 mL = 10 µg) may be prepared by diluting 1 mL of each single element stock in the

combination list to 100 mL with ASTM type I water containing 1% (v/v) nitric acid.

7.4.1 Preparation of calibration standards - fresh multielement calibration standards should be prepared every two weeks or as needed. Dilute each of the stock multielement standard solutions A and B to levels appropriate to the operating range of the instrument using ASTM type I water containing 1% (v/v) nitric acid. The element concentrations in the standards should be sufficiently high to produce good measurement precision and to accurately define the slope of the response curve. Concentrations of 200 µg/L are suggested. If the direct addition procedure is being used (Method A, Sect. 9.2), add internal standards (Sect. 7.5) to the calibration standards and store in Teflon bottles. Calibration standards should be verified initially using a quality control sample (Sect. 7.8).

7.5 INTERNAL STANDARDS STOCK SOLUTION, 1 mL = 100 µg. Dilute 10 mL of scandium, yttrium, indium, terbium and bismuth stock standards (Sect. 7.3) to 100 mL with ASTM type I water, and store in a Teflon bottle. Use this solution concentrate for addition to blanks, calibration standards and samples, or dilute by an appropriate amount using 1% (v/v) nitric acid, if the internal standards are being added by peristaltic pump (Method B, Sect. 9.2).

7.6 BLANKS - Three types of blanks are required for this method. A calibration blank is used to establish the analytical calibration curve, the laboratory reagent blank is used to assess possible contamination from the sample preparation procedure and to assess spectral background and the rinse blank is used to flush the instrument between samples in order to reduce memory interferences.

7.6.1 Calibration blank - Consists of 1% (v/v) nitric acid in ASTM type I water. If the direct addition procedure (Method A, Sect. 9.2), is being used add internal standards.

7.6.2 Laboratory reagent blank (LRB) - Must contain all the reagents in the same volumes as used in processing the samples. The LRB must be carried through the entire sample digestion and preparation scheme. If the direct addition procedure (Method A, Sect. 9.2) is being used, add internal standards to the solution after preparation is complete.

7.6.3 Rinse blank - Consists of 2% (v/v) nitric acid in ASTM type I water.

7.7 TUNING SOLUTION - This solution is used for instrument tuning and mass calibration prior to analysis. The solution is prepared by mixing beryllium, magnesium, cobalt, indium and lead stock solutions (Sect. 7.3) in 1% (v/v) nitric acid to produce a concentration of

100 µg/L of each element. Internal standards are not added to this solution.

7.8 QUALITY CONTROL SAMPLE (QCS) - The QCS should be obtained from a source outside the laboratory. Dilute an appropriate aliquot of analytes (concentrations not to exceed 1000 µg/L), in 1% (v/v) nitric acid. If the direct addition procedure (Method A, Sect. 9.2) is being used, add internal standards after dilution, mix and store in a Teflon bottle.

7.9 LABORATORY FORTIFIED BLANK (LFB) - To an aliquot of LRB, add aliquots from multielement stock standards A and B (Sect. 7.4) to produce a final concentration of 100 µg/L for each analyte. The LFB must be carried through the entire sample digestion and preparation scheme. If the direct addition procedure (Method A, Sect. 9.2) is being used, add internal standards to this solution after preparation has been completed.

8. SAMPLE COLLECTION, PRESERVATION AND STORAGE

8.1 Prior to sample collection, consideration should be given to the type of data required so that appropriate preservation and pretreatment steps can be taken. Filtration, acid preservation, etc., should be performed at the time of sample collection or as soon thereafter as practically possible.

8.2 For the determination of dissolved elements, the sample should be filtered through a 0.45-µm membrane filter. Use a portion of the sample to rinse the filter assembly, discard and then collect the required volume of filtrate. Acidify the filtrate with (1+1) nitric acid immediately following filtration to pH < 2.

8.3 For the determination of total recoverable elements in aqueous samples, acidify with (1+1) nitric acid at the time of collection to pH < 2 (normally, 3 mL of (1+1) nitric acid per liter of sample is sufficient for most ambient and drinking water samples). The sample should not be filtered prior to analysis.

NOTE: Samples that cannot be acid preserved at the time of collection because of sampling limitations or transport restrictions, should be acidified with nitric acid to pH < 2 upon receipt in the laboratory. Following acidification, the sample should be held for 16 h before withdrawing an aliquot for sample processing.

8.4 Solid samples usually require no preservation prior to analysis other than storage at 4°C.

9. CALIBRATION AND STANDARDIZATION

9.1 CALIBRATION - Demonstration and documentation of acceptable initial calibration is required before any samples are analyzed and is required periodically throughout sample analysis as dictated by results of continuing calibration checks. After initial calibration is successful, a calibration check is required at the beginning and end of each period during which analyses are performed, and at requisite intervals.

9.1.1 Initiate proper operating configuration of instrument and data system. Allow a period of not less than 30 min for the instrument to warm up. During this process conduct mass calibration and resolution checks using the tuning solution. Resolution at low mass is indicated by magnesium isotopes 24,25,26. Resolution at high mass is indicated by lead isotopes 206,207,208. For good performance adjust spectrometer resolution to produce a peak width of approximately 0.75 amu at 5% peak height. Adjust mass calibration if it has shifted by more than 0.1 amu from unit mass.

9.1.2 Instrument stability must be demonstrated by running the tuning solution (Sect. 7.7) a minimum of five times with resulting relative standard deviations of absolute signals for all analytes of less than 5%.

9.1.3 Prior to initial calibration, set up proper instrument software routines for quantitative analysis. The instrument must be calibrated for the analytes to be determined using the calibration blank (Sect. 7.6.1) and calibration standards A and B (Sect. 7.4.1) prepared at one or more concentration levels. A minimum of three replicate integrations are required for data acquisition. Use the average of the integrations for instrument calibration and data reporting.

9.1.4 The rinse blank should be used to flush the system between solution changes for blanks, standards and samples. Allow sufficient rinse time to remove traces of the previous sample or a minimum of 1 min. Solutions should be aspirated for 30 sec prior to the acquisition of data to allow equilibrium to be established.

9.2 INTERNAL STANDARDIZATION - Internal standardization must be used in all analyses to correct for instrument drift and physical interferences. A list of acceptable internal standards is provided in Table 3. For full mass range scans, a minimum of three internal standards must be used. Procedures described in this method for general application, detail the use of five internal standards; scandium, yttrium, indium, terbium and bismuth. These were used to generate the precision and recovery data attached to this method. Internal standards must be present in all samples, standards and

blanks at identical levels. This may be achieved by directly adding an aliquot of the internal standards to the CAL standard, blank or sample solution (Method A, Sect. 9.2), or alternatively by mixing with the solution prior to nebulization using a second channel of the peristaltic pump and a mixing coil (Method B, Sect. 9.2). The concentration of the internal standard should be sufficiently high that good precision is obtained in the measurement of the isotope used for data correction and to minimize the possibility of correction errors if the internal standard is naturally present in the sample. A concentration of 200 µg/L of each internal standard is recommended. Internal standards should be added to blanks, samples and standards in a like manner, so that dilution effects resulting from the addition may be disregarded.

9.3 INSTRUMENT PERFORMANCE - Check the performance of the instrument and verify the calibration using data gathered from analyses of calibration blanks, calibration standards and the quality control sample (QCS).

9.3.1 After the calibration has been established, it must be initially verified for all analytes by analyzing the QCS (Sect. 7.8). If measurements exceed ± 10% of the established QCS value, the analysis should be terminated, the source of the problem identified and corrected, the instrument recalibrated and the calibration reverified before continuing analyses.

9.3.2 To verify that the instrument is properly calibrated on a continuing basis, run the calibration blank and calibration standards as surrogate samples after every ten analyses. The results of the analyses of the standards will indicate whether the calibration remains valid. If the indicated concentration of any analyte deviates from the true concentration by more than 10%, reanalyze the standard. If the analyte is again outside the 10% limit, the instrument must be recalibrated and the previous ten samples reanalyzed. The instrument responses from the calibration check may be used for recalibration purposes. If the sample matrix is responsible for the calibration drift, it is recommended that the previous ten samples are reanalyzed in groups of five between calibration checks to prevent a similar drift situation from occurring.

10. QUALITY CONTROL

10.1 Each laboratory using this method is required to operate a formal quality control (QC) program. The minimum requirements of this program consist of an initial demonstration of laboratory capability, and the analysis of laboratory reagent blanks, fortified blanks and samples as a continuing check on performance. The

laboratory is required to maintain performance records that define the quality of the data thus generated.

10.2 INITIAL DEMONSTRATION OF PERFORMANCE

10.2.1 The initial demonstration of performance is used to characterize instrument performance (method detection limits and linear calibration ranges) for analyses conducted by this method.

10.2.2 Method detection limits (MDL) should be established for all analytes, using reagent water (blank) fortified at a concentration of two to five times the estimated detection limit. To determine MDL values, take seven replicate aliquots of the fortified reagent water and process through the entire analytical method. Perform all calculations defined in the method and report the concentration values in the appropriate units. Calculate the MDL as follows:

$$MDL = (t) \times (S)$$

where, t = Student's t value for a 99% confidence level and a standard deviation estimate with n-1 degrees of freedom [t = 3.14 for seven replicates].

S = standard deviation of the replicate analyses.

MDLs should be determined every six months or whenever a significant change in background or instrument response is expected (e.g., detector change).

10.2.3 Linear calibration ranges - Linear calibration ranges are primarily detector limited. The upper limit of the linear calibration range should be established for each analyte by determining the signal responses from a minimum of three different concentration standards, one of which is close to the upper limit of the linear range. Care should be taken to avoid potential damage to the detector during this process. The linear calibration range which may be used for the analysis of samples should be judged by the analyst from the resulting data. Linear calibration ranges should be determined every six months or whenever a significant change in instrument response is expected (e.g., detector change).

10.3 ASSESSING LABORATORY PERFORMANCE - REAGENT AND FORTIFIED BLANKS

10.3.1 Laboratory reagent blank (LRB) - The laboratory must analyze at least one LRB (Sect. 7.6.2) with each set of samples. LRB data are used to assess contamination from the laboratory environment and to characterize spectral background from the reagents used in sample processing. If an analyte value in the reagent blank exceeds its determined MDL, then laboratory

or reagent contamination should be suspected. Any determined source of contamination should be corrected and the samples reanalyzed.

10.3.2 Laboratory fortified blank (LFB) - The laboratory must analyze at least one LFB (Sect. 7.9) with each batch of samples. Calculate accuracy as percent recovery (Sect. 10.4.2) If the recovery of any analyte falls outside the control limits (Sect. 10.3.3), that analyte is judged out of control, and the source of the problem should be identified and resolved before continuing analyses.

10.3.3 Until sufficient LFB data become available (usually a minimum of 20 to 30 analyses), the laboratory should assess laboratory performance against recovery limits of 85-115%. When sufficient internal performance data becomes available, develop control limits from the percent mean recovery (x) and the standard deviation (S) of the mean recovery. These data are used to establish upper and lower control limits as follows:

$$\text{UPPER CONTROL LIMIT} = x + 3S$$
$$\text{LOWER CONTROL LIMIT} = x - 3S$$

After each five to ten new recovery measurements, new control limits should be calculated using only the most recent twenty to 30 data points.

10.4 ASSESSING ANALYTE RECOVERY - LABORATORY FORTIFIED SAMPLE MATRIX

10.4.1 The laboratory must add a known amount of analyte to a minimum of 10% of the routine samples or one sample per sample set, whichever is greater. Ideally for water samples, the analyte concentration should be the same as that used in the LFB (Sect. 10.3.2). For solid samples, the concentration added should be 50 mg/kg equivalent (100 µg/L in the analysis solution). Over time, samples from all routine sample sources should be fortified.

10.4.2 Calculate the percent recovery for each analyte, corrected for background concentrations measured in the unfortified sample, and compare these values to the control limits established in Sect. 10.3.3 for the analyses of LFBs. Recovery calculations are not required if the concentration of the analyte added is less than 10% of the sample background concentration. Percent recovery may be calculated in units appropriate to the matrix, using the following equation:

$$R = \frac{C_s - C}{s} \times 100$$

where, R = percent recovery
C_s = fortified sample concentration
C = sample background concentration
s = concentration equivalent of fortifier added to sample.

10.4.3 If recovery of any analyte falls outside the designated range and laboratory performance for that analyte is shown to be in control (Sect. 10.3), the recovery problem encountered with the fortified sample is judged to be matrix related, not system related. The result for that analyte in the unfortified sample must be labelled "suspect/matrix" to inform the data user that the results are suspect due to matrix effects.

10.5 INTERNAL STANDARDS RESPONSES - The analyst is expected to monitor the responses from the internal standards throughout the sample set being analyzed. Ratios of the internal standards responses against each other should also be monitored routinely. This information may be used to detect potential problems caused by mass dependent drift, errors incurred in adding the internal standards or increases in the concentrations of individual internal standards caused by background contributions from the sample. The absolute response of any one internal standard should not deviate more than 60-125% of the original response in the calibration blank. If deviations greater than this are observed, use the following test procedure:

10.5.1 Flush the instrument with the rinse blank and monitor the responses in the calibration blank. If the responses of the internal standards are now within the limit, take a fresh aliquot of the sample, dilute by a further factor of two, add the internal standards and reanalyze.

10.5.2 If test (Sect. 10.5.1) is not satisfied, or if it is a blank or calibration standard that is out of limits, terminate the analysis, and determine the cause of the drift. Possible causes of drift may be a partially blocked sampling cone or a change in the tuning condition of the instrument.

11. PROCEDURE

11.1 SAMPLE PREPARATION - DISSOLVED ELEMENTS

11.1.1 For determination of dissolved elements in drinking water, ground and surface waters, take a 100 mL aliquot of the filtered acid preserved sample, and add 1 mL of concentrated nitric acid. If the direct addition procedure (Method A) is being used, add internal standards and mix. The sample is now ready for analysis. Allowance for sample dilution should be made in the calculations.

NOTE: If a precipitate is formed during acidification, transport or storage, the sample aliquot must be treated using the procedure in Sect. 11.2.1 prior to analysis.

11.2 SAMPLE PREPARATION - TOTAL RECOVERABLE ELEMENTS

11.2.1 For determination of total recoverable elements in water or wastewater, take a 100 mL aliquot from a well mixed, acid preserved sample containing not more than 0.25% (w/v) total solids and transfer to a 250-mL Griffin beaker (if total solids are greater than 0.25% reduce the size of the aliquot by a proportionate amount). Add 1 mL of conc. nitric acid and 0.5 mL conc. hydrochloric acid. Heat on a hot plate at 85°C until the volume has been reduced to approximately 20 mL, ensuring that the sample does not boil. A spare beaker containing 20 mL of water can be used as a guage. (NOTE: Adjust the temperature control of the hot plate such that an uncovered beaker containing 50 mL of water located in the center of the hot plate can be maintained at a temperature no higher than 85°C. Evaporation time for 100 mL of sample at 85°C is approximately 2 h with the rate of evaporation increasing rapidly as the sample volume approaches 20 mL). Cover the beaker with a watch glass and reflux for 30 min. Slight boiling may occur but vigorous boiling should be avoided. Allow to cool and quantitatively transfer to either a 50-mL volumetric flask or 50-mL class A stoppered graduated cylinder. Dilute to volume with ASTM type I water and mix. Centrifuge the sample or allow to stand overnight to separate insoluble material. Prior to analysis, pipette 20 mL into a 50-mL volumetric flask, dilute to volume with ASTM type I water and mix. If the direct addition procedure (Method A, Sect. 9.2) is being used, add internal standards and mix. The sample is now ready for analysis. Because the stability of diluted samples cannot be fully characterized, all analyses should be performed as soon as possible after the completed preparation.

11.2.2 For determination of total recoverable elements in solid samples (sludge, soils, and sediments), mix the sample thoroughly to achieve homogeneity and weigh accurately a 1.0 ± 0.01 g portion of the sample. Transfer to a 250-mL Phillips beaker. Add 4 mL (1+1) nitric acid and 10 mL (1+4) HCl. Cover with a watch glass, and reflux the sample on a hot plate for 30 min. Very slight boiling may occur, however, vigorous boiling must be avoided to prevent the loss of the $HCl-H_2O$ azeotrope. (NOTE: Adjust the temperature control of the hot plate such that an uncovered Griffin beaker containing 50 mL of water located in the center of the hot plate can be maintained at a temperature of approximately but no higher than 85°C). Allow the sample to cool, and quantitatively transfer to a 100-mL volumetric flask. Dilute

to volume with ASTM type I water and mix. Centrifuge the sample or allow to stand overnight to separate insoluble material. Prior to analysis, pipette 10 mL into a 50-mL volumetric flask and dilute to volume with ASTM type I water. If the direct addition procedure (Method A, Sect. 9.2) is being used, add internal standards and mix. The sample is now ready for analysis. Because the effects of various matrices on the stability of diluted samples cannot be characterized, all analyses should be performed as soon as possible after the completed preparation.

NOTE: Determine the percent solids in the sample for use in calculations and for reporting data on a dry weight basis.

11.3 For every new or unusual matrix, it is highly recommended that a semi-quantitative analysis be carried out to screen for high element concentrations. Information gained from this may be used to prevent potential damage to the detector during sample analysis and to identify elements which may be higher than the linear range. Matrix screening may be carried out by using intelligent software, if available, or by diluting the sample by a factor of 500 and analyzing in a semi-quantitative mode. The sample should also be screened for background levels of all elements chosen for use as internal standards in order to prevent bias in the calculation of the analytical data.

11.4 Initiate instrument operating configuration. Tune and calibrate the instrument for the analytes of interest (Sect. 9).

11.5 Establish instrument software run procedures for quantitative analysis. For all sample analyses, a minimum of three replicate integrations are required for data acquisition. Discard any integrations which are considered to be statistical outliers and use the average of the integrations for data reporting.

11.6 All masses which might affect data quality must be monitored during the analytical run. As a minimum, those masses prescribed in Table 4 must be monitored in the same scan as is used for the collection of the data. This information should be used to correct the data for identified interferences.

11.7 The rinse blank should be used to flush the system between samples. Allow sufficient time to remove traces of the previous sample or a minimum of one minute. Samples should be aspirated for 30 sec prior to the collection of data.

11.8 Samples having concentrations higher than the established linear dynamic range should be diluted into range and reanalyzed. The sample should first be analyzed for the trace elements in the sample, protecting the detector from the high concentration elements, if necessary, by the selection of appropriate scanning windows. The sample should then be diluted for the determination of

the remaining elements. Alternatively, the dynamic range may be adjusted by selecting an alternative isotope of lower natural abundance, provided quality control data for that isotope have been established. The dynamic range must not be adjusted by altering instrument conditions to an uncharacterized state.

12. CALCULATIONS

12.1 Elemental equations recommended for sample data calculations are listed in Table 5. Sample data should be reported in units of µg/L for aqueous samples or mg/kg dry weight for solid samples. Do not report element concentrations below the determined MDL.

12.2 For data values less than ten, two significant figures should be used for reporting element concentrations. For data values greater than or equal to ten, three significant figures should be used.

12.3 Reported values should be calibration blank subtracted. For aqueous samples prepared by total recoverable procedure (Sect. 11.2.1), multiply solution concentrations by the dilution factor 1.25. For solid samples prepared by total recoverable procedure (Sect. 11.2.2), multiply solution concentrations (µg/L in the analysis solution) by the dilution factor 0.5. If additional dilutions were made to any samples, the appropriate factor should be applied to the calculated sample concentrations.

12.4 Data values should be corrected for instrument drift or sample matrix induced interferences by the application of internal standardization. Corrections for characterized spectral interferences should be applied to the data. Chloride interference corrections should be made on all samples, regardless of the addition of hydrochloric acid, as the chloride ion is a common constituent of environmental samples.

12.5 If an element has more than one monitored isotope, examination of the concentration calculated for each isotope, or the isotope ratios, will provide useful information for the analyst in detecting a possible spectral interference. Consideration should therefore be given to both primary and secondary isotopes in the evaluation of the element concentration. In some cases, secondary isotopes may be less sensitive or more prone to interferences than the primary recommended isotopes, therefore differences between the results do not necessarily indicate a problem with data calculated for the primary isotopes.

12.6 The QC data obtained during the analyses provide an indication of the quality of the sample data and should be provided with the sample results.

13. PRECISION AND ACCURACY

13.1 Instrument operating conditions used for single laboratory testing of the method are summarized in Table 6. Total recoverable MDLs determined using the procedure described in Sect. 10.2.2, are listed in Table 7.

13.2 Data obtained from single laboratory testing of the method are summarized in Table 8 for five water samples representing drinking water, surface water, ground water and waste effluent. Samples were prepared using the procedure described in Sect. 11.2.1. For each matrix, five replicates were analyzed and the average of the replicates used for determining the sample background concentration for each element. Two further pairs of duplicates were fortified at different concentration levels. For each method element, the sample background concentration, mean percent recovery, the standard deviation of the percent recovery and the relative percent difference between the duplicate fortified samples are listed in Table 8.

13.3 Data obtained from single laboratory testing of the method are summarized in Table 9 for three solid samples consisting of SRM 1645 River Sediment, EPA Hazardous Soil and EPA Electroplating Sludge. Samples were prepared using the procedure described in Sect. 11.2.2. For each method element, the sample background concentration, mean percent recovery, the standard deviation of the percent recovery and the relative percent difference between the duplicate fortified samples were determined as for Sect. 13.2.

14. REFERENCES

1. A. L. Gray and A. R. Date, *Analyst* 108 1033 (1983).
2. R. S. Houk et al. *Anal Chem.* 52 2283 (1980).
3. R. S. Houk, *Anal. Chem.* 58 97A (1986).
4. J. J. Thompson and R. S. Houk, *Appl. Spec.* 41 801 (1987).
5. "OSHA Safety and Health Standards, General Industry," (29 CFR 1910), Occupational Safety and Health Administration, OSHA 2206, revised January 1976.
6. "Proposed OSHA Safety and Health Standards, Laboratories," Occupational Safety and Health Administration, Federal Register, July 24, 1986.
7. Code of Federal Regulations 40, Ch. 1, Pt. 136 Appendix B.

TABLE 1: ESTIMATED INSTRUMENT DETECTION LIMITS

ELEMENT	RECOMMENDED ANALYTICAL MASS	ESTIMATED IDL (μg/L)
Aluminum	27	0.05
Antimony	121	0.08
Arsenic	75	0.9
Barium	137	0.5
Beryllium	9	0.1
Cadmium	111	0.1
Chromium	52	0.07
Cobalt	59	0.03
Copper	63	0.03
Lead	206.207,208	0.08
Manganese	55	0.1
Molybdenum	98	0.1
Nickel	60	0.2
Selenium	82	5
Silver	107	0.05
Thallium	205	0.09
Thorium	232	0.03
Uranium	238	0.02
Vanadium	51	0.02
Zinc	66	0.2

Instrument detection limits (3σ) estimated from seven replicate integrations of the blank (1% v/v nitric acid) following calibration of the instrument with three replicate integrations of a multi-element standard.

TABLE 2: COMMON MOLECULAR ION INTERFERENCES IN ICP-MS

BACKGROUND MOLECULAR IONS		
Molecular Ion	Mass	Element Interference[a]
NH^+	15	
OH^+	17	
OH_2^+	18	
C_2^+	24	
CN^+	26	
CO^+	28	
N_2^+	28	
N_2H^+	29	
NO^+	30	
NOH^+	31	
O_2^+	32	
O_2H^+	33	
$^{36}ArH^+$	37	
$^{38}ArH^+$	39	
$^{40}ArH^+$	41	
CO_2^+	44	
CO_2H^+	45	Sc
ArC^+, ArO^+	52	Cr
ArN^+	54	Cr
$ArNH^+$	55	Mn
ArO^+	56	
$ArOH^+$	57	
$^{40}Ar^{36}Ar^+$	76	Se
$^{40}Ar^{38}Ar^+$	78	Se
$^{40}Ar_2^+$	80	Se

[a] method elements or internal standards affected by the molecular ions.

TABLE 2 (Continued).

MATRIX MOLECULAR IONS

CHLORIDE Molecular Ion	Mass	Element Interference
$^{35}ClO^+$	51	V
$^{35}ClOH^+$	52	Cr
$^{37}ClO^+$	53	Cr
$^{37}ClOH^+$	54	Cr
$Ar^{35}Cl^+$	75	As
$Ar^{37}Cl^+$	77	Se

SULPHATE Molecular Ion	Mass	Element Interference
$^{32}SO^+$	48	
$^{32}SOH^+$	49	
$^{34}SO^+$	50	V,Cr
$^{34}SOH^+$	51	V
SO_2^+, S_2^+	64	Zn
$Ar^{32}S^+$	72	
$Ar^{34}S^+$	74	

PHOSPHATE Molecular Ion	Mass	Element Interference
PO^+	47	
POH^+	48	
PO_2^+	63	Cu
ArP^+	71	

GROUP I, II METALS Molecular Ion	Mass	Element Interference
$ArNa^+$	63	Cu
ArK^+	79	
$ArCa^+$	80	

MATRIX OXIDES* Molecular Ion	Masses	Element Interference
TiO	62-66	Ni,Cu,Zn
ZrO	106-112	Ag,Cd
MoO	108-116	Cd

* Oxide interferences will normally be very small and will only impact the method elements when present at relatively high concentrations. Some examples of matrix oxides are listed of which the analyst should be aware. It is recommended that Ti and Zr isotopes are monitored in solid waste samples, which are likely to contain high levels of these elements. Mo is monitored as a method analyte.

TABLE 3: INTERNAL STANDARDS AND LIMITATIONS OF USE

Internal Standard	Mass	Possible Limitation
^{6}Lithium	6	a
Scandium	45	polyatomic ion interference
Yttrium	89	a,b
Rhodium	103	
Indium	115	isobaric interference by Sn
Terbium	159	
Holmium	165	
Lutetium	175	
Bismuth	209	a

a May be present in environmental samples.
b In some instruments Yttrium may form measurable amounts of YO^{+} (105 amu) and YOH^{+} (106 amu). If this is the case, care should be taken in the use of the cadmium elemental correction equation.

Internal standards recommended for use with this method are shown in bold face. Preparation procedures for these are included in section 7.3.

TABLE 4: RECOMMENDED ANALYTICAL ISOTOPES AND ADDITIONAL MASSES WHICH MUST BE MONITORED

Isotope	Element of Interest
27	Aluminum
121,123	Antimony
75	Arsenic
135,137	Barium
9	Beryllium
106,108,111,114	Cadmium
52,53	Chromium
59	Cobalt
63,65	Copper
206,207,208	Lead
55	Manganese
95,97,98	Molybdenum
60,62	Nickel
77,82	Selenium
107,109	Silver
203,205	Thallium
232	Thorium
238	Uranium
51	Vanadium
66,67,68	Zinc
83	Krypton
99	Ruthenium
105	Palladium
118	Tin

NOTE: Isotopes recommended for analytical determination are underlined.

TABLE 5: RECOMMENDED ELEMENTAL EQUATIONS FOR DATA CALCULATIONS

Element	Elemental Equation	Note
Al	$(1.000)(^{27}C)$	
Sb	$(1.000)(^{121}C)$	
As	$(1.000)(^{75}C)-(3.127)[(^{77}C)-(0.815)(^{82}C)]$	(1)
Ba	$(1.000)(^{137}C)$	
Be	$(1.000)(^{9}C)$	
Cd	$(1.000)(^{111}C)-(1.073)[(^{108}C)-(0.712)(^{106}C)]$	(2)
Cr	$(1.000)(^{52}C)$	(3)
Co	$(1.000)(^{59}C)$	
Cu	$(1.000)(^{63}C)$	
Pb	$(1.000)(^{206}C)+(1.000)(^{207}C)+(1.000)(^{208}C)$	(4)
Mn	$(1.000)(^{55}C)$	
Mo	$(1.000)(^{98}C)-(0.146)(^{99}C)$	(5)
Ni	$(1.000)(^{60}C)$	
Se	$(1.000)(^{82}C)$	(6)
Ag	$(1.000)(^{107}C)$	
Tl	$(1.000)(^{205}C)$	
Th	$(1.000)(^{232}C)$	
U	$(1.000)(^{238}C)$	
V	$(1.000)(^{51}C)-(3.127)[(^{53}C)-(0.113)(^{52}C)]$	(7)
Zn	$(1.000)(^{66}C)$	

Cont.

TABLE 5 (Continued)

INTERNAL STANDARDS

Element	Elemental Equation	Note
Bi	$(1.000)(^{209}C)$	
In	$(1.000)(^{115}C)-(0.016)(^{118}C)$	(8)
Sc	$(1.000)(^{45}C)$	
Tb	$(1.000)(^{159}C)$	
Y	$(1.000)(^{89}C)$	

C - calibration blank subtracted counts at specified mass.
(1) - correction for chloride interference with adjustment for Se77. ArCl 75/77 ratio may be determined from the reagent blank.
(2) - correction for MoO interference. An additional isobaric elemental correction should be made if palladium is present.
(3) - in 0.4% v/v HCl, the background from ClOH will normally be small. However the contribution may be estimated from the reagent blank.
(4) - allowance for isotopic variability of lead isotopes.
(5) - isobaric elemental correction for ruthenium.
(6) - some argon supplies contain krypton as an impurity. Selenium is corrected for Kr82 by background subtraction.
(7) - correction for chloride interference with adjustment for Cr53. ClO 51/53 ratio may be determined from the reagent blank.
(8) - isobaric elemental correction for tin.

TABLE 6: INSTRUMENT OPERATING CONDITIONS FOR PRECISION AND RECOVERY DATA

Instrument	VG PlasmaQuad Type I
Plasma forward power	1.35 kW
Coolant flow rate	13.5 L/min
Auxiliary flow rate	0.6 L/min
Nebulizer flow rate	0.78 L/min
Solution uptake rate	0.6 mL/min
Spray chamber temperature	15°C
Data Acquisition	
Detector mode	Pulse counting
Replicate integrations	3
Mass range	8 - 240 amu
Dwell time	320 μs
Number of MCA channels	2048
Number of scan sweeps	85
Total acquisition time	3 minutes per sample

TABLE 7: TOTAL RECOVERABLE METHOD DETECTION LIMITS

ELEMENT	RECOMMENDED ANALYTICAL MASS	MDL* AQUEOUS µg/L	MDL* SOLIDS mg/kg
Aluminum	27	1.0	0.4
Antimony	121	0.4	0.2
Arsenic	75	1.4	0.6
Barium	137	0.8	0.4
Beryllium	9	0.3	0.1
Cadmium	111	0.5	0.2
Chromium	52	0.9	0.4
Cobalt	59	0.09	0.04
Copper	63	0.5	0.2
Lead	206,207,208	0.6	0.3
Manganese	55	0.1	0.05
Molybdenum	98	0.3	0.1
Nickel	60	0.5	0.2
Selenium	82	7.9	3.2
Silver	107	0.1	0.05
Thallium	205	0.3	0.1
Thorium	232	0.1	0.05
Uranium	238	0.1	0.05
Vanadium	51	2.5	1.0
Zinc	66	1.8	0.7

* MDL concentrations are computed for original matrix with allowance for sample dilution during preparation.

TABLE 8 : PRECISION AND RECOVERY DATA IN AQUEOUS MATRICES

DRINKING WATER

Element	Sample Concn. (µg/L)	Low Spike (µg/L)	Average Recovery R (%)	S(R)	RPD	High Spike (µg/L)	Average Recovery R (%)	S(R)	RPD
Al	175	50	115.8	5.9	0.4	200	102.7	1.6	1.1
Sb	<0.4	10	99.1	0.7	2.0	100	100.8	0.7	2.0
As	<1.4	50	99.7	0.8	2.2	200	102.5	1.1	2.9
Ba	43.8	50	94.8	3.9	5.8	200	95.6	0.8	1.7
Be	<0.3	10	113.5	0.4	0.9	100	111.0	0.7	1.8
Cd	<0.5	10	97.0	2.8	8.3	100	101.5	0.4	1.0
Cr	<0.9	10	111.0	3.5	9.0	100	99.5	0.1	0.2
Co	0.11	10	94.4	0.4	1.1	100	93.6	0.5	1.4
Cu	3.6	10	101.8	8.8	17.4	100	91.6	0.3	0.3
Pb	0.87	10	97.8	2.0	2.8	100	99.0	0.8	2.2
Mn	0.96	10	96.9	1.8	4.7	100	95.8	0.6	1.8
Mo	1.9	10	99.4	1.6	3.4	100	98.6	0.4	1.0
Ni	1.9	10	100.2	5.7	13.5	100	95.2	0.5	1.3
Se	<7.9	50	99.0	1.8	5.3	200	93.5	3.5	10.7
Ag	<0.1	50	100.7	1.5	4.2	200	99.0	0.4	1.0
Tl	<0.3	10	97.5	0.4	1.0	100	98.5	1.7	4.9
Th	<0.1	10	109.0	0.7	1.8	100	106.0	1.4	3.8
U	0.23	10	110.7	1.4	3.5	100	107.8	0.7	1.9
V	<2.5	50	101.4	0.1	0.4	200	97.5	0.7	2.1
Zn	5.2	50	103.4	3.3	7.7	200	96.4	0.5	1.0

S(R) Standard deviation of percent recovery.
RPD Relative percent difference between duplicate spike determinations.
< Sample concentration below established method detection limit.

TABLE 8 : PRECISION AND RECOVERY DATA IN AQUEOUS MATRICES (Cont).

WELL WATER

Element	Sample Concn. (µg/L)	Low Spike (µg/L)	Average Recovery R (%)	S(R)	RPD	High Spike (µg/L)	Average Recovery R (%)	S(R)	RPD
Al	34.3	50	100.1	3.9	0.8	200	102.6	1.1	1.3
Sb	0.46	10	98.4	0.9	1.9	100	102.5	0.7	1.9
As	<1.4	50	110.0	6.4	16.4	200	101.3	0.2	0.5
Ba	106	50	95.4	3.9	3.3	200	104.9	1.0	1.6
Be	<0.3	10	104.5	0.4	1.0	100	101.4	1.2	3.3
Cd	1.6	10	88.6	1.7	3.8	100	98.6	0.6	1.6
Cr	<0.9	10	111.0	0.0	0.0	100	103.5	0.4	1.0
Co	2.4	10	100.6	1.0	1.6	100	104.1	0.4	0.9
Cu	37.4	10	104.3	5.1	1.5	100	100.6	0.8	1.5
Pb	3.5	10	95.2	2.5	1.5	100	99.5	1.4	3.9
Mn	2770	10	*	*	1.8	100	*	*	0.7
Mo	2.1	10	103.8	1.1	1.6	100	102.9	0.7	1.9
Ni	11.4	10	116.5	6.3	6.5	100	99.6	0.3	0.0
Se	<7.9	50	127.3	8.4	18.7	200	101.3	0.2	0.5
Ag	<0.1	50	99.2	0.4	1.0	200	101.5	1.4	3.9
Tl	<0.3	10	93.9	0.1	0.0	100	100.4	1.8	5.0
Th	<0.1	10	103.0	0.7	1.9	100	104.5	1.8	4.8
U	1.8	10	106.0	1.1	1.6	100	109.7	2.5	6.3
V	<2.5	50	105.3	0.8	2.1	200	105.8	0.2	0.5
Zn	554	50	*	*	1.2	200	102.1	5.5	3.2

S(R) Standard deviation of percent recovery.
RPD Relative percent difference between duplicate spike determinations.
< Sample concentration below established method detection limit.
* Spike concentration <10% of sample background concentration.

TABLE 8 : PRECISION AND RECOVERY DATA IN AQUEOUS MATRICES (Cont).

POND WATER

Element	Sample Concn. (µg/L)	Low Spike (µg/L)	Average Recovery R (%)	S(R)	RPD	High Spike (µg/L)	Average Recovery R (%)	S(R)	RPD
Al	610	50	*	*	1.7	200	78.2	9.2	5.5
Sb	<0.4	10	101.1	1.1	2.9	100	101.5	3.0	8.4
As	<1.4	50	100.8	2.0	5.6	200	96.8	0.9	2.6
Ba	28.7	50	102.1	1.8	2.4	200	102.9	3.7	9.0
Be	<0.3	10	109.1	0.4	0.9	100	114.4	3.9	9.6
Cd	<0.5	10	106.6	3.2	8.3	100	105.8	2.8	7.6
Cr	2.0	10	107.0	1.0	1.6	100	100.0	1.4	3.9
Co	0.79	10	101.6	1.1	2.7	100	101.7	1.8	4.9
Cu	5.4	10	107.5	1.4	1.9	100	98.1	2.5	6.8
Pb	1.9	10	108.4	1.5	3.2	100	106.1	0.0	0.0
Mn	617	10	*	*	1.1	100	139.0	11.1	4.0
Mo	0.98	10	104.2	1.4	3.5	100	104.0	2.1	5.7
Ni	2.5	10	102.0	2.3	4.7	100	102.5	2.1	5.7
Se	<7.9	50	102.7	5.6	15.4	200	105.5	1.4	3.8
Ag	0.12	50	102.5	0.8	2.1	200	105.2	2.7	7.1
Tl	<0.3	10	108.5	3.2	8.3	100	105.0	2.8	7.6
Th	0.19	10	93.1	3.5	10.5	100	93.9	1.6	4.8
U	0.30	10	107.0	2.8	7.3	100	107.2	1.8	4.7
V	3.5	50	96.1	5.2	14.2	200	101.5	0.2	0.5
Zn	6.8	50	99.8	1.7	3.7	200	100.1	2.8	7.7

S(R) Standard deviation of percent recovery.
RPD Relative percent difference between duplicate spike determinations.
< Sample concentration below established method detection limit.
* Spike concentration <10% of sample background concentration.

TABLE 8 : PRECISION AND RECOVERY DATA IN AQUEOUS MATRICES (Cont).

SEWAGE TREATMENT PRIMARY EFFLUENT

Element	Sample Concn. (µg/L)	Low Spike (µg/L)	Average Recovery R (%)	S(R)	RPD	High Spike (µg/L)	Average Recovery R (%)	S(R)	RPD
Al	1150	50	*	*	3.5	200	100.0	13.8	1.5
Sb	1.5	10	95.7	0.4	0.9	100	104.5	0.7	1.9
As	<1.4	50	104.2	4.5	12.3	200	101.5	0.7	2.0
Ba	202	50	79.2	9.9	2.5	200	108.6	4.6	5.5
Be	<0.3	10	110.5	1.8	4.5	100	106.4	0.4	0.9
Cd	9.2	10	101.2	1.3	0.0	100	102.3	0.4	0.9
Cr	128	10	*	*	1.5	100	102.1	1.7	0.4
Co	13.4	10	95.1	2.7	2.2	100	99.1	1.1	2.7
Cu	171	10	*	*	2.4	100	105.2	7.1	0.7
Pb	17.8	10	95.7	3.8	1.1	100	102.7	1.1	2.5
Mn	199	10	*	*	1.5	100	103.4	2.1	0.7
Mo	136	10	*	*	1.4	100	105.7	2.4	2.1
Ni	84.0	10	88.4	16.3	4.1	100	98.0	0.9	0.0
Se	<7.9	50	112.0	10.9	27.5	200	108.8	3.0	7.8
Ag	10.9	50	97.1	0.7	1.5	200	102.6	1.4	3.7
Tl	<0.3	10	97.5	0.4	1.0	100	102.0	0.0	0.0
Th	0.11	10	15.4	1.8	30.3	100	29.3	0.8	8.2
U	0.71	10	109.4	1.8	4.3	100	109.3	0.7	1.8
V	<2.5	50	90.9	0.9	0.6	200	99.4	2.1	6.0
Zn	163	50	85.8	3.3	0.5	200	102.0	1.5	1.9

S(R) Standard deviation of percent recovery.
RPD Relative percent difference between duplicate spike determinations.
< Sample concentration below established method detection limit.
* Spike concentration <10% of sample background concentration.

TABLE 8 : PRECISION AND RECOVERY DATA IN AQUEOUS MATRICES (Cont).

INDUSTRIAL EFFLUENT

Element	Sample Concn. (µg/L)	Low Spike (µg/L)	Average Recovery R (%)	S(R)	RPD	High Spike (µg/L)	Average Recovery R (%)	S(R)	RPD
Al	44.7	50	98.8	8.7	5.7	200	90.4	2.1	2.2
Sb	2990	10	*	*	0.3	100	*	*	0.0
As	<1.4	50	75.1	1.8	6.7	200	75.0	0.0	0.0
Ba	100	50	96.7	5.5	3.4	200	102.9	1.1	0.7
Be	<0.3	10	103.5	1.8	4.8	100	100.0	0.0	0.0
Cd	10.1	10	106.5	4.4	2.4	100	97.4	1.1	2.8
Cr	171	10	*	*	0.0	100	127.7	2.4	1.7
Co	1.3	10	90.5	3.2	8.7	100	90.5	0.4	1.3
Cu	101	10	*	*	0.9	100	92.5	2.0	1.6
Pb	294	10	*	*	2.6	100	108.4	2.1	0.0
Mn	154	10	*	*	2.8	100	103.6	3.7	1.6
Mo	1370	10	*	*	1.4	100	*	*	0.7
Ni	17.3	10	107.4	7.4	5.0	100	88.2	0.7	1.0
Se	15.0	50	129.5	9.3	15.1	200	118.3	1.9	3.6
Ag	<0.1	50	91.8	0.6	1.7	200	87.0	4.9	16.1
Tl	<0.3	10	90.5	1.8	5.5	100	98.3	1.0	2.8
Th	0.29	10	109.6	1.2	2.7	100	108.7	0.0	0.0
U	0.17	10	104.8	2.5	6.6	100	109.3	0.4	0.9
V	<2.5	50	74.9	0.1	0.3	200	72.0	0.0	0.0
Zn	43.4	50	85.0	4.0	0.6	200	97.6	1.0	0.4

S(R) Standard deviation of percent recovery.
RPD Relative percent difference between duplicate spike determinations.
< Sample concentration below established method detection limit.
* Spike concentration <10% of sample background concentration.

TABLE 9 : PRECISION AND RECOVERY DATA IN SOLID MATRICES

EPA HAZARDOUS SOIL #884

Element	Sample Concn. (mg/kg)	Low+ Spike (mg/kg)	Average Recovery R (%)	S(R)	RPD	High+ Spike (mg/kg)	Average Recovery R (%)	S(R)	RPD
Al	5170	20	*	*	-	100	*	*	-
Sb	5.4	20	69.8	2.5	4.7	100	70.4	1.8	6.5
As	8.8	20	104.7	5.4	9.1	100	102.2	2.2	5.4
Ba	113	20	54.9	63.6	18.6	100	91.0	9.8	0.5
Be	0.6	20	100.1	0.6	1.5	100	102.9	0.4	1.0
Cd	1.8	20	97.3	1.0	1.4	100	101.7	0.4	1.0
Cr	83.5	20	86.7	16.1	8.3	100	105.5	1.3	0.0
Co	7.1	20	98.8	1.2	1.9	100	102.9	0.7	1.8
Cu	115	20	86.3	13.8	3.4	100	102.5	4.2	4.6
Pb	152	20	85.0	45.0	13.9	100	151.7	25.7	23.7
Mn	370	20	*	*	12.7	100	85.2	10.4	2.2
Mo	4.8	20	95.4	1.5	2.9	100	95.2	0.7	2.0
Ni	19.2	20	101.7	3.8	1.0	100	102.3	0.8	0.8
Se	<3.2	20	79.5	7.4	26.4	100	100.7	9.4	26.5
Ag	1.1	20	96.1	0.6	0.5	100	94.8	0.8	2.3
Tl	0.24	20	94.3	1.1	3.1	100	97.9	1.0	2.9
Th	1.0	20	69.8	0.6	1.3	100	76.0	2.2	7.9
U	1.1	20	100.1	0.2	0.0	100	102.9	0.0	0.0
V	17.8	20	109.2	4.2	2.3	100	106.7	1.3	2.4
Zn	128	20	87.0	27.7	5.5	100	113.4	12.9	14.1

S(R) Standard deviation of percent recovery.
RPD Relative percent difference between duplicate spike determinations.
< Sample concentration below established method detection limit.
* Spike concentration <10% of sample background concentration.
- Not determined.
+ Equivalent.

TABLE 9 : PRECISION AND RECOVERY DATA IN SOLID MATRICES (Cont).

NBS 1645 RIVER SEDIMENT

Element	Sample Concn. (mg/kg)	Low+ Spike (mg/kg)	Average Recovery R (%)	S(R)	RPD	High+ Spike (mg/kg)	Average Recovery R (%)	S(R)	RPD
Al	5060	20	*	*	-	100	*	*	-
Sb	21.8	20	73.9	6.5	9.3	100	81.2	1.5	3.9
As	67.2	20	104.3	13.0	7.6	100	107.3	2.1	2.9
Ba	54.4	20	105.6	4.9	2.8	100	98.6	2.2	3.9
Be	0.59	20	88.8	0.2	0.5	100	87.9	0.1	0.2
Cd	8.3	20	92.9	0.4	0.0	100	95.7	1.4	3.9
Cr	29100	20	*	*	-	100	*	*	-
Co	7.9	20	97.6	1.3	2.6	100	103.1	0.0	0.0
Cu	112	20	121.0	9.1	1.5	100	105.2	2.2	1.8
Pb	742	20	*	*	-	100	-	-	-
Mn	717	20	*	*	-	100	-	-	-
Mo	17.1	20	89.8	8.1	12.0	100	98.4	0.7	0.9
Ni	41.8	20	103.7	6.5	4.8	100	102.2	0.8	0.0
Se	<3.2	20	108.3	14.3	37.4	100	93.9	5.0	15.1
Ag	1.8	20	94.8	1.6	4.3	100	96.2	0.7	1.9
Tl	1.2	20	91.2	1.3	3.6	100	94.4	0.4	1.3
Th	0.90	20	91.3	0.9	2.6	100	92.3	0.9	2.8
U	0.79	20	95.6	1.8	5.0	100	98.5	1.2	3.5
V	21.8	20	91.8	4.6	5.7	100	100.7	0.6	0.8
Zn	1780	20	*	*	-	100	*	*	-

S(R) Standard deviation of percent recovery.
RPD Relative percent difference between duplicate spike determinations.
< Sample concentration below established method detection limit.
* Spike concentration <10% of sample background concentration.
- Not determined.
+ Equivalent.

TABLE 9 : PRECISION AND RECOVERY DATA IN SOLID MATRICES (Cont).

EPA ELECTROPLATING SLUDGE #286

Element	Sample Concn. (mg/kg)	Low+ Spike (mg/kg)	Average Recovery R (%)	S(R)	RPD	High+ Spike (mg/kg)	Average Recovery R (%)	S(R)	RPD
Al	5110	20	*	*	-	100	*	*	-
Sb	8.4	20	55.4	1.5	4.1	100	61.0	0.2	0.9
As	41.8	20	91.0	2.3	1.7	100	94.2	0.8	1.5
Ba	27.3	20	1.8	7.1	8.3	100	0	1.5	10.0
Be	0.25	20	92.0	0.9	2.7	100	93.4	0.3	0.9
Cd	112	20	85.0	5.2	1.6	100	88.5	0.8	0.5
Cr	7980	20	*	*	-	100	*	*	-
Co	4.1	20	89.2	1.8	4.6	100	88.7	1.5	4.6
Cu	740	20	*	*	6.0	100	61.7	20.4	5.4
Pb	1480	20	*	*	-	100	*	*	-
Mn	295	20	*	*	-	100	-	-	-
Mo	13.3	20	82.9	1.2	1.3	100	89.2	0.4	1.0
Ni	450	20	*	*	6.8	100	83.0	10.0	4.5
Se	3.5	20	89.7	3.7	4.2	100	91.0	6.0	18.0
Ag	5.9	20	89.8	2.1	4.6	100	85.1	0.4	1.1
Tl	1.9	20	96.9	0.9	2.4	100	98.9	0.9	2.4
Th	3.6	20	91.5	1.3	3.2	100	97.4	0.7	2.0
U	2.4	20	107.7	2.0	4.6	100	109.6	0.7	1.8
V	21.1	20	105.6	1.8	2.1	100	97.4	1.1	2.5
Zn	13300	20	*	*	-	100	*	*	-

S(R) Standard deviation of percent recovery.
RPD Relative percent difference between duplicate spike determinations.
< Sample concentration below established method detection limit.
* Spike concentration <10% of sample background concentration.
- Not determined.
+ Equivalent.

METHOD 525.2

DETERMINATION OF ORGANIC COMPOUNDS IN DRINKING WATER BY LIQUID-SOLID EXTRACTION AND CAPILLARY COLUMN GAS CHROMATOGRAPHY/MASS SPECTROMETRY

Revision 1.0

March 1994

J.W. Eichelberger, T.D. Behymer, W.L. Budde -- Method 525,
Revision 1.0, 2.0, 2.1 (1988)

J.W. Eichelberger, T.D. Behymer, and W.L. Budde -- Method 525.1
Revision 2.2 (July 1991)

J.W. Eichelberger, J.W. Munch, and J.A. Shoemaker
Method 525.2 -- Revision 1.0 (February, 1994)

ENVIRONMENTAL MONITORING SYSTEMS LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
U.S. ENVIRONMENTAL PROTECTION AGENCY
CINCINNATI, OHIO 45268

METHOD 525.2

DETERMINATION OF ORGANIC COMPOUNDS IN DRINKING WATER BY LIQUID-SOLID EXTRACTION AND CAPILLARY COLUMN GAS CHROMATOGRAPHY/MASS SPECTROMETRY

1.0 SCOPE AND APPLICATION

1.1 This is a general purpose method that provides procedures for determination of organic compounds in finished drinking water, source water, or drinking water in any treatment stage. The method is applicable to a wide range of organic compounds that are efficiently partitioned from the water sample onto a C_{18} organic phase chemically bonded to a solid matrix in a disk or cartridge, and sufficiently volatile and thermally stable for gas chromatography. Single-laboratory accuracy and precision data have been determined with two instrument systems using both disks and cartridges for the following compounds:

Analyte	MW[1]	Chemical Abstracts Service Registry Number
Acenaphthylene	152	208-96-8
Alachlor	269	15972-60-8
Aldrin	362	309-00-2
Ametryn	227	834-12-8
Anthracene	178	120-12-7
Atraton	211	1610-17-9
Atrazine	215	1912-24-9
Benz[a]anthracene	228	56-55-3
Benzo[b]fluoranthene	252	205-82-3
Benzo[k]fluoranthene	252	207-08-9
Benzo[a]pyrene	252	50-32-8
Benzo[g,h,i]perylene	276	191-24-2
Bromacil	260	314-40-9
Butachlor	311	23184-66-9
Butylate	217	2008-41-5
Butylbenzylphthalate	312	85-68-7
Carboxin[2]	235	5234-68-4
Chlordane components:		
Alpha-chlordane	406	5103-71-9
Gamma-chlordane	406	5103-74-2
Trans nonachlor	440	39765-80-5
Chlorneb	206	2675-77-6
Chlorobenzilate	324	510-15-6
Chlorpropham	213	101-21-3
Chlorothalonil	264	1897-45-6
Chlorpyrifos	349	2921-88-2

Analyte	MW[1]	Chemical Abstracts Service Registry Number
2-Chlorobiphenyl	188	2051-60-7
Chrysene	228	218-01-9
Cyanazine	240	21725-46-2
Cycloate	215	1134-23-2
Dacthal(DCPA)	330	1861-32-1
DDD, 4,4'-	318	72-54-8
DDE, 4,4'-	316	72-55-9
DDT, 4,4'-	352	50-29-3
Diazinon[2]	304	333-41-5
Dibenz[a,h]anthracene	278	53-70-3
Di-n-butylphthalate	278	84-74-2
2,3-Dichlorobiphenyl	222	16605-91-7
Dichlorvos	220	62-73-7
Dieldrin	378	60-57-1
Diethylphthalate	222	84-66-2
Di(2-ethylhexyl)adipate	370	103-23-1
Di(2-ethylhexyl)phthalate	390	117-81-7
Dimethylphthalate	194	131-11-3
2,4-Dinitrotoluene	182	121-14-2
2,6-Dinitrotoluene	182	606-20-2
Diphenamid	239	957-51-7
Disulfoton[2]	274	298-04-4
Disulfoton sulfoxide[2]	290	2497-07-6
Disulfoton sulfone	306	2497-06-5
Endosulfan I	404	959-98-8
Endosulfan II	404	33213-65-9
Endosulfan sulfate	420	1031-07-8
Endrin	378	72-20-8
Endrin aldehyde	378	7421-93-4
EPTC	189	759-94-4
Ethoprop	242	13194-48-4
Etridiazole	246	2593-15-9
Fenamiphos[2]	303	22224-92-6
Fenarimol	330	60168-88-9
Fluorene	166	86-73-7
Fluridone	328	59756-60-4
Heptachlor	370	76-44-8
Heptachlor epoxide	386	1024-57-3
2,2',3,3',4,4',6-Heptachloro-biphenyl	392	52663-71-5
Hexachlorobenzene	282	118-74-1
2,2',4,4',5,6'-Hexachlorobiphenyl	358	60145-22-4
Hexachlorocyclohexane, alpha	288	319-84-6
Hexachlorocyclohexane, beta	288	319-85-7
Hexachlorocyclohexane, delta	288	319-86-8

Analyte	MW[1]	Chemical Abstracts Service Registry Number
Hexachlorocyclopentadiene	270	77-47-4
Hexazinone	252	51235-04-2
Indeno[1,2,3,c,d]pyrene	276	193-39-5
Isophorone	138	78-59-1
Lindane	288	58-89-9
Merphos[2]	298	150-50-5
Methoxychlor	344	72-43-5
Methyl paraoxon	247	950-35-6
Metolachlor	283	51218-45-2
Metribuzin	214	21087-64-9
Mevinphos	224	7786-34-7
MGK 264	275	113-48-4
Molinate	187	2212-67-1
Napropamide	271	15299-99-7
Norflurazon	303	27314-13-2
2,2',3,3',4,5',6,6'-Octa-chlorobiphenyl	426	40186-71-8
Pebulate	203	1114-71-2
2,2',3',4,6-Pentachlorobiphenyl	324	60233-25-2
Pentachlorophenol	264	87-86-5
Phenanthrene	178	85-01-8
Permethrin, cis-	390	54774-45-7
Permethrin, trans	390	51877-74-8
Prometon	225	1610-18-0
Prometryn	241	7287-19-6
Pronamide	255	23950-58-5
Propachlor	211	1918-16-7
Propazine	229	139-40-2
Pyrene	202	129-00-0
Simazine	201	122-34-9
Simetryn	213	1014-70-6
Stirofos	364	22248-79-9
Tebuthiuron	228	34014-18-1
Terbacil	216	5902-51-2
Terbufos[2]	288	13071-79-9
Terbutryn	241	886-50-0
2,2',4,4'-Tetrachlorobiphenyl	290	2437-79-8
Toxaphene		8001-35-2
Triademefon	293	43121-43-3
2,4,5-Trichlorobiphenyl	256	15862-07-4
Tricyclazole	189	41814-78-2
Trifluralin	335	1582-09-8
Vernolate	203	1929-77-7
Aroclor 1016		12674-11-2
Aroclor 1221[3]		11104-28-2

Analyte	MW[1]	Chemical Abstracts Service Registry Number
Aroclor 1232[3]		11141-16-5
Aroclor 1242[3]		53469-21-9
Aroclor 1248[3]		12672-29-6
Aroclor 1254		11097-69-1
Aroclor 1260		11096-82-5

[1]Monoisotopic molecular weight calculated from the atomic masses of the isotopes with the smallest masses.
[2]Only qualitative identification of this analyte is possiblebecause of its instability in aqueous matrices. Merphos, carboxin, disulfoton, and disulfoton sulfoxide showed instability within one hour of fortification. Diazinon, fenamiphos, and terbufos showed significant losses within seven days under the sample storage conditions specified in this method.
[3]This method was validated using Aroclors 1016, 1254, and 1260 which were selected to represent these Aroclors. The extraction conditions and determinative techniques should produce accuracy and precision data comparable to those for the Aroclors tested.

Attempting to determine all of the above analytes in all samples is not practical and not necessary in most cases. If all the analytes must be determined, multiple calibration mixtures will be required.

1.2 Method detection limit (MDL) is defined as the statistically calculated minimum amount that can be measured with 99% confidence that the reported value is greater than zero[1]. The MDL is compound dependent and is particularly dependent on extraction efficiency and sample matrix. MDLs for all method analytes are listed in Tables 3 through 6. These MDLs are not necessarily required by regulation, but were demonstrated in the validation of the method. The concentration calibration range demonstrated in this method is 0.1-10 µg/L for most analytes.

2.0 SUMMARY OF METHOD

Organic compound analytes, internal standards, and surrogates are extracted from a water sample by passing 1 L of sample water through a cartridge or disk containing a solid matrix with a chemically bonded C_{18} organic phase (liquid-solid extraction, LSE). The organic compounds are eluted from the LSE cartridge or disk with small quantities of ethyl acetate followed by methylene chloride, and this extract is concentrated further by evaporation of some of the solvent. The sample components are separated, identified, and measured by injecting an aliquot of the concentrated extract into a high resolution fused silica capillary column of a gas chromatography/mass spectrometry (GC/MS) system. Compounds eluting from the GC column are identified by comparing their measured mass spectra and retention times to reference spectra and retention times in a data base. Reference spectra and retention times for analytes are obtained by the measurement of calibration standards

under the same conditions used for samples. The concentration of each identified component is measured by relating the MS response of the quantitation ion produced by that compound to the MS response of the quantitation ion produced by a compound that is used as an internal standard. Surrogate analytes, whose concentrations are known in every sample, are measured with the same internal standard calibration procedure.

3.0 DEFINITIONS

3.1 Internal Standard (IS) -- A pure analyte(s) added to a sample, extract, or standard solution in known amount(s) and used to measure the relative responses of other method analytes and surrogates that are components of the same solution. The internal standard must be an analyte that is not a sample component.

3.2 Surrogate Analyte (SA) -- A pure analyte(s), which is extremely unlikely to be found in any sample, and which is added to a sample aliquot in known amount(s) before extraction or other processing, and is measured with the same procedures used to measure other sample components. The purpose of the SA is to monitor method performance with each sample.

3.3 Laboratory Duplicates (LD1 and LD2) -- Two aliquots of the same sample taken in the laboratory and analyzed separately with identical procedures. Analyses of LD1 and LD2 indicate precision associated with laboratory procedures, but not with sample collection, preservation, or storage procedures.

3.4 Field Duplicates (FD1 and FD2) -- Two separate samples collected at the same time and place under identical circumstances, and treated exactly the same throughout field and laboratory procedures. Analyses of FD1 and FD2 give a measure of the precision associated with sample collection, preservation, and storage, as well as with laboratory procedures.

3.5 Laboratory Reagent Blank (LRB) -- An aliquot of reagent water or other blank matrix that is treated exactly as a sample including exposure to all glassware, equipment, solvents, reagents, internal standards, and surrogates that are used with other samples. The LRB is used to determine if method analytes or other interferences are present in the laboratory environment, the reagents, or the apparatus.

3.6 Field Reagent Blank (FRB) -- An aliquot of reagent water or other blank matrix that is placed in a sample container in the laboratory and treated as a sample in all respects, including shipment to the sampling site, exposure to sampling site conditions, storage, preservation, and all analytical procedures. The purpose of the FRB is to determine if method analytes or other interferences are present in the field environment.

3.7 Instrument Performance Check Solution (IPC) -- A solution of one or more method analytes, surrogates, internal standards, or other test substances used to evaluate the performance of the instrument system with respect to a defined set of method criteria.

3.8 Laboratory Fortified Blank (LFB) -- An aliquot of reagent water or other blank matrix to which known quantities of the method analytes are added in the laboratory. The LFB is analyzed exactly like a sample, and its purpose is to determine whether the methodology is in control, and whether the laboratory is capable of making accurate and precise measurements.

3.9 Laboratory Fortified Sample Matrix (LFM) -- An aliquot of an environmental sample to which known quantities of the method analytes are added in the laboratory. The LFM is analyzed exactly like a sample, and its purpose is to determine whether the sample matrix contributes bias to the analytical results. The background concentrations of the analytes in the sample matrix must be determined in a separate aliquot and the measured values in the LFM corrected for background concentrations.

3.10 Stock Standard Solution (SSS) -- A concentrated solution containing one or more method analytes prepared in the laboratory using assayed reference materials or purchased from a reputable commercial source.

3.11 Primary Dilution Standard Solution (PDS) -- A solution of several analytes prepared in the laboratory from stock standard solutions and diluted as needed to prepare calibration solutions and other needed analyte solutions.

3.12 Calibration Standard (CAL) -- A solution prepared from the primary dilution standard solution or stock standard solutions and the internal standards and surrogate analytes. The CAL solutions are used to calibrate the instrument response with respect to analyte concentration.

3.13 Quality Control Sample (QCS) -- A solution of method analytes of known concentrations which is used to fortify an aliquot of LRB or sample matrix. The QCS is obtained from a source external to the laboratory and different from the source of calibration standards. It is used to check laboratory performance with externally prepared test materials.

4.0 INTERFERENCES

4.1 During analysis, major contaminant sources are reagents and liquid- solid extraction devices. Analyses of field and laboratory reagent blanks provide information about the presence of contaminants.

4.2 Interfering contamination may occur when a sample containing low concentrations of compounds is analyzed immediately after a sample containing relatively high concentrations of compounds. Syringes and splitless injection port liners must be cleaned carefully or replaced as needed. After analysis of a sample containing high concentrations of compounds, a

laboratory reagent blank should be analyzed to ensure that accurate values are obtained for the next sample.

5.0 SAFETY

5.1 The toxicity or carcinogenicity of chemicals used in this method has not been precisely defined; each chemical should be treated as a potential health hazard, and exposure to these chemicals should be minimized. Each laboratory is responsible for maintaining awareness of OSHA regulations regarding safe handling of chemicals used in this method. Additional references to laboratory safety are cited[2-4].

5.2 Some method analytes have been tentatively classified as known or suspected human or mammalian carcinogens. Pure standard materials and stock standard solutions of these compounds should be handled with suitable protection to skin, eyes, etc.

6.0 EQUIPMENT AND SUPPLIES

6.1 All glassware must be meticulously cleaned. This may be accomplished by washing with detergent and water, rinsing with water, distilled water, or solvents, air-drying, and heating (where appropriate) in a muffle furnace. Volumetric glassware should never be heated to the temperatures obtained in a muffle furnace.

6.2 Sample Containers -- 1 L or 1 qt amber glass bottles fitted with Teflon-lined screw caps. Amber bottles are highly recommended since some of the method analytes are very sensitive to light and are oxidized or decomposed upon exposure.

6.3 Volumetric Flasks -- Various sizes.

6.4 Laboratory or Aspirator Vacuum System -- Sufficient capacity to maintain a minimum vacuum of approximately 13 cm (5 in.) of mercury for cartridges. A greater vacuum (66 cm [26 in.] of mercury) may be used with disks.

6.5 Micro Syringes -- Various sizes.

6.6 Vials -- Various sizes of amber vials with Teflon-lined screw caps.

6.7 Drying Column -- The drying tube should contain about 5-7 g of anhydrous sodium sulfate to prohibit residual water from contaminating the extract. Any small tube may be used, such as a syringe barrel, a glass dropper, etc. as long as no sodium sulfate passes through the column into the extract.

6.8 Analytical Balance -- Capable of weighing 0.0001 g accurately.

6.9 Fused Silica Capillary Gas Chromatography Column -- Any capillary column that provides adequate resolution, capacity, accuracy, and precision (Section 10.0) can be used. Medium polar, low bleed columns are recommended for use with this method to provide adequate chromatography and minimize column bleed. A 30 m X 0.25 mm id fused silica capillary column coated with a 0.25 µm bonded film of polyphenylmethylsilicone (J&W DB-5.MS) was used to develop this method. Any column which provides analyte separations equivalent to or better than this column may be used.

6.10 Gas Chromatograph/Mass Spectrometer/Data system (GC/MS/DS)

6.10.1 The GC must be capable of temperature programming and be equipped for splitless/split injection. On-column capillary injection is acceptable if all the quality control specifications in Sections 9.0 and 10.0 are met. The injection tube liner should be quartz and about 3 mm in diameter. The injection system must not allow the analytes to contact hot stainless steel or other metal surfaces that promote decomposition.

6.10.2 The GC/MS interface should allow the capillary column or transfer line exit to be placed within a few mm of the ion source. Other interfaces, for example the open split interface, are acceptable as long as the system has adequate sensitivity (see Section 10.0 for calibration requirements).

6.10.3 The mass spectrometer must be capable of electron ionization at a nominal electron energy of 70 eV to produce positive ions. The spectrometer must be capable of scanning at a minimum from 45-450 amu with a complete scan cycle time (including scan overhead) of 1.0 second or less. (Scan cycle time = total MS data acquisition time in seconds divided by number of scans in the chromatogram). The spectrometer must produce a mass spectrum that meets all criteria in Table 1 when an injection of approximately 5 ng of DFTPP is introduced into the GC. An average spectrum across the DFTPP GC peak may be used to test instrument performance.

6.10.4 An interfaced data system is required to acquire, store, reduce, and output mass spectral data. The computer software must have the capability of processing stored GC/MS data by recognizing a GC peak within any given retention time window, comparing the mass spectrum from the GC peak with spectral data in a user-created data base, and generating a list of tentatively identified compounds with their retention times and scan numbers. The software must also allow integration of the ion abundance of any specific ion between specified time or scan number limits, calculation of response factors as defined in Section 10.2.6 (or construction of a linear regression calibration curve), calculation of response factor statistics (mean and standard deviation), and calculation of concentrations of analytes using either the calibration curve or the equation in Section 12.0.

6.11 Standard Filter Apparatus -- ALL GLASS OR TEFLON LINED. These should be used to carry out disk extractions when no automatic system or manifold is utilized.

6.12 A manifold system or an automatic or robotic commercially available sample preparation system designed for either cartridges or disks may be utilized in this method if all quality control requirements discussed in Section 9.0 are met.

7.0 REAGENTS AND STANDARDS

7.1 Helium Carrier Gas -- As contaminant free as possible.

7.2 Liquid-Solid Extraction (LSE) Cartridges -- Cartridges are inert non-leaching plastic, for example polypropylene, or glass, and must not contain plasticizers, such as phthalate esters or adipates, that leach into the ethyl acetate and methylene chloride eluant. The cartridges are packed with about 1 gram of silica, or other inert inorganic support, whose surface is modified by chemically bonded octadecyl (C_{18}) groups. The packing must have a narrow size distribution and must not leach organic compounds into the eluting solvent. One liter of water should pass through the cartridge in about two hours with the assistance of a slight vacuum of about 13 cm (5 in.) of mercury. Section 9.0 provides criteria for acceptable LSE cartridges which are available from several commercial suppliers.

The extraction disks contain octadecyl bonded silica uniformly enmeshed in an inert matrix. The disks used to generate the data in this method were 47 mm in diameter and 0.5 mm in thickness. Other disk sizes are acceptable and larger disks may be used for special problems or when sample compositing is carried out. As with cartridges, the disks should not contain any organic compounds, either from the matrix or the bonded silica, which will leach into the ethyl acetate and methylene chloride eluant. One liter of reagent water should pass through the disks in 5-20 minutes using a vacuum of about 66 cm (26 in.) of mercury. Section 9.0 provides criteria for acceptable LSE disks which are available commercially.

7.3 Solvents

7.3.1 Methylene chloride, ethyl acetate, acetone, toluene and methanol -- High purity pesticide quality or equivalent.

7.3.2 Reagent water -- Water in which an interference is not observed at the method detection limit of the compound of interest. Prepare reagent water by passing tap water through a filter bed containing about 0.5 kg of activated carbon or by using a water purification system. Store in clean, narrow-mouth bottles with Teflon-lined septa and screw caps.

7.4 Hydrochloric Acid -- 6 N.

7.5 Sodium Sulfate -- Anhydrous. Soxhlet extracted with methylene chloride for a minimum of four hours or heated to 400°C for two hours in a muffle furnace.)

7.6 Stock Standard Solutions -- Individual solutions of analytes, surrogates, and internal standards may be purchased from commercial suppliers or prepared from pure materials. To prepare, add 10 mg (weighed on an analytical balance to 0.1 mg) of the pure material to 1.9 mL of methanol, ethyl acetate, or acetone in a 2 mL volumetric flask, dilute to the mark, and transfer the solution to an amber glass vial. If the analytical standard is available only in quantities smaller than 10 mg, reduce the volume of solvent accordingly. Some polycyclic aromatic hydrocarbons are not soluble in methanol, ethyl acetate, or acetone, and their stock standard solutions are prepared in toluene. Methylene chloride should be avoided as a solvent for standards because its high vapor pressure leads to rapid evaporation and concentration changes. Methanol, ethyl acetate, and acetone are not as volatile as methylene chloride, but their solutions must also be handled with care to avoid evaporation. If compound purity is confirmed by the supplier at >96%, the weighed amount can be used without correction to calculate the concentration of the solution (5 µg/µL). Store the amber vials in a dark cool place.

7.7 Primary Dilution Standard Solution -- The stock standard solutions are used to prepare a primary dilution standard solution that contains multiple analytes. Mixtures of these analytes to be used as primary dilution standards may be purchased from commercial suppliers. Do not put every method analyte in a single primary dilution standard because chromatographic separation will be extremely difficult, if not impossible. Two or three primary dilution standards would be more appropriate. The recommended solvent for these standards is acetone or ethyl acetate. Aliquots of each of the stock standard solutions are combined to produce the primary dilution in which the concentration of the analytes is at least equal to the concentration of the most concentrated calibration solution, that is, 10 ng/µL. Store the primary dilution standard solution in an amber vial in a dark cool place, and check frequently for signs of degradation or evaporation, especially just before preparing calibration solutions.

7.8 Fortification Solution of Internal Standards and Surrogates -- Prepare an internal standard solution of acenaphthene-D_{10}, phenanthrene-D_{10}, and chrysene-D_{12}, in methanol, ethyl acetate, or acetone at a concentration of 500 µg/mL of each. This solution is used in the preparation of the calibration solutions. Dilute a portion of this solution by 10 to a concentration of 50 µg/mL and use this solution to fortify the actual water samples (see Sections 11.1.3 and 11.2.3). Similarly, prepare a surrogate compound solution. Surrogate compounds used in developing this method are 1,3-dimethyl-2-nitrobenzene, perylene-D_{12}, and triphenylphosphate. Other surrogates, for example pyrene-D_{10} may be used in this solution as needed (a 100 µL aliquot of this 50 µg/mL solution added to 1 L of water gives a concentration of 5 µg/L of each internal standard or surrogate). Store these solutions in an amber vial in a dark cool place. These two solutions may be combined or made as a single solution.

7.9 GC/MS Performance Check Solution -- Prepare a solution in methylene chloride of the following compounds at 5 ng/µL of each: DFTPP and endrin, and 4,4'-DDT. Store this solution in an amber vial in a dark cool place. DFTPP is less stable in acetone or ethyl acetate than it is in methylene chloride.

7.10 Calibration Solutions (CAL1 through CAL6) -- Prepare a series of six concentration calibration solutions in ethyl acetate which contain analytes of interest (except pentachlorophenol, toxaphene, and the Aroclor compounds) at suggested concentrations of 10, 5, 2, 1, 0.5, and 0.1 ng/µL, with a constant concentration of 5 ng/µL of each internal standard and surrogate in each CAL solution. It should be noted that CAL1 through CAL6 are prepared by combining appropriate aliquots of a primary dilution standard solution (Section 7.7) and the fortification solution (500 µg/mL) of internal standards and surrogates (Section 7.8). All calibration solutions should contain at least 80% ethyl acetate to avoid gas chromatographic problems. IF ALL METHOD ANALYTES ARE TO BE DETERMINED, TWO OR THREE SETS OF CALIBRATION SOLUTIONS WILL LIKELY BE REQUIRED. Pentachlorophenol is included in this solution at a concentration four times the other analytes. Toxaphene CAL solutions should be prepared as separate solutions at concentrations of 250, 200, 100, 50, 25, and 10 ng/µL. Aroclor CAL solutions should be prepared individually at concentrations of 25, 10, 5, 2.5, 1., and 0.5 ng/µL. Store these solutions in amber vials in a dark cool place. Check these solutions regularly for signs of degradation, for example, the appearance of anthraquinone from the oxidation of anthracene.

7.11 Reducing Agent -- Sodium sulfite, anhydrous. Sodium thiosulfate is not recommended as it may produce a residue of elemental sulfur that can interfere with some analytes.

7.12 Fortification Solution for Recovery Standard -- Prepare a solution of terphenyl-D_{14} at a concentration of 500 µg/mL in methylene chloride or ethyl acetate. These solutions are also commercially available. An aliquot of this solution should be added to each extract to check on the recovery of the internal standards in the extraction process.

8.0 SAMPLE COLLECTION, PRESERVATION, AND STORAGE

8.1 Sample Collection -- When sampling from a water tap, open the tap and allow the system to flush until the water temperature has stabilized (usually about two minutes). Adjust the flow to about 500 mL/min and collect samples from the flowing stream. Keep samples sealed from collection time until analysis. When sampling from an open body of water, fill the sample container with water from a representative area. Sampling equipment, including automatic samplers, must be free of plastic tubing, gaskets, and other parts that may leach interfering analytes into the water sample. Automatic samplers that composite samples over time should use refrigerated glass sample containers if possible.

8.2 Sample Dechlorination and Preservation -- All samples should be iced or refrigerated at 4°C and kept in the dark from the time of collection until extraction. Residual chlorine should be reduced at the sampling site by addition of 40-50 mg of sodium sulfite (this may be added as a solid with stirring or shaking until dissolved) to each water sample. It is very important that the sample be dechlorinated prior to adding acid to lower the pH of the sample. Adding sodium sulfite and HCl to the sample bottles prior to shipping to the sampling site is not permitted. Hydrochloric acid should be used at the sampling site to retard the microbiological degradation of some analytes in water. The sample pH is adjusted to <2 with 6 N hydrochloric acid. This is the same pH used in the extraction, and is required to support the recovery of acidic compounds like pentachlorophenol.

8.2.1 If cyanizine is to be determined, a separate sample must be collected. Cyanazine degrades in the sample when it is stored under acidic conditions or when sodium sulfite is present in the stored sample. Samples collected for cyanazine determination MUST NOT be dechlorinated or acidified when collected. They should be iced or refrigerated as described above and analyzed within 14 days. However, these samples MUST be dechlorinated and acidified immediately prior to fortification with internal standards and extraction using the same quantities of acid and sodium sulfite described above.

8.2.2 Atraton and prometon are not efficiently extracted from water at pH 2 due to what appears to be their ionization in solution under acidic conditions. In order to determine these analytes accurately, a separate sample must be collected and dechlorinated with sodium sulfite, but no acid should be added. At neutral pH, these two compounds are recovered from water with efficiencies greater than 90%. The data in Tables 3, 4, 5, 6, and 8 are from samples extracted at pH 2.

8.3 Holding Time -- Results of the time/storage study of all method analytes showed that all but six compounds are stable for 14 days in water samples when the samples are dechlorinated, preserved, and stored as described in Section 8.2. Therefore, samples must be extracted within 14 days and the extracts analyzed within 30 days of sample collection. If the following analytes are to be determined, the samples cannot be held for 14 days but must be extracted immediately after collection and preservation: carboxin, diazinon, disulfoton, disulfoton sulfoxide, fenamiphos, and terbufos.

8.4 Field Blanks

8.4.1 Processing of a field reagent blank (FRB) is recommended along with each sample set, which is composed of the samples collected from the same general sample site at approximately the same time. At the laboratory, fill a sample container with reagent water, seal, and ship to the sampling site along with the empty sample containers. Return the FRB to the laboratory with the filled sample bottles.

8.4.2 When sodium sulfite and hydrochloric acid are added to samples, use the same procedure to add the same amounts to the FRB.

9.0 QUALITY CONTROL

9.1 Quality control (QC) requirements are the initial demonstration of laboratory capability followed by regular analyses of laboratory reagent blanks, laboratory fortified blanks, and laboratory fortified matrix samples. The laboratory must maintain records to document the quality of the data generated. Additional quality control practices are recommended.

9.2 Initial demonstration of low disk or cartridge system background. Before any samples are analyzed, or any time a new supply of cartridges or disks is received from a supplier, it must be demonstrated that a laboratory reagent blank (LRB) is reasonably free of contamination that would prevent the determination of any analyte of concern. In this same experiment, it must be demonstrated that the particle size and packing of the LSE cartridges or the preparation of the disks are acceptable. Consistent flow rate with all samples is an indication of acceptable particle size distribution, packing, and proper preparation.

9.2.1 A source of potential contamination is the liquid-solid extraction (LSE) cartridge or disk which could contain phthalate esters, silicon compounds, and other contaminants that could prevent the determination of method analytes[5]. Although disks are generally made of an inert matrix, they may still contain phthalate material. Generally, phthalate esters can be leached from the cartridges into ethyl acetate and methylene chloride and produce a variable background in the water sample. If the background contamination is sufficient to prevent accurate and precise measurements, the condition must be corrected before proceeding with the initial demonstration.

9.2.2 Other sources of background contamination are solvents, reagents, and glassware. Background contamination must be reduced to an acceptable level before proceeding with the next section. In general, background from method analytes should be below the method detection limits.

9.2.3 One liter of water should pass through a cartridge in about two hours with a partial vacuum of about 13 cm (5 in.) of mercury. Using full aspirator or pump vacuum, approximately 5-20 minutes will normally be required to pass one liter of drinking water through a disk. The extraction time should not vary unreasonably among LSE cartridges or disks.

9.3 Initial Demonstration of Laboratory Accuracy and Precision -- Analyze a minimum of four replicates of a laboratory fortified blank containing each analyte of concern at a suggested concentration in the range of 2-5 µg/L (see

regulations and maximum contaminant levels for guidance on appropriate concentrations).

9.3.1 Prepare each replicate by adding sodium sulfite and HCl according to Section 8.2, then adding an appropriate aliquot of the primary dilution standard solution, or another certified quality control sample, to reagent water. Analyze each replicate according to the procedures described in Section 11.0.

9.3.2 Calculate the measured concentration of each analyte in each replicate, the mean concentration of each analyte in all replicates, and mean accuracy (as mean percentage of true value) for each analyte, and the precision (as relative standard deviation, RSD) of the measurements for each analyte.

9.3.3 For each analyte and surrogate, the mean accuracy, expressed as a percentage of the true value, should be 70-130% and the RSD should be <30%.

9.3.4 Analyze seven replicate laboratory fortified blanks which have been fortified with all analytes of interest at approximately 0.5 µg/L. Calculate the MDL of each analyte using the procedure described in Section 13.1.2[1]. It is recommended that these analyses be performed over a period of three or four days to produce more realistic method detection limits.

9.3.5 Develop and maintain a system of control charts to plot the precision and accuracy of analyte and surrogate measurements as a function of time. Charting of surrogate recoveries is an especially valuable activity since these are present in every sample and the analytical results will form a significant record of data quality.

9.4 Monitor the integrated areas of the quantitation ions of the internal standards and surrogates in continuing calibration checks (see Section 10.3). In laboratory fortified blanks or samples, the integrated areas of internal standards and surrogates will not be constant because the volume of the extract will vary (and is difficult to keep constant). But the ratios of the areas should be reasonably constant in laboratory fortified blanks and samples. The addition of 10 µL of the recovery standard, terphenyl-D_{14} (500 µg/mL), to the extract is recommended to be used to monitor the recovery of the internal standards in laboratory fortified blanks and samples. Internal standard recovery should be in excess of 70%.

9.5 With each batch of samples processed as a group within a 12-hour work shift, analyze a laboratory reagent blank to determine the background system contamination. Any time a new batch of LSE cartridges or disks is received, or new supplies of other reagents are used, repeat the demonstration of low background described in Section 9.2.

9.6 With each batch of samples processed as a group within a work shift, analyze a single laboratory fortified blank (LFB) containing each analyte of concern at a concentration as determined in Section 9.3. If more than 20 samples are included in a batch, analyze a LFB for every 20 samples. Use the procedures described in Section 9.3.3 to evaluate the accuracy of the measurements. If acceptable accuracy cannot be achieved, the problem must be located and corrected before additional samples are analyzed. Add the results to the on-going control charts to document data quality.

9.7 Determine that the sample matrix does not contain materials that adversely affect method performance. This is accomplished by analyzing replicates of laboratory fortified matrix samples and ascertaining that the precision, accuracy, and method detection limits of analytes are in the same range as obtained with laboratory fortified blanks. If a variety of different sample matrices are analyzed regularly, for example, drinking water from groundwater and surface water sources, matrix independence should be established for each. A laboratory fortified sample matrix should be analyzed for every 20 samples processed in the same batch.

9.8 With each set of samples, a field reagent blank (FRB) should be analyzed. The results of this analysis will help define contamination resulting from field sampling and transportation activities.

9.9 At least quarterly, analyze a quality control sample from an external source. If measured analyte concentrations are not of acceptable accuracy (Section 9.3.3), check the entire analytical procedure to locate and correct the problem source.

9.10 Numerous other quality control measures are incorporated into other parts of this procedure, and serve to alert the analyst to potential problems.

10.0 CALIBRATION AND STANDARDIZATION

10.1 Demonstration and documentation of acceptable initial calibration is required before any samples are analyzed and is required intermittently throughout sample analysis as dictated by results of continuing calibration checks. After initial calibration is successful, a continuing calibration check is required each day or at the beginning of each period in which analyses are performed not to exceed 12 hours. Additional periodic calibration checks are good laboratory practice.

10.2 Initial Calibration

10.2.1 Calibrate the mass and abundance scales of the MS with calibration compounds and procedures prescribed by the manufacturer with any modifications necessary to meet the requirements in Section 10.2.2.

10.2.2 Inject into the GC/MS system a 1 µL aliquot of the 5 ng/µL solution of DFTPP, endrin and 4,4'-DDT. If desired, the endrin and DDT degradation checks may be performed simultaneously with the DFTPP

check or in a separate injection. Acquire a mass spectrum that includes data for m/z 45-450. Use GC conditions that produce a narrow (at least five scans per peak) symmetrical peak for each compound (Sections 10.2.3.1 and 10.2.3.2). If the DFTPP mass spectrum does not meet all criteria in Table 1, the MS must be retuned and adjusted to meet all criteria before proceeding with calibration. A single spectrum or an average spectrum across the GC peak may be used to evaluate the performance of the system. Locate any degradation products of endrin (endrin ketone [EK] and endrin aldehyde [EA]) and 4,4'-DDT (4,4'-DDE and 4,4'-DDD) at their appropriate retention times and m/z ratios (Table 2). Endrin ketone can be located at ≈1.1 to 1.2 times the endrin retention time with prominent m/z 67 and 317 ions in the mass spectrum. If degradation of either endrin or DDT exceeds 20%, maintenance is required on the GC injection port and possibly other areas of the system before proceeding with the calibration. Calculate percent breakdown using peak areas based on total ion current (TIC) as follows:

% 4,4'-DDT breakdown =

$$\frac{\sum \text{TIC area of DDT degradation peaks (DDE+DDD)}}{\sum \text{TIC area of total DDT peaks (DDT+DDE+DDD)}} \times 100$$

% endrin breakdown =

$$\frac{\sum \text{TIC area of endrin degradation peaks (EA+EK)}}{\sum \text{TIC area of total endrin peaks (endrin+EA+EK)}} \times 100$$

10.2.3 Inject a 1 µL aliquot of a medium concentration calibration solution, for example 0.5-2 µg/L, and acquire and store data from m/z 45-450 with a total cycle time (including scan overhead time) of 1.0 second or less. Cycle time should be adjusted to measure at least five or more spectra during the elution of each GC peak.

10.2.3.1 The following are suggested multi-ramp temperature program GC conditions. Adjust the helium carrier gas flow rate to about 33 cm/sec. Inject at 45°C and hold in splitless mode for one minute. Heat rapidly to 130°C. At three minutes start the temperature program: 130-180°C at 12°/min; 180-240°C at 7°/min; 240-320°C at 12°/min. Start data acquisition at four minutes.

10.2.3.2 Single ramp linear temperature program suggested GC conditions. Adjust the helium carrier gas flow rate to about 33 cm/sec. Inject at 40°C and hold in splitless mode for one minute. Heat rapidly to 160°C. At three minutes start the temperature program: 160-320°C

at 6°/min; hold at 320° for two minutes. Start data acquisition at three minutes.

10.2.4 Performance criteria for the medium calibration -- Examine the stored GC/MS data with the data system software.

10.2.4.1 GC performance -- Anthracene and phenanthrene should be separated by baseline. Benz[a]anthracene and chrysene should be separated by a valley whose height is less than 25% of the average peak height of these two compounds. If the valley between benz[a]anthracene and chrysene exceeds 25%, the GC column requires maintenance. See Section 10.3.6.

10.2.4.2 MS sensitivity -- The GC/MS/DS peak identification software should be able to recognize a GC peak in the appropriate retention time window for each of the compounds in the calibration solution, and make correct identifications. If fewer than 99% of the compounds are recognized, system maintenance is required. See Section 10.3.6.

10.2.5 If all performance criteria are met, inject a 1 µL aliquot of each of the other CAL solutions using the same GC/MS conditions.

10.2.5.1 Some GC/MS systems may not be sensitive enough to detect some of the analytes in the two lowest concentration CAL solutions. In this case, the analyst should prepare additional CAL solutions at slightly higher concentrations to obtain at least five calibration points that bracket the expected analyte concentration range.

10.2.6 Calculate a response factor (RF) for each analyte of interest and surrogate for each CAL solution using the internal standard whose retention time is nearest the retention time of the analyte or surrogate. Table 2 contains suggested internal standards for each analyte and surrogate, and quantitation ions for all compounds. This calculation is supported in acceptable GC/MS data system software (Section 6.10.4), and many other software programs. The RF is a unitless number, but units used to express quantities of analyte and internal standard must be equivalent.

$$RF = \frac{(A_x)\ (Q_{is})}{(A_{is})\ (Q_x)}$$

where: A_x = integrated abundance of the quantitation ion of the analyte.
A_{is} = integrated abundance of the quantitation ion internal standard.
Q_x = quantity of analyte injected in ng or concentration units.
Q_{is} = quantity of internal standard injected in ng or concentration units.

10.2.6.1 For each analyte and surrogate, calculate the mean RF from the analyses of the six CAL solutions. Calculate the standard deviation (SD) and the relative standard deviation (RSD) from each mean: RSD = 100 (SD/M). If the RSD of any analyte or surrogate mean RF exceeds 30%, either analyze additional aliquots of appropriate CAL solutions to obtain an acceptable RSD of RFs over the entire concentration range, or take action to improve GC/MS performance. See Section 10.3.6.

10.2.7 As an alternative to calculating mean response factors, use the GC/MS data system software or other available software to generate a linear regression calibration curve.

10.3 Continuing Calibration Check -- Verify the MS tune and initial calibration at the beginning of each 12-hour work shift during which analyses are performed using the following procedure.

10.3.1 Inject a 1 µL aliquot of the 5 ng/µL solution of DFTPP, endrin, and 4,4'-DDT. Acquire a mass spectrum for DFTPP that includes data for m/z 45-450. Ensure that all criteria in Section 10.2.2 are met.

10.3.2 Inject a 1 µL aliquot of a medium concentration calibration solution and analyze with the same conditions used during the initial calibration.

10.3.3 Demonstrate acceptable performance for the criteria shown in Section 10.2.4.

10.3.4 Determine that the absolute areas of the quantitation ions of the internal standards and surrogate(s) have not decreased by more than 30% from the areas measured in the most recent continuing calibration check, or by more than 50% from the areas measured during initial calibration. If these areas have decreased by more than these amounts, adjustments must be made to restore system sensitivity. These adjustments may require cleaning of the MS ion source, or other maintenance as indicated in Section 10.3.6, and recalibration. Control charts are useful aids in documenting system sensitivity changes.

10.3.5 Calculate the RF for each analyte and surrogate from the data measured in the continuing calibration check. The RF for each analyte and surrogate must be within 30% of the mean value measured in the initial calibration. Alternatively, if a linear regression is used, the calculated amount for each analyte must be ±30% of the true value. If these conditions do not exist, remedial action should be taken which may require recalibration.

10.3.5.1 Because of the large number of compounds on the analyte list, it is possible for a few analytes of interest to be outside the continuing calibration criteria. If analytes that missed the calibration check are detected in samples, they may be quantified using a single point calibration. The single point standards should be prepared at concentrations that produce responses close (±20%) to those of the unknowns. If the same analyte misses the continuing calibration check on three consecutive work shifts, remedial action MUST be taken. If more than 10% of the analytes of interest miss the continuing calibration check on a single day, remedial action MUST be taken.

10.3.6 Some possible remedial actions -- Major maintenance such as cleaning an ion source, cleaning quadrupole rods, replacing filament assemblies, etc. require returning to the initial calibration step.

10.3.6.1 Check and adjust GC and/or MS operating conditions; check the MS resolution, and calibrate the mass scale.

10.3.6.2 Clean or replace the splitless injection liner; silanize a new injection liner.

10.3.6.3 Flush the GC column with solvent according to manufacturer's instructions.

10.3.6.4 Break off a short portion (about 1 M) of the column from the end near the injector; or replace GC column. This action will cause a change in retention times.

10.3.6.5 Prepare fresh CAL solutions, and repeat the initial calibration step.

10.3.6.6 Clean the MS ion source and rods (if a quadrupole).

10.3.6.7 Replace any components that allow analytes to come into contact with hot metal surfaces.

10.3.6.8 Replace the MS electron multiplier, or any other faulty components.

11.0 PROCEDURE

11.1 Cartridge Extraction

11.1.1 This procedure may be carried out in the manual mode or in the automated mode (Section 6.12) using a robotic or automatic sample preparation device. If an automatic system is used to prepare samples, follow the manufacturer's operating instructions, but follow this procedure. If the manual mode is used, a suggested setup of the extraction apparatus is shown in Figure 1A. The reservoir is not required, but recommended for convenient operation. Water drains from the reservoir through the LSE cartridge and into a syringe needle which is inserted through a rubber stopper into the suction flask. A slight vacuum of approximately 13 cm (5 in.) of mercury is used during all operations with the apparatus. About two hours should be required to draw a liter of water through the cartridge.

11.1.2 Elute each cartridge with a 5 mL aliquot of ethyl acetate followed by a 5 mL aliquot of methylene chloride. Let the cartridge drain dry after each flush. Then elute the cartridge with a 10 mL aliquot of methanol, but DO NOT allow the methanol to elute below the top of the cartridge packing. Add 10 mL of reagent water to the cartridge, but before the reagent water level drops below the top edge of the packing, begin adding sample to the solvent reservoir.

11.1.3 Pour the water sample into the 2 L separatory funnel with the stopcock closed, add 5 mL methanol, and mix well. If a vacuum manifold is used instead of the separatory funnel, the sample may be transferred directly to the cartridge after the methanol is added to the sample. Residual chlorine should not be present as a reducing agent should have been added at the time of sampling. Also the pH of the sample should be about 2. If residual chlorine is present and/or the pH is >2, the sample may be invalid. Add a 100 µL aliquot of the fortification solution (50 µg/mL) for internal standards and surrogates, and mix immediately until homogeneous. The resulting concentration of these compounds in the water should be 5 µg/L.

11.1.4 Periodically transfer a portion of the sample into the solvent reservoir. The water sample will drain into the cartridge, and from the exit into the suction flask. Maintain the packing material in the cartridge immersed in water at all times. After all of the sample has passed through the LSE cartridge, draw air or nitrogen through the cartridge for 10 minutes.

11.1.5 Transfer the 125 mL solvent reservoir and LSE cartridge (from Figure 1A) to the elution apparatus if used (Figure 1B). The same 125 mL solvent reservoir is used for both apparatus. Rinse the inside of the 2 L separatory funnel and the sample jar with 5 mL of ethyl acetate and elute the cartridge with this rinse into the collection tube. Wash

the inside of the separatory funnel and the sample jar with 5 mL methylene chloride and elute the cartridge, collecting the rinse in the same collection tube. Small amounts of residual water from the sample container and the LSE cartridge may form an immiscible layer with the eluate. Pass the eluate through the drying column (Section 6.7) which is packed with approximately 5-7 g of anhydrous sodium sulfate and collect in a second vial. Wash the sodium sulfate with at least 2 mL methylene chloride and collect in the same vial. Concentrate the extract in a warm water bath under a gentle stream of nitrogen. Do not concentrate the extract to less than 0.5 mL, as this will result in losses of analytes. Make any volume adjustments with ethyl acetate. It is recommended that an aliquot of the recovery standard be added to the concentrated extract to check the recovery of the internal standards (see Section 7.12).

11.2 Disk Extraction

11.2.1 This procedure was developed using the standard 47 mm diameter disks. Larger disks (90 mm diameter) may be used if sample compositing is being done or special matrix problems are encountered. If larger disks are used, the washing solvent volume is 15 mL, the conditioning solvent volume is 15 mL, and the elution solvent volume is two 15 mL aliquots.

11.2.1.1 Extractions using the disks may be carried out either in the manual or automatic mode (Section 6.12) using an automatic sample preparation device. If an automatic system is used to prepare samples, follow the manufacturer's operating instructions, but follow this procedure. Insert the disk into the filter apparatus (Figure 2) or sample preparation unit. Wash the disk with 5 mL of a 1:1 mixture of ethyl acetate (EtAc) and methylene chloride (MeCl2) by adding the solvent to the disk, drawing about half through the disk, allowing it to soak the disk for about a minute, then drawing the remaining solvent through the disk.

NOTE: Soaking the disk may not be desirable when disks other than Teflon are used. Instead, apply a constant, low vacuum in this section and Section 11.2.1.2 to ensure adequate contact time between solvent and disk.

11.2.1.2 Pre-wet the disk with 5 mL methanol (MeOH) by adding the MeOH to the disk and allowing it to soak for about a minute, then drawing most of the remaining MeOH through. A layer of MeOH must be left on the surface of the disk, which should not be allowed to go dry from this point until the end of the sample extraction. THIS IS

A CRITICAL STEP FOR A UNIFORM FLOW AND GOOD RECOVERY.

11.2.1.3 Rinse the disk with 5 mL reagent water by adding the water to the disk and drawing most through, again leaving a layer on the surface of the disk.

11.2.2 Add 5 mL MeOH per liter of water to the sample. Mix well.

11.2.3 Add 100 µL of the internal standard and surrogate compound fortification solution (50 µg/mL) to the sample and shake or mix until the sample is homogeneous. The resulting concentration of these compounds in the water should be 5 µg/L.

11.2.4 Add the water sample to the reservoir and apply full vacuum to begin the extraction. Particulate-free water may pass through the disk in as little as five minutes without reducing analyte recoveries. Extract the entire sample, draining as much water from the sample container as possible. Dry the disk by maintaining vacuum for about 10 min.

11.2.5 Remove the filtration top, but do not disassemble the reservoir and fritted base. If a suction flask is being used, empty the water from the flask, and insert a suitable collection tube to contain the eluant. The only constraint on the sample tube is that it fit around the drip tip of the fritted base. Reassemble the apparatus.

11.2.6 Add 5 mL of ethyl acetate to the sample bottle, and rinse the inside walls thoroughly. Allow the solvent to settle to the bottom of the bottle, then transfer it to the disk. A disposable pipet or syringe may be used to do this, rinsing the sides of the glass filtration reservoir in the process. Draw about half of the solvent through the disk, release the vacuum, and allow the disk to soak for a minute. Draw the remaining solvent through the disk.

NOTE: Soaking the disk may not be desirable if disks other than Teflon are used. Instead, apply a constant, low vacuum in this section and Section 11.2.7 to ensure adequate contact time between solvent and disk.

11.2.7 Repeat the above step (Section 11.2.6) with methylene chloride.

11.2.8 Using a syringe or disposable pipet, rinse the filtration reservoir with two 3 mL portions of 1:1 EtAc:MeCl2. Draw the solvent through the disk and into the collector tube. Pour the combined eluates (Sections 11.2.6, 11.2.7, and 11.2.8) through the drying tube (Section 6.7) containing about 5-7 g of anhydrous sodium sulfate. Rinse the drying tube and sodium sulfate with two 3 mL portions of 1:1 EtAc:MeCl2 mixture. Collect all the extract and washings in a concentrator tube.

11.2.9 While gently heating the extract in a water bath or a heating block, concentrate to between 0.5 and 1 mL under a gentle stream of nitrogen. Do not concentrate the extract to less than 0.5 mL, since this will result in losses of analytes. Make any volume adjustments with ethyl acetate. It is recommended that an aliquot of the recovery standard be added to the concentrated extract to check the recovery of the internal standards (see Section 7.12).

11.3 Analyze a 1-2 µL aliquot with the GC/MS system under the same conditions used for the initial and continuing calibrations (Section 10.2.3).

11.4 At the conclusion of data acquisition, use the same software that was used in the calibration procedure to tentatively identify peaks in predetermined retention time windows of interest. Use the data system software to examine the ion abundances of components of the chromatogram.

11.5 Identification of Analytes -- Identify a sample component by comparison of its mass spectrum (after background subtraction) to a reference spectrum in the user-created data base. The GC retention time of the sample component should be within five seconds of the retention time observed for that same compound in the most recently analyzed continuing calibration check standard.

11.5.1 In general, all ions that are present above 10% relative abundance in the mass spectrum of the standard should be present in the mass spectrum of the sample component and should agree within absolute 20%. For example, if an ion has a relative abundance of 30% in the standard spectrum, its abundance in the sample spectrum should be in the range of 10-50%. Some ions, particularly the molecular ion, are of special importance, and should be evaluated even if they are below 10% relative abundance.

11.5.2 Identification is hampered when sample components are not resolved chromatographically and produce mass spectra containing ions contributed by more than one analyte. When GC peaks obviously represent more than one sample component (i.e., broadened peak with shoulder(s) or valley between two or more maxima), appropriate analyte spectra and background spectra can be selected by examining plots of characteristic ions for tentatively identified components. When analytes coelute (i.e., only one GC peak is apparent), the identification criteria can be met but each analyte spectrum will contain extraneous ions contributed by the coeluting compound.

11.5.3 Structural isomers that produce very similar mass spectra can be explicitly identified only if they have sufficiently different GC retention times. See Section 10.2.4.1. Acceptable resolution is achieved if the height of the valley between two isomer peaks is less than 25% of the average height of the two peak heights. Otherwise, structural isomers

are identified as isomeric pairs. Benzo[b] and benzo[k]fluoranthene may be measured as an isomeric pair. MGK 264 is made up of two structural isomers. These are listed separately in the data tables.

12.0 DATA ANALYSIS AND CALCULATIONS

12.1 Complete chromatographic resolution is not necessary for accurate and precise measurements of analyte concentrations if unique ions with adequate intensities are available for quantitation. In validating this method, concentrations were calculated by measuring the characteristic ions listed in Table 2.

12.1.1 Calculate analyte and surrogate concentrations.

$$C_x = \frac{(A_x)\ (Q_{is})}{(A_{is})\ (RF)\ (V)}$$

where: C_x =concentration of analyte or surrogate in µg/L in the water sample.
A_x = integrated abundance of the quantitation ion of the analyte in the sample.
A_{is} = integrated abundance of the quantitation ion of the internal standard in the sample.
Q_{is} = total quantity (in micrograms) of internal standard added to the water sample.
V = original water sample volume in liters.
RF = mean response factor of analyte from the initial calibration.

12.1.2 Alternatively, use the GC/MS system software or other available proven software to compute the concentrations of the analytes and surrogates from the linear regression curves.

12.1.3 Calculations should utilize all available digits of precision, but final reported concentrations should be rounded to an appropriate number of significant figures (one digit of uncertainty). Experience indicates that three significant figures may be used for concentrations above 99 µg/L, two significant figures for concentrations between 1-99 µg/L, and one significant figure for lower concentrations.

13.0 METHOD PERFORMANCE

13.1 Single laboratory accuracy and precision data (Tables 3-6) for each listed analyte were obtained at a concentration of 0.5 µg/L and/or 5 µg/L in reagent water utilizing both the disk and the cartridge technology and two different GC/MS systems, an ion trap detector and a quadrupole mass spectrometer. Table 8 lists accuracy and precision data from replicate determinations of method analytes in tap water using liquid-solid cartridge extractions and the ion trap mass spectrometer. Any type of GC/MS system may be used to

perform this method if it meets the requirement in Section 6.10 and the quality control criteria in Section 9.0. The multi-component analytes (i.e., toxaphene and Aroclors) were studied at higher concentrations (see Tables 5 and 6). The average recoveries in the tables represent eight replicate analyses done over a minimum of a two-day period.

13.1.2 With these data, the method detection limits (MDL) in the tables were calculated using the formula:

$$MDL = S\ t_{(n-1,1-alpha\ =\ 0.99)}$$

where: $t_{(n-1,1-alpha\ =\ 0.99)}$ = Student's t value for the 99% confidence level with n-1 degrees of freedom.
n = number of replicates.
S = standard deviation of replicate analyses.

13.2 Problem Compounds

13.2.1 Some polycyclic aromatic hydrocarbons (PAH), including the labeled PAHs used in this method as internal standards, are rapidly oxidized and/or chlorinated in water containing residual chlorine. Therefore, residual chlorine must be reduced at the time of sampling. These same types of compounds, especially anthracene, benz[a]anthracene, and benzo[a]pyrene, are susceptible to photodegradation. Therefore, care should be taken to avoid exposing standards, samples, and extracts to direct light. Low recoveries of some PAH compounds have been observed when the cartridge or disk was air dried longer than 10 minutes (Sections 11.1.4 and 11.2.4). Drying times longer than 10 minutes should be avoided, or nitrogen may be used to dry the cartridge or disk to minimize the possible oxidation of these analytes during the drying step.

13.2.2 Merphos is partially converted to DEF in aqueous matrices, and also when introduced into a hot gas chromatographic injection system. The efficiency of this conversion appears to be unpredictable and not reproducible. Therefore, merphos cannot be quantified and can only be identified by the presence of DEF in the sample.

13.2.3 Several of the nitrogen and/or phosphorus containing pesticides listed as method analytes are difficult to chromatograph and appear as broad, asymmetrical peaks. These analytes, whose peak shapes are typically poor, are listed in Table 7. The method performance for these analytes is strongly dependent on chromatographic efficiency and performance. Poor peak shapes for these analytes will affect the linearity of the calibration curves and result in poor accuracy at low concentrations. Also listed in Table 7 are precision and accuracy data generated at a mid-concentration level for these analytes. In most cases, the data at

this concentration meet the quality control criteria requirements of the method.

13.2.4 Phthalate esters and other background components appear in variable quantities in laboratory and field reagent blanks, and generally cannot be accurately measured at levels below about 2 µg/L. Subtraction of the concentration in the blank from the concentration in the sample at or below the 2 µg/L level is not recommended because the concentration of the background in the blank is highly variable.

13.2.5 Atraton and prometon are not efficiently extracted from the water at pH 2 due to what appears to be their ionization occurring in solution under acidic conditions. In order to determine these analytes accurately, a separate sample must be collected and dechlorinated with sodium sulfite, but no HCl should be added at the time of collection. At neutral pH, these two compounds are recovered from water with efficiencies greater than 90%. The data in Tables 3, 4, 5, 6, and 8 are from samples extracted at pH 2.

13.2.6 Carboxin, disulfoton, and disulfoton sulfoxide were found to be unstable in water and began to degrade almost immediately. These analytes may be identified by this method but not accurately measured.

13.2.7 Low recoveries of metribuzin were observed in samples fortified with relatively high concentrations of additional method analytes. In samples fortified with approximately 80 analytes at 5 µg/L each, metribuzin was recovered at about 50% efficiency. This suggests that metribuzin may break through the C-18 phase in highly contaminated samples resulting in low recoveries.

13.2.8 If cyanazine is to be determined, a separate sample must be collected. Cyanazine degrades in the sample when it is stored under acidic conditions or when sodium sulfite is present in the stored sample. Samples collected for cyanazine determination MUST NOT be dechlorinated or acidified when collected. They should be iced or refrigerated and analyzed within 14 days. However, these samples MUST be dechlorinated and acidified immediately prior to fortification with internal standards and extraction using the same quantities of acid and sodium sulfite described in Section 8.0.

14.0 POLLUTION PREVENTION

14.1 This method utilizes the new liquid-solid extraction (LSE) technology to remove the analytes from water. It requires the use of very small volumes of organic solvent and very small quantities of pure analytes, thereby eliminating the potential hazards to both the analyst and the environment involved with the use of large volumes of organic solvents in conventional liquid-liquid extractions.

14.2 For information about pollution prevention that may be applicable to laboratory operations, consult "Less Is Better: Laboratory Chemical Management for Waste Reduction" available from the American Chemical Society's Department of Government Relations and Science Policy, 1155 16th Street N.W., Washington, D.C. 20036.

15.0 WASTE MANAGEMENT

15.1 It is the laboratory's responsibility to comply with all federal, state, and local regulations governing waste management, particularly the hazardous waste identification rules and land disposal restrictions. The laboratory using this method has the responsibility to protect the air, water, and land by minimizing and controlling all releases from fume hoods and bench operations. Compliance is also required with any sewage discharge permits and regulations. For further information on waste management, consult "The Waste Management Manual for Laboratory Personnel," also available from the American Chemical Society at the address in Section 14.2.

16.0 REFERENCES

1. Glaser, J.A., Foerst, D.L., McKee, G.D., Quave, S.A., and Budde, W.L. "Trace Analyses for Wastewaters," Environ. Sci. Technol. 1981 15, 1426-1435. or 40 CFR, Part 136, Appendix B.

2. "Carcinogens - Working With Carcinogens," Department of Health, Education, and Welfare, Public Health Service, Center for Disease Control, National Institute for Occupational Safety and Health, Publication No. 77-206, August 1977.

3. "OSHA Safety and Health Standards, General Industry," (29 CFR 1910), Occupational Safety and Health Administration, OSHA 2206, (Revised, January 1976).

4. "Safety in Academic Chemistry Laboratories," American Chemical Society Publication, Committee on Chemical Safety, 3rd Edition, 1979.

5. Junk, G.A., Avery, M.J., and Richard, J.J. "Interferences in Solid-Phase Extraction Using C-18 Bonded Porous Silica Cartridges," Anal. Chem. 1988, 60, 1347.

TABLE 1. ION ABUNDANCE CRITERIA FOR BIS(PERFLUOROPHENYL)PHENYL PHOSPHINE (DECAFLUOROTRIPHENYLPHOSPHINE, DFTPP)

Mass (M/z)	Relative Abundance Criteria	Purpose of Checkpoint[1]
51	10-80% of the base peak	low mass sensitivity
68	<2% of mass 69	low mass resolution
70	<2% of mass 69	low mass resolution
127	10-80% of the base peak	low-mid mass sensitivity
197	<2% of mass 198	mid-mass resolution
198	base peak or >50% of 442	mid-mass resolution and sensitivity
199	5-9% of mass 198	mid-mass resolution and isotope ratio
275	10-60% of the base peak	mid-high mass sensitivity
365	>1% of the base peak	baseline threshold
441	Present and < mass 443	high mass resolution
442	base peak or >50% of 198	high mass resolution and sensitivity
443	15-24% of mass 442	high mass resolution and isotope ratio

[1]All ions are used primarily to check the mass measuring accuracy of the mass spectrometer and data system, and this is the most important part of the performance test. The three resolution checks, which include natural abundance isotope ratios, constitute the next most important part of the performance test. The correct setting of the baseline threshold, as indicated by the presence of low intensity ions, is the next most important part of the performance test. Finally, the ion abundance ranges are designed to encourage some standardization to fragmentation patterns.

TABLE 2. RETENTION TIME DATA, QUANTITATION IONS, AND INTERNAL STANDARD REFERENCES FOR METHOD ANALYTES

Compound	Retention Time (min:sec) A[a]	Retention Time (min:sec) B[b]	Quantitation Ion	IS Reference #
Internal Standards				
acenaphthene-d10	7:47	7:01	164	
chrysene-d12	21:33	18:09	240	
phenanthrene-d10	11:37	10:13	188	
Surrogates				
1,3-dimethyl-2-nitrobenzene	5:16	4:33	134	1
perylene-d12	26:60	21:31	264	3
triphenylphosphate	20:25	17:25	326 / 325	3
Target Analytes				
acenaphthylene	7:30	6:46	152	1
alachlor	12:59	11:24	160	2
aldrin	14:24	12:31	66	2
ametryn	13:11	11:35	227 / 170	2
anthracene	11:50	10:24	178	2
aroclor 1016		7:30-14:00	152+256+292	2
aroclor 1254		11:00-18:00	220+326+360	2
arochlor 1260		13:10-21:00	326+360+394	2
atraton	10:31	9:25	196 / 169	1
atrazine	10:49	9:38	200 / 215	1 / 2
benz[a]anthracene	21:31	18:08	228	3
benzo[b]fluoranthene	25:33	20:44	252	3
benzo[k]fluoranthene	25:45	20:48	252	3
benzo[g,h,i]perylene	31:16	24:18	276	3
benzo[a]pyrene	25:24	21:25	252	3
bromacil	13:46	12:03	205	2
butachlor	16:25	14:16	176 / 160	2
butylate	6:60	6:23	57 / 146	1
butylbenzylphthalate	19:39	16:53	149	2 / 3
carboxin	17:37	15:13	143	2
chlordane, (alpha-chlordane)	16:43	14:28	375 / 373	2 / 3
chlordane, (gamma-chlordane)	16:19	14:05	373	2 / 3
chlordane, (trans-nonachlor)	16:47	14:30	409	2 / 3
chlorneb	7:47	7:05	191	1
chlorobenzilate	18:22	15:52	139	2
2-chlorobiphenyl	7:53	7:08	188	1
chlorpropham	9:33	8:36	127	1

TABLE 2. RETENTION TIME DATA, QUANTITATION IONS, AND INTERNAL STANDARD REFERENCES FOR METHOD ANALYTES

Compound	Retention Time (min:sec) A[a]	Retention Time (min:sec) B[b]	Quantitation Ion	IS Reference #
chlorpyrifos	14:10	12:23	197 / 97	2
chlorthalonil	11:38	10:15	266	2
chrysene	21:39	18:13	228	3
cyanazine	14:14	12:28	225 / 68	2
cycloate	9:23	8:26	83 / 154	1
DCPA	14:20	12:30	301	2
4,4-DDD	18:40	16:05	235 / 165	2
4,4'-DDT	19:52	17:00	235 / 165	2
4,4'-DDE	17:20	14:59	246	2
DEF	17:24	15:05	57 / 169	2
diazinon	11:19	10:05	137 / 179	2
dibenz[[a,h]anthracene	30:32	23:47	278	3
di-n-butylphthalate	13:49	12:07	149	2
2,3-dichlorobiphenyl	10:20	9:12	222 / 152	1
dichlorvos	5:31	4:52	109	1
dieldrin	17:35	15:09	79	2
di(2-ethylhexyl)adipate	20:11	17:19	129	2 / 3
di(2-ethylhexyl)phthalate	22:11	18:39	149	2 / 3
diethylphthalate	8:68	7:53	149	1
dimethylphthalate	7:13	6:34	163	1
2,4-dinitrotoluene	8:08	7:22	165	1
2,6-dinitrotoluene	7:19	6:40	165	1
diphenamid	14:52	12:58	72 / 167	2
disulfoton	11:43	10:22	88	2
disulfoton sulfone	16:28	14:17	213 / 153	2
disulfoton sulfoxide	6:09	5:31	97	1
endosulfan I	16:44	14:26	195	2
endosulfan II	18:35	15:59	195	2
endosulfan sulfate	19:47	16:54	272	2
endrin	19:15	15:42	67 / 81	2
endrin aldehyde	19:02	16:20	67	2
EPTC	6:23	5:46	128	1
ethoprop	9:19	8:23	158	1
etridiazole	7:14	6:37	211 / 183	1
fenamiphos	16:48	14:34	303 / 154	2
fenarimol	23:26	19:24	139	3
fluorene	8:59	8:03	166	1
fluridone	26:51	21:26	328	3
HCH, alpha	10:19	9:10	181	1
HCH, beta	10:57	9:41	181	2
HCH, delta	11:57	10:32	181	2

TABLE 2. RETENTION TIME DATA, QUANTITATION IONS, AND INTERNAL STANDARD REFERENCES FOR METHOD ANALYTES

Compound	Retention Time (min:sec) A[a]	Retention Time (min:sec) B[b]	Quantitation Ion	IS Reference #
HCH, gamma (Lindane)	11:13	9:54	181	2
heptachlor	13:19	11:37	100	2
heptachlor epoxide	15:34	13:29	81	2
2,2',3,3',4,4',6-heptachlorobiphenyl	21:23	18:04	394 / 396	3
hexachlorobenzene	10:27	9:15	284	1
2,2',4,4',5,6'-hexachlorobiphenyl	17:32	15:09	360	2
hexachlorocyclopentadiene	5:16	5:38	237	1
hexazinone	20:00	17:06	171	2
indeno[1,2,3,c,d]pyrene	30:26	23:43	276	3
isophorone	4:54	4:10	82	1
merphos	15:38	13:35	209 / 153	2
metolachlor	14:07	12:20	162	2
methoxychlor	21:36	18:14	227	3
methyl paraoxon	11:57	10:22	109	2
metribuzin	12:46	11:13	198	2
mevinphos	5:54	6:19	127	1
MGK 264 - isomer a	15:18	13:00	164 / 66	2
MGK 264 - isomer b	14:55	13:19	164	2
molinate	8:19	7:30	126	1
napropamide	16:53	14:37	72	2
norflurazon	19:31	16:46	145	2
2,2',3',4,6-octachlorobiphenyl	21:33	18:11	430 / 428	3
pebulate	7:18	6:40	128	1
2,2',3',4,6-pentachlorobiphenyl	15:37	13:33	326	2
pentachlorophenol	11:01	9:45	266	2
permethrin, cis	24:25	20:01	183	3
permethrin, trans	24:39	20:10	183	3
phenanthrene	11:41	10:16	178	2
prometon	10:39	9:32	225 / 168	2
prometryn	13:15	11:39	241 / 184	2
pronamide	11:19	10:02	173	2
propachlor	9:00	8:07	120	1
propazine	10:54	9:43	214 / 172	2
pyrene	16:41	14:24	202	2
simazine	10:41	9:33	201 / 186	2
simetryn	13:04	11:29	213	2
stirofos	16:20	14:11	109	2
tebuthiuron	8:00	7:16	156	1
terbacil	11:44	10:24	161	2
terbufos	11:14	9:58	57	2
terbutryn	13:39	11:58	226 / 185	2

TABLE 2. RETENTION TIME DATA, QUANTITATION IONS, AND INTERNAL STANDARD REFERENCES FOR METHOD ANALYTES

Compound	Retention Time (min:sec) A[a]	Retention Time (min:sec) B[b]	Quantitation Ion	IS Reference #
2,2',4,4'-tetrachlorobiphenyl	14:02	12:14	292	2
toxaphene		13:00-21:00	159	2
triademefon	14:30	12:40	57	2
2,4,5-trichlorobiphenyl	12:44	10:53	256	2
tricyclazole	17:15	14:51	189	2
trifluralin	9:31	8:37	306	1
vernolate	7:10	6:32	128	1

[a]Single-ramp linear temperature program conditions (Section 10.2.3.2).
[b]Multi-ramp linear temperature program conditions (Section 10.2.3.1).

TABLE 3. ACCURACY AND PRECISION DATA FROM EIGHT DETERMINATIONS OF THE METHOD ANALYTES IN REAGENT WATER USING LIQUID-SOLID C-18 CARTRIDGE EXTRACTION AND THE QUADRUPOLE MASS SPECTROMETER

Compound	True Conc. (µg/L)	Mean Observed Conc. (µg/L)	Relative Standard Deviation (%)	Mean Method Accuracy (% of True Conc.)	MDL (µg/L)
Surrogates					
1,3-dimethyl-2-nitrobenzene	5.0	4.7	3.9	94	
perylene-d12	5.0	4.9	4.8	98	
triphenylphosphate	5.0	5.5	6.3	110	
Target Analytes					
acenaphthylene	0.50	0.45	8.2	91	0.11
alachlor	0.50	0.47	12	93	0.16
aldrin	0.50	0.40	9.3	80	0.11
ametryn	0.50	0.44	6.9	88	0.092
anthracene	0.50	0.53	4.3	106	0.068
atraton	0.50	0.35	15	70	0.16
atrazine	0.50	0.54	4.8	109	0.078
benz[a]anthracene	0.50	0.41	16	82	0.20
benzo[b]fluoranthene	0.50	0.49	20	98	0.30
benzo[k]fluoranthene	0.50	0.51	35	102	0.54
benzo[g,h,i]perylene	0.50	0.72	2.2	144	0.047
benzo[a]pyrene	0.50	0.58	1.9	116	0.032
bromacil	0.50	0.54	6.4	108	0.10
butachlor	0.50	0.62	4.1	124	0.076
butylate	0.50	0.52	4.1	105	0.064
butylbenzylphthalate	0.50	0.77	11	154	0.25
carboxin	5.0	3.8	12	76	1.4
chlordane (alpha-chlordane)	0.50	0.36	11	72	0.12
chlordane (gamma-chlordane)	0.50	0.40	8.8	80	0.11
chlordane (trans-nonachlor)	0.50	0.43	17	87	0.22
chlorneb	0.50	0.51	5.7	102	0.088
chlorobenzilate	5.0	6.5	6.9	130	1.3
2-chlorobiphenyl	0.50	0.40	7.2	80	0.086
chlorpropham	0.50	0.61	6.2	121	0.11
chlorpyrifos	0.50	0.55	2.7	110	0.044
chlorthalonil	0.50	0.57	6.9	113	0.12
chrysene	0.50	0.39	7.0	78	0.082
cyanazine	0.50	0.71	8.0	141	0.17
cycloate	0.50	0.52	6.1	104	0.095
DCPA	0.50	0.55	5.8	109	0.094
4,4'-DDE	0.50	0.40	6.3	80	0.075
4,4'-DDT	0.50	0.79	3.5	159	0.083
4,4-DDD	0.50	0.54	4.4	107	0.071

TABLE 3. ACCURACY AND PRECISION DATA FROM EIGHT DETERMINATIONS OF THE METHOD ANALYTES IN REAGENT WATER USING LIQUID-SOLID C-18 CARTRIDGE EXTRACTION AND THE QUADRUPOLE MASS SPECTROMETER

Compound	True Conc. (µg/L)	Mean Observed Conc. (µg/L)	Relative Standard Deviation (%)	Mean Method Accuracy (% of True Conc.)	MDL (µg/L)
diazinon	0.50	0.41	8.8	83	0.11
dibenz[a,h]anthracene	0.50	0.53	0.5	106	0.010
di-n-butylphthalate	ND	ND	ND	ND	ND
2,3-dichlorobiphenyl	0.50	0.40	11	80	0.14
dichlorvos	0.50	0.55	9.1	110	0.15
dieldrin	0.50	0.48	3.7	96	0.053
di-(2-ethylhexyl) adipate	0.50	0.42	7.1	84	0.090
di(2-ethylhexyl) phthalate	ND	ND	ND	ND	ND
diethylphthalate	0.50	0.59	9.6	118	0.17
dimethylphthalate	0.50	0.60	3.2	120	0.058
2,4-dinitrotoluene	0.50	0.60	5.6	119	0.099
2,6-dinitrotoluene	0.50	0.60	8.8	121	0.16
diphenamid	0.50	0.54	2.5	107	0.041
disulfoton	5.0	3.99	5.1	80	0.62
disulfoton sulfone	0.50	0.74	3.2	148	0.070
disulfoton sulfoxide	0.50	0.58	12	116	0.20
endosulfan I	0.50	0.55	18	110	0.30
endosulfan II	0.50	0.50	29	99	0.44
endosulfan sulfate	0.50	0.62	7.2	124	0.13
endrin	0.50	0.54	18	108	0.29
endrin aldehyde	0.50	0.43	15	87	0.19
EPTC	0.50	0.50	7.2	100	0.11
ethoprop	0.50	0.62	6.1	123	0.11
etridiazole	0.50	0.69	7.6	139	0.16
fenamiphos	5.0	5.2	6.1	103	0.95
fenarimol	5.0	6.3	6.5	126	1.2
fluorene	0.50	0.46	4.2	93	0.059
fluridone	5.0	5.1	3.6	102	0.55
HCH, alpha	0.50	0.51	13	102	0.20
HCH, beta	0.50	0.51	20	102	0.31
HCH, delta	0.50	0.56	13	112	0.21
HCH, gamma (Lindane)	0.50	0.63	8.0	126	0.15
heptachlor	0.50	0.41	12	83	0.15
heptachlor epoxide	0.50	0.35	5.5	70	0.053
2,2',3,3',4,4',6-heptachlorobiphenyl	0.50	0.35	10	71	0.11
hexachlorobenzene	0.50	0.39	11	78	0.13
2,2',4,4',5,6'-hexachlorobiphenyl	0.50	0.37	9.6	73	0.11
hexachlorocyclopentadiene	0.50	0.43	5.6	86	0.072
hexazinone	0.50	0.70	5.0	140	0.11

TABLE 3. ACCURACY AND PRECISION DATA FROM EIGHT DETERMINATIONS OF THE METHOD ANALYTES IN REAGENT WATER USING LIQUID-SOLID C-18 CARTRIDGE EXTRACTION AND THE QUADRUPOLE MASS SPECTROMETER

Compound	True Conc. (µg/L)	Mean Observed Conc. (µg/L)	Relative Standard Deviation (%)	Mean Method Accuracy (% of True Conc.)	MDL (µg/L)
indeno[1,2,3,c,d]pyrene	0.50	0.69	2.7	139	0.057
isophorone	0.50	0.44	3.2	88	0.042
methoxychlor	0.50	0.62	4.2	123	0.077
methyl paraoxon	0.50	0.57	10	115	0.17
metolachlor	0.50	0.37	8.0	75	0.090
metribuzin	0.50	0.49	11	97	0.16
mevinphos	0.50	0.57	12	114	0.20
MGK 264 - isomer a	0.33	0.39	3.4	116	0.040
MGK 264 - isomer b	0.17	0.16	6.4	96	0.030
molinate	0.50	0.53	5.5	105	0.087
napropamide	0.50	0.58	3.5	116	0.060
norflurazon	0.50	0.63	7.1	126	0.13
2,2',3,3',4,5',6,6'-octachlorobiphenyl	0.50	0.50	8.7	101	0.13
pebulate	0.50	0.49	5.4	98	0.080
2,2',3',4,6-pentachlorobiphenyl	0.50	0.30	16	61	0.15
pentachlorophenol	ND	ND	ND	ND	ND
permethrin, cis	0.25	0.30	3.7	121	0.034
permethrin, trans	0.75	0.82	2.7	109	0.067
phenathrene	0.50	0.46	4.3	92	0.059
prometon	0.50	0.30	42	60	0.38
prometryn	0.50	0.46	56	92	0.078
pronamide	0.50	0.54	5.9	108	0.095
propachlor	0.50	0.49	7.5	98	0.11
propazine	0.50	0.54	7.1	108	0.12
pyrene	0.50	0.38	5.7	77	0.066
simazine	0.50	0.55	9.1	109	0.15
simetryn	0.50	0.52	8.2	105	0.13
stirofos	0.50	0.75	5.8	149	0.13
tebuthiuron	5.0	6.8	14	136	2.8
terbacil	5.0	4.9	14	97	2.1
terbufos	0.50	0.53	6.1	106	0.096
terbutryn	0.50	0.47	7.6	95	0.11
2,2',4,4'-tetrachlorobiphenyl	0.50	0.36	4.1	71	0.044
trademefon	0.50	0.57	20	113	0.33
2,4,5-trichlorobiphenyl	0.50	0.38	6.7	75	0.075

TABLE 3. ACCURACY AND PRECISION DATA FROM EIGHT DETERMINATIONS OF THE METHOD ANALYTES IN REAGENT WATER USING LIQUID-SOLID C-18 CARTRIDGE EXTRACTION AND THE QUADRUPOLE MASS SPECTROMETER

Compound	True Conc. (µg/L)	Mean Observed Conc. (µg/L)	Relative Standard Deviation (%)	Mean Method Accuracy (% of True Conc.)	MDL (µg/L)
tricyclazole	5.0	4.6	19	92	2.6
trifluralin	0.50	0.63	5.1	127	0.096
vernolate	0.50	0.51	5.5	102	0.084

ND = Not determined.

[a]Data from samples extracted at pH 2 - for accurate determination of this analyte, a separate sample must be extracted at ambient pH.

TABLE 4. ACCURACY AND PRECISION DATA FROM EIGHT DETERMINATIONS OF THE METHOD ANALYTES IN REAGENT WATER USING LIQUID-SOLID C-18 DISK EXTRACTION AND THE QUADRUPOLE MASS SPECTROMETER

Compound	True Conc. (µg/L)	Mean Observed Conc. (µg/L)	Relative Standard Deviation (%)	Mean Method Accuracy (% of True Conc.)	MDL (µg/L)
Surrogates					
1,3-dimethyl-2-nitrobenzene	5.0	4.6	2.6	93	
perylene-d12	5.0	4.8	1.6	95	
triphenylphosphate	5.0	5.0	2.5	101	
Target Analytes					
acenaphthylene	0.50	0.47	8.4	94	0.12
alachlor	0.50	0.50	5.8	100	0.087
aldrin	0.50	0.39	13	78	0.16
ametryn	0.50	0.38	28	76	0.32
anthracene	0.50	0.49	13	98	0.18
atraton	0.50	0.07	139	19	0.40
atrazine	0.50	0.60	3.7	119	0.065
benz[a]anthracene	0.50	0.38	6.1	76	0.070
benzo[b]fluoranthene	0.50	0.61	2.5	121	0.046
benzo[k]fluoranthene	0.50	0.61	27	122	0.50
benzo[g,h,i]perylene	0.50	0.69	1.4	138	0.029
benzo[a]pyrene	0.50	0.58	6.1	116	0.11
bromacil	0.50	0.49	23	99	0.34
butachlor	0.50	0.63	2.1	127	0.039
butylate	0.50	0.50	4.9	99	0.073
butylbenzylphthalate	0.50	0.78	5.5	156	0.13
carboxin	5.0	2.7	12	54	0.98
chlordane (alpha-chlordane)	0.50	0.37	5.5	74	0.061
chlordane (gamma-chlordane)	0.50	0.40	4.2	80	0.050
chlordane (trans-nonachlor)	0.50	0.45	7.8	90	0.11
chlorneb	0.50	0.51	7.3	100	0.11
chlorobenzilate	5.0	7.9	8.4	156	2.0
2-chlorobiphenyl	0.50	0.42	1.9	84	0.023
chlorpropham	0.50	0.68	5.4	134	0.11
chlorpyrifos	0.50	0.61	6.5	119	0.12
chlorthalonil	0.50	0.59	6.5	116	0.11
chrysene	0.50	0.35	3.6	71	0.038
cyanazine	0.50	0.68	15	136	0.31
cycloate	0.50	0.53	4.9	106	0.077
DCPA	0.50	0.55	4.5	110	0.073
4,4'-DDE	0.50	0.48	4.9	96	0.070
4,4'-DDT	0.50	0.93	3.2	187	0.090
4,4-DDD	0.50	0.67	14	137	0.28

TABLE 4. ACCURACY AND PRECISION DATA FROM EIGHT DETERMINATIONS OF THE METHOD ANALYTES IN REAGENT WATER USING LIQUID-SOLID C-18 DISK EXTRACTION AND THE QUADRUPOLE MASS SPECTROMETER

Compound	True Conc. (µg/L)	Mean Observed Conc. (µg/L)	Relative Standard Deviation (%)	Mean Method Accuracy (% of True Conc.)	MDL (µg/L)
diazinon	0.50	0.56	6.8	109	0.11
dibenz[a,h]anthracene	0.50	0.61	15	122	0.28
di-n-butylphthalate	ND	ND	ND	ND	ND
2,3-dichlorobiphenyl	0.50	0.46	8.1	93	0.11
dichlorvos	0.50	0.54	5.6	108	0.092
dieldrin	0.50	0.52	7.8	104	0.12
di-(2-ethylhexyl) adipate	ND	ND	ND	ND	ND
di(2-ethylhexyl) phthalate	ND	ND	ND	ND	ND
diethylphthalate	0.50	0.66	10	132	0.20
dimethylphthalate	0.50	0.57	8.3	114	0.14
2,4-dinitrotoluene	0.50	0.54	5.7	109	0.093
2,6-dinitrotoluene	0.50	0.48	4.9	96	0.071
diphenamid	0.50	0.60	3.8	118	0.067
disulfoton	5.0	4.8	9.4	96	1.3
disulfoton sulfone	0.50	0.82	2.8	164	0.070
disulfoton sulfoxide	0.50	0.68	8.9	136	0.18
endosulfan I	0.50	0.65	10	132	0.20
endosulfan II	0.50	0.60	21	122	0.38
endosulfan sulfate	0.50	0.67	6.1	133	0.12
endrin	0.50	0.58	18	116	0.31
endrin aldehyde	0.50	0.51	16	101	0.24
EPTC	0.50	0.50	3.8	100	0.056
ethoprop	0.50	0.69	2.3	138	0.048
etridiazole	0.50	0.74	4.0	149	0.090
fenamiphos	5.0	6.3	8.8	124	1.6
fenarimol	5.0	7.5	5.5	150	1.2
fluorene	0.50	0.47	8.1	94	0.11
fluridone	5.0	5.7	4.5	114	0.77
HCH, alpha	0.50	0.54	12	107	0.20
HCH, beta	0.50	0.57	17	112	0.28
HCH, delta	0.50	0.61	8.2	120	0.15
HCH, gamma (Lindane)	0.50	0.62	6.6	124	0.12
heptachlor	0.50	0.40	12	80	0.14
heptachlor epoxide	0.50	0.36	8.7	71	0.093
2,2',3,3',4,4',6-heptachlorobiphenyl	0.50	0.36	13	71	0.14
hexachlorobenzene	0.50	0.47	8.3	95	0.12
2,2',4,4',5,6'-hexachlorobiphenyl	0.50	0.41	11	83	0.13
hexachlorocyclopentadiene	0.50	0.42	12	84	0.16
hexazinone	0.50	0.85	5.6	169	0.14

TABLE 4. ACCURACY AND PRECISION DATA FROM EIGHT DETERMINATIONS OF THE METHOD ANALYTES IN REAGENT WATER USING LIQUID-SOLID C-18 DISK EXTRACTION AND THE QUADRUPOLE MASS SPECTROMETER

Compound	True Conc. (µg/L)	Mean Observed Conc. (µg/L)	Relative Standard Deviation (%)	Mean Method Accuracy (% of True Conc.)	MDL (µg/L)
indeno[1,2,3,c,d]pyrene	0.50	0.69	2.4	138	0.050
isophorone	0.50	0.41	4.2	83	0.052
methoxychlor	0.50	0.58	1.9	117	0.033
methyl paraoxon	0.50	0.62	14	122	0.25
metolachlor	0.50	0.38	7.5	75	0.084
metribuzin	0.50	0.54	3.9	107	0.062
mevinphos	0.50	0.72	3.7	143	0.079
MGK 264 - isomer a	0.33	0.40	8.8	119	0.10
MGK 264 - isomer b	0.17	0.17	5.9	103	0.030
molinate	0.50	0.53	3.2	105	0.050
napropamide	0.50	0.64	5.9	126	0.11
norflurazon	0.50	0.70	4.2	141	0.089
2,2',3,3',4,5',6,6'-octachlorobiphenyl	0.50	0.51	4.2	102	0.064
pebulate	0.50	0.48	5.8	96	0.084
2,2',3',4,6-pentachlorobiphenyl	0.50	0.35	4.2	70	0.044
pentachlorophenol	2.0	1.9	16	95	.89
permethrin,cis	0.25	0.32	3.3	126	0.031
permethrin,trans	0.75	0.89	1.9	118	0.051
phenathrene	0.50	0.48	5.0	95	0.071
prometon	0.50	0.21	66	45	0.44
prometryn	0.50	0.46	24	93	0.33
pronamide	0.50	0.58	7.1	113	0.12
propachlor	0.50	0.49	5.4	98	0.079
propazine	0.50	0.59	5.0	117	0.088
pyrene	0.50	0.40	3.2	79	0.038
simazine	0.50	0.60	10	120	0.18
simetryn	0.50	0.41	15	83	0.19
stirofos	0.50	0.84	3.2	168	0.081
tebuthiuron	5.0	9.3	8.6	187	2.4
terbacil	5.0	5.0	11	100	1.7
terbufos	0.50	0.62	4.2	123	0.077
terbutryn	0.50	0.46	23	94	0.32
2,2',4,4'-tetrachlorobiphenyl	0.50	0.40	7.4	79	0.088
trialemefon	0.50	0.73	7.2	145	0.16
2,4,5-trichlorobiphenyl	0.50	0.44	5.3	89	0.071

TABLE 4. ACCURACY AND PRECISION DATA FROM EIGHT DETERMINATIONS OF THE METHOD ANALYTES IN REAGENT WATER USING LIQUID-SOLID C-18 DISK EXTRACTION AND THE QUADRUPOLE MASS SPECTROMETER

Compound	True Conc. (µg/L)	Mean Observed Conc. (µg/L)	Relative Standard Deviation (%)	Mean Method Accuracy (% of True Conc.)	MDL (µg/L)
tricyclazole	5.0	6.8	12	137	2.4
trifluralin	0.50	0.62	2.6	124	0.048
vernolate	0.50	0.51	3.4	100	0.051

ND = Not determined.

[a]Data from samples extracted at pH 2 - for accurate determination of this analyte, a separate sample must be extracted at ambient pH.

TABLE 5. ACCURACY AND PRECISION DATA FROM EIGHT DETERMINATIONS OF THE METHOD ANALYTES IN REAGENT WATER USING LIQUID-SOLID C-18 CARTRIDGE EXTRACTION AND THE ION TRAP MASS SPECTROMETER

Compound	True Conc. (µg/L)	Mean Observed Conc. (µg/L)	Relative Standard Deviation (%)	Mean Method Accuracy (% of True Conc.)	MDL (µg/L)
Surrogates					
1,3-dimethyl-2-nitrobenzene	5.0	4.9	8.4	98	
perylene-d12	5.0	4.3	18	86	
triphenylphosphate	5.0	4.8	13	96	
Target Analytes					
acenaphthylene	0.50	0.50	8.8	100	0.13
alachlor	0.50	0.58	4.0	115	0.069
aldrin	0.50	0.42	3.5	85	0.045
ametryn	0.50	0.46	3.3	91	0.045
anthracene	0.50	0.42	3.8	84	0.048
aroclor 1016	1.0	1.1	4.4	113	0.15
aroclor 1254[a]	1.0	1.1	17	110	0.59
aroclor 1260	1.0	0.96	9.3	96	0.27
atraton	0.50	0.35	11	70	0.12
atrazine	0.50	0.55	5.0	109	0.081
benz[a]anthracene	0.50	0.43	7.3	85	0.093
benzo[b]fluoranthene	0.50	0.44	16	88	0.21
benzo[k]fluoranthene	0.50	0.34	22	68	0.23
benzo[g,h,i]perylene	0.50	0.38	31	76	0.35
benzo[a]pyrene	0.50	0.36	21	73	0.23
bromacil	0.50	0.45	9.1	90	0.12
butachlor	0.50	0.67	12	133	0.24
butylate	0.50	0.52	5.2	104	0.082
butylbenzylphthalate[b]	5.0	5.7	7.7	114	1.4
carboxin	0.50	0.58	22	117	0.38
chlordane, (alpha-chlordane)	0.50	0.47	12	95	0.17
chlordane, (gamma-chlordane)	0.50	0.50	10	99	0.16
chlordane, (trans-nonachlor)	0.50	0.48	11	96	0.16
chlorneb	0.50	0.51	8.1	103	0.13
chlorobenzilate	0.50	0.61	9.7	123	0.17
2-chlorobiphenyl	0.50	0.47	4.8	94	0.068
chlorpropham	0.50	0.55	8.1	109	0.13
chlorpyrifos	0.50	0.50	2.4	99	0.035
chlorthalonil	0.50	0.62	5.3	123	0.098
chrysene	0.50	0.50	9.2	99	0.14
cyanazine	0.50	0.49	13	97	0.19
cycloate	0.50	0.52	7.6	103	0.12
DCPA	0.50	0.55	7.2	109	0.12

TABLE 5. ACCURACY AND PRECISION DATA FROM EIGHT DETERMINATIONS OF THE METHOD ANALYTES IN REAGENT WATER USING LIQUID-SOLID C-18 CARTRIDGE EXTRACTION AND THE ION TRAP MASS SPECTROMETER

Compound	True Conc. (µg/L)	Mean Observed Conc. (µg/L)	Relative Standard Deviation (%)	Mean Method Accuracy (% of True Conc.)	MDL (µg/L)
4,4'-DDD	0.50	0.52	3.6	103	0.055
4,4'-DDE	0.50	0.41	5.8	81	0.070
4,4'-DDT	0.50	0.54	2.4	108	0.039
diazinon	0.50	0.37	2.7	75	0.030
dibenz[a,h]anthracene	0.50	0.37	29	74	0.32
di-n-butylphthalate[b]	5.0	6.2	4.6	124	0.89
2,3-dichlorobiphenyl	0.50	0.45	5.8	90	0.079
dichlorvos	0.50	0.53	8.0	106	0.13
dieldrin	0.50	0.50	10	100	0.15
di(2-ethylhexyl)adipate	0.50	0.59	18	117	0.31
di(2-ethylhexyl)phthalate[b]	5.0	6.5	6.6	130	7.9
diethylphthalate	0.50	0.63	15	126	0.28
dimethylphthalate	0.50	0.51	9.5	102	0.14
2,4-dinitrotoluene	0.50	0.45	18	91	0.24
2,6-dinitrotoluene	0.50	0.40	17	80	0.20
diphenamid	0.50	0.55	6.5	111	0.11
disulfoton	0.50	0.62	9.8	124	0.18
disulfoton sulfone	0.50	0.64	3.5	128	0.068
disulfoton sulfoxide	0.50	0.57	8.6	114	0.15
endosulfan I	0.50	0.60	6.1	121	0.11
endosulfan II	0.50	0.64	3.9	128	0.074
endosulfan sulfate	0.50	0.58	5.4	116	0.093
endrin	0.50	0.62	18	124	0.34
endrin aldehyde	0.50	0.58	8.7	116	0.15
EPTC	0.50	0.53	7.7	105	0.12
ethoprop	0.50	0.62	10	124	0.19
etridiazole	0.50	0.61	6.5	122	0.12
fenamiphos	0.50	0.67	12	133	0.24
fenarimol	0.50	0.74	11	148	0.25
fluorene	0.50	0.49	9.0	98	0.13
fluridone	5.0	5.2	2.5	105	0.18
HCH, alpha	0.50	0.55	6.8	109	0.11
HCH,beta	0.50	0.54	5.3	107	0.085
HCH,delta	0.50	0.52	3.1	105	0.049
HCH, gamma (Lindane)	0.50	0.53	5.3	105	0.084
heptachlor	0.50	0.50	4.1	100	0.061
heptachlorepoxide	0.50	0.54	8.2	108	0.13
2,2',3,3',4,4',6-heptachlorobiphenyl	0.50	0.45	11	90	0.15
hexachlorobenzene	0.50	0.41	6.0	82	0.074

TABLE 5. ACCURACY AND PRECISION DATA FROM EIGHT DETERMINATIONS OF THE METHOD ANALYTES IN REAGENT WATER USING LIQUID-SOLID C-18 CARTRIDGE EXTRACTION AND THE ION TRAP MASS SPECTROMETER

Compound	True Conc. (µg/L)	Mean Observed Conc. (µg/L)	Relative Standard Deviation (%)	Mean Method Accuracy (% of True Conc.)	MDL (µg/L)
2,2',4,4',5,6'-hexachlorobiphenyl	0.50	0.40	15	80	0.18
hexachlorocyclopentadiene	0.50	0.34	13	68	0.13
hexazinone	0.50	0.80	5.6	159	0.14
indeno[1,2,3,c,d]pyrene	0.50	0.36	28	71	0.30
isophorone	0.50	0.54	7.9	107	0.13
methoxychlor	0.50	0.58	7.7	115	0.13
methyl paraoxon	0.50	0.85	3.7	170	0.094
metolachlor	0.50	0.58	4.8	117	0.085
metribuzin	0.50	0.54	14	108	0.22
mevinphos	0.50	0.47	12	95	0.17
MGK 264 - isomer a	0.33	0.38	9.5	113	0.11
MGK 264 - isomer b	0.16	0.18	5.4	105	0.029
molinate	0.50	0.55	5.2	111	0.086
napropamide	0.50	0.63	10	127	0.20
norflurazon	0.50	0.82	3.8	165	0.093
2,2',3,3',4,5',6,6'-octachlorobiphenyl	0.50	0.49	19	99	0.28
pebulate	0.50	0.56	6.1	112	0.10
2,2',3',4,6-pentachlorobiphenyl	0.50	0.43	8.7	86	0.11
pentachlorophenol	2.0	2.4	10	119	0.72
permethrin,cis	0.25	0.45	3.2	179	0.043
permethrin,trans	0.75	1.1	2.2	153	0.074
phenanthrene	0.50	0.48	4.8	96	0.069
prometon	0.50	0.24	27	48	0.20
prometryn	0.50	0.46	3.0	92	0.041
pronamide	0.50	0.56	5.3	113	0.089
propachlor	0.50	0.56	8.6	112	0.14
propazine	0.50	0.52	4.3	103	0.066
pyrene	0.50	0.47	11	95	0.16
simazine	0.50	0.48	8.8	96	0.13
simetryn	0.50	0.48	2.9	96	0.042
stirofos	0.50	0.80	3.9	160	0.093
tebuthiuron	0.50	0.67	7.4	134	0.15
terbacil	0.50	0.59	12	119	0.22
terbufos	0.50	0.46	11	92	0.15
terbutryn	0.50	0.48	2.6	97	0.038
2,2',4,4'-tetrachlorobiphenyl	0.50	0.40	6.4	81	0.077
toxaphene	10	11	4.9	118	1.7
triademefon	0.50	0.73	6.4	146	0.14

TABLE 5. ACCURACY AND PRECISION DATA FROM EIGHT DETERMINATIONS OF THE METHOD ANALYTES IN REAGENT WATER USING LIQUID-SOLID C-18 CARTRIDGE EXTRACTION AND THE ION TRAP MASS SPECTROMETER

Compound	True Conc. (µg/L)	Mean Observed Conc. (µg/L)	Relative Standard Deviation (%)	Mean Method Accuracy (% of True Conc.)	MDL (µg/L)
2,4,5-trichlorobiphenyl	0.50	0.44	3.3	88	0.043
tricyclazole	0.50	0.63	16	127	0.31
trifluralin	0.50	0.62	13	124	0.24
vernolate	0.50	0.50	9.3	101	0.14

[a]Seven replicates.
[b]Seven replicates in fortified tap water.
[c]Data from samples extracted at pH 2 - for accurate determination of this analyte, a separate sample must be extracted at ambient pH.

TABLE 6. ACCURACY AND PRECISION DATA FROM EIGHT DETERMINATIONS OF THE METHOD ANALYTES IN REAGENT WATER USING LIQUID-SOLID C-18 DISK EXTRACTION AND THE ION TRAP MASS SPECTROMETER

Compound	True Conc. (µg/L)	Mean Observed Conc. (µg/L)	Relative Standard Deviation (%)	Mean Method Accuracy (% of True Conc.)	MDL (µg/L)
Surrogates					
1,3-dimethyl-2-nitrobenzene	5.0	4.9	10	98	
perylene-d12	5.0	4.9	4.5	98	
triphenylphosphate	5.0	5.9	8.1	117	
Target Analytes					
acenaphthylene	0.50	0.51	4.5	102	0.068
alachlor	0.50	0.54	6.6	108	0.11
aldrin	0.50	0.45	6.3	90	0.085
ametryn	0.50	0.41	23	82	0.29
anthracene	0.50	0.39	15	79	0.18
aroclor 1016	1.0	0.94	7.5	94	0.21
aroclor 1254	1.0	0.94	7.4	94	0.20
aroclor 1260[a]	1.0	1.2	13	125	0.53
atraton	0.50	0.10	46	21	0.14
atrazine	0.50	0.56	4.6	111	0.076
benz[a]anthracene	0.50	0.44	7.4	88	0.098
benzo[b]fluoranthene	0.50	0.50	9.1	100	0.14
benzo[k]fluoranthene	0.50	0.46	2.2	91	0.031
benzo[g,h,i]perylene	0.50	0.47	7.9	95	0.11
benzo[a]pyrene	0.50	0.44	12	89	0.16
bromacil	0.50	0.49	4.4	99	0.066
butachlor	0.50	0.66	5.1	132	0.10
butylate	0.50	0.50	5.4	100	0.082
butylbenzylphthalate[b]	5.0	5.7	7.7	114	1.4
carboxin	0.50	0.40	38.1	79	0.45
chlordane, (alpha-chlordane)	0.50	0.50	4.3	101	0.065
chlordane, (gamma-chlordane)	0.50	0.51	7.2	102	0.11
chlordane, (trans-nonachlor)	0.50	0.52	6.2	104	0.097
chlorneb	0.50	0.54	6.3	108	0.10
chlorobenzilate	0.50	0.59	9.7	117	0.17
2-chlorobiphenyl	0.50	0.50	4.7	100	0.070
chlorpropham	0.50	0.55	4.7	111	0.079
chlorpyrifos	0.50	0.54	11	109	0.18
chlorthalonil	0.50	0.59	4.4	119	0.079
chrysene	0.50	0.48	6.1	96	0.088
cyanazine	0.50	0.52	8.3	105	0.13
cycloate	0.50	0.51	4.1	102	0.063
DCPA	0.50	0.53	3.2	105	0.051

TABLE 6. ACCURACY AND PRECISION DATA FROM EIGHT DETERMINATIONS OF THE METHOD ANALYTES IN REAGENT WATER USING LIQUID-SOLID C-18 DISK EXTRACTION AND THE ION TRAP MASS SPECTROMETER

Compound	True Conc. (µg/L)	Mean Observed Conc. (µg/L)	Relative Standard Deviation (%)	Mean Method Accuracy (% of True Conc.)	MDL (µg/L)
4,4'-DDD	0.50	0.63	16	127	0.31
4,4'-DDE	0.50	0.48	3.7	96	0.054
4,4'-DDT	0.50	0.58	7.2	117	0.13
diazinon	0.50	0.50	4.5	101	0.068
dibenz[a,h]anthracene	0.50	0.47	9.9	94	0.14
di-n-butylphthalate[b]	5.0	5.7	3.3	115	0.59
2,3-dichlorobiphenyl	0.50	0.50	2.6	100	0.039
dichlorvos	0.50	0.50	8.7	99	0.13
dieldrin	0.50	0.53	7.0	106	0.11
di(2-ethylhexyl)adipate[b]	5.0	5.4	7.5	107	1.3
di(2-ehtylhexyl)phthalate[b]	5.0	5.7	2.6	114	0.46
diethylphthalate	0.50	0.68	5.0	137	0.10
dimethylphthalate	0.50	0.51	5.0	102	0.077
2,6-dinitrotoluene	0.50	0.28	6.4	56	0.054
2,4-dinitrotoluene	0.50	0.30	8.1	59	0.072
diphenamid	0.50	0.56	6.4	112	0.11
disulfoton	0.50	0.70	5.3	139	0.11
disulfoton sulfone	0.50	0.64	5.9	128	0.11
disulfoton sulfoxide	0.50	0.60	3.8	119	0.068
endosulfan I	0.50	0.61	4.9	122	0.089
endosulfan II	0.50	0.66	6.1	131	0.12
endosulfan sulfate	0.50	0.57	9.0	115	0.16
endrin	0.50	0.68	7.9	137	0.16
endrin aldehyde	0.50	0.57	2.8	114	0.048
EPTC	0.50	0.48	5.2	97	0.076
ethoprop	0.50	0.61	7.5	122	0.14
etridiazole	0.50	0.54	4.2	108	0.067
fenamiphos	0.50	0.67	10	133	0.20
fenarimol	0.50	0.59	5.8	118	0.10
fluorene	0.50	0.53	3.4	106	0.054
fluridone	5.0	5.2	2.3	104	0.16
HCH, alpha	0.50	0.55	5.0	110	0.083
HCH, gamma (Lindane)	0.50	0.50	3.2	100	0.047
HCH,beta	0.50	0.54	4.1	109	0.068
HCH,delta	0.50	0.53	3.6	106	0.058
heptachlor	0.50	0.49	4.0	98	0.059
heptachlorepoxide	0.50	0.50	3.2	100	0.048
2,2,',3',4,4',6-heptachlorobiphenyl	0.50	0.46	7.3	92	0.10
hexachlorobenzene	0.50	0.49	3.4	97	0.049

TABLE 6. ACCURACY AND PRECISION DATA FROM EIGHT DETERMINATIONS OF THE METHOD ANALYTES IN REAGENT WATER USING LIQUID-SOLID C-18 DISK EXTRACTION AND THE ION TRAP MASS SPECTROMETER

Compound	True Conc. (µg/L)	Mean Observed Conc. (µg/L)	Relative Standard Deviation (%)	Mean Method Accuracy (% of True Conc.)	MDL (µg/L)
2,2',4,4',5,6'-hexachlorobiphenyl	0.50	0.50	5.3	99	0.079
hexachlorocyclopentadiene	0.50	0.37	9.3	73	0.10
hexazinone	0.50	0.75	4.2	150	0.094
indeno[1,2,3,c,d]pyrene	0.50	0.48	7.3	96	0.10
isophorone	0.50	0.51	4.3	102	0.066
methoxychlor	0.50	0.52	6.7	104	0.10
methyl paraoxon	0.50	0.75	4.5	151	0.10
metolachlor	0.50	0.57	3.2	114	0.054
metribuzin	0.50	0.53	5.7	107	0.090
mevinphos	0.50	0.56	6.2	112	0.10
MGK 264 - isomer a	0.33	0.38	6.7	113	0.076
MGK 264 - isomer b	0.16	0.18	5.3	110	0.029
molinate	0.50	0.53	3.8	105	0.060
napropamide	0.50	0.58	7.9	116	0.14
norflurazon	0.50	0.71	4.3	142	0.091
2,2',3,3',4,5',6,6'-octachlorobiphenyl	0.50	0.47	5.3	94	0.076
pebulate	0.50	0.56	7.1	112	0.11
2,2',3',4,6-pentachlorobiphenyl	0.50	0.49	4.0	97	0.059
pentachlorophenol	2.0	2.2	15	111	1.0
permethrin,cis	0.25	0.37	3.1	149	0.035
permethrin,trans	0.75	0.84	1.6	112	0.039
phenanthrene	0.50	0.49	6.3	97	0.092
prometon	0.50	0.16	63	32	0.30
prometryn	0.50	0.46	23	91	0.32
pronamide	0.50	0.56	3.9	111	0.064
propachlor	0.50	0.58	5.7	115	0.098
propazine	0.50	0.53	4.7	106	0.074
pyrene	0.50	0.52	5.2	104	0.080
simazine	0.50	0.54	2.8	107	0.045
simetryn	0.50	0.36	20	71	0.22
stirofos	0.50	0.72	3.7	144	0.080
tebuthiuron	0.50	0.67	7.9	133	0.16
terbacil	0.50	0.64	12	129	0.23
terbufos	0.50	0.57	6.8	113	0.11
terbutryn	0.50	0.46	24	93	0.34
2,2',,4'-tetrachlorobiphenyl	0.50	0.46	7.4	91	0.10
toxaphene[c]	10	12	2.7	122	1.0
trialemefon	0.50	0.71	7.3	142	0.16
2,4,5-trichlorobiphenyl	0.50	0.48	4.5	97	0.066

TABLE 6. ACCURACY AND PRECISION DATA FROM EIGHT DETERMINATIONS OF THE METHOD ANALYTES IN REAGENT WATER USING LIQUID-SOLID C-18 DISK EXTRACTION AND THE ION TRAP MASS SPECTROMETER

Compound	True Conc. (µg/L)	Mean Observed Conc. (µg/L)	Relative Standard Deviation (%)	Mean Method Accuracy (% of True Conc.)	MDL (µg/L)
tricyclazole	0.50	0.65	14	130	0.27
trifluralin	0.50	0.59	7.8	117	0.14
vernolate	0.50	0.50	3.2	99	0.047

[a]Six replicates.
[b]Seven replicates.
[c]Seven replicates in fortified tap water.
[d]Data from samples extracted at pH 2 - for accurate determination of this analyte, a separate sample must be extracted at ambient pH.

TABLE 7. ACCURACY AND PRECISION DATA FROM EIGHT DETERMINATIONS AT 5 µg/L IN REAGENT WATER OF POORLY CHROMATOGRAPHED NITROGEN AND PHOSPHOROUS CONTAINING PESTICIDES

	Ion Trap Mass Spectrometer				Quadrupole Mass Spectrometer			
	Cartridge		Disk		Cartridge		Disk	
Compound	Relative Standard Deviation (%)	Mean Method Accuracy (% of True Conc.)	Relative Standard Deviation (%)	Mean Method Accuracy (% of True Conc.)	Relative Standard Deviation (%)	Mean Method Accuracy (% of True Conc.)	Relative Standard Deviation (%)	Mean Method Accuracy (% of True Conc.)
fenamiphos	7.7	99	4.5	108	6.1	103	8.8	124
fenarimol	2.0	104	10	110	6.5	126	5.5	150
fluridone	2.5	105	2.3	104	3.6	102	4.5	114
hexazinone	4.2	106	9.7	116	5.3	104	8.3	127
norflurazon	4.1	111	9.6	119	3.2	98	11.1	113
stirofos	8.2	114	12	124	4.1	110	11.1	125
tebuthiuron	9.5	119	5.3	145	13	136	8.6	182
triademeton	7.8	113	10	128	3.7	100	9.8	118
tricyclazole	16	81	9.5	99	19	92	12	137

TABLE 8. ACCURACY AND PRECISION DATA FROM SEVEN DETERMINATIONS OF THE METHOD ANALYTES IN TAP WATER USING LIQUID-SOLID C-18 CARTRIDGE EXTRACTION AND THE ION TRAP MASS SPECTROMETER

Compound	True Conc.	Mean	% RSD	% REC
acenaphthylene	5.0	5.2	5.3	104
alachlor	5.0	5.5	6.9	110
aldrin	5.0	4.4	14	88
ametryn	5.0	4.2	3.4	83
anthracene	5.0	4.3	5.2	87
atraton	5.0	2.2	28	43
atrazine	5.0	5.6	6.2	111
benz[a]anthracene	5.0	4.9	8.8	97
benzo[b]fluoranthene	5.0	5.7	7.5	114
benzo[k]fluoranthene	5.0	5.7	2.9	113
benzo[g,h,i]perylene	5.0	5.6	7.1	113
benzo[a]pyrene	5.0	6.1	4.6	121
bromacil	5.0	3.5	5.1	69
butachlor	5.0	5.4	7.5	109
butylate	5.0	5.1	4.5	102
butylbenzylphthalate	5.0	7.2	8.3	144
carboxin	5.0	1.0	23	20
chlordane, (alpha-chlordane)	5.0	5.2	8.9	104
chlordane, (gamma-chlordane)	5.0	5.1	8.0	102
chlordane, (trans-nonachlor)	5.0	5.6	7.4	111
chlorneb	5.0	5.2	3.0	105
chlorobenzilate	5.0	5.7	4.4	114
2-chlorobiphenyl	5.0	5.8	5.4	115
chlorpropham	5.0	6.3	4.9	127
chlorpyrifos	5.0	5.3	7.2	107
chlorthalonil	5.0	5.4	9.9	108
chrysene	5.0	5.5	3.9	110
cyanazine	5.0	6.1	13	122
cycloate	5.0	5.6	1.5	112
DCPA	5.0	5.4	5.0	107
4,4'-DDD	5.0	5.3	6.5	105
4,4'-DDE	5.0	5.2	6.6	104
4,4'-DDT	5.0	5.6	9.6	111
diazinon	5.0	4.9	8.7	98
dibenz[a,h]anthracene	5.0	5.9	7.5	118
di-n-butylphthalate	5.0	6.2	4.6	124
2,3-dichlorobiphenyl	5.0	5.3	7.4	106
dichlorvos	5.0	2.8	7.3	56
dieldrin	5.0	5.3	7.2	105
di(2-ethylhexyl) adipate	5.0	6.7	10	134
di(2-ethylhexyl) phthalate	5.0	6.5	6.6	130

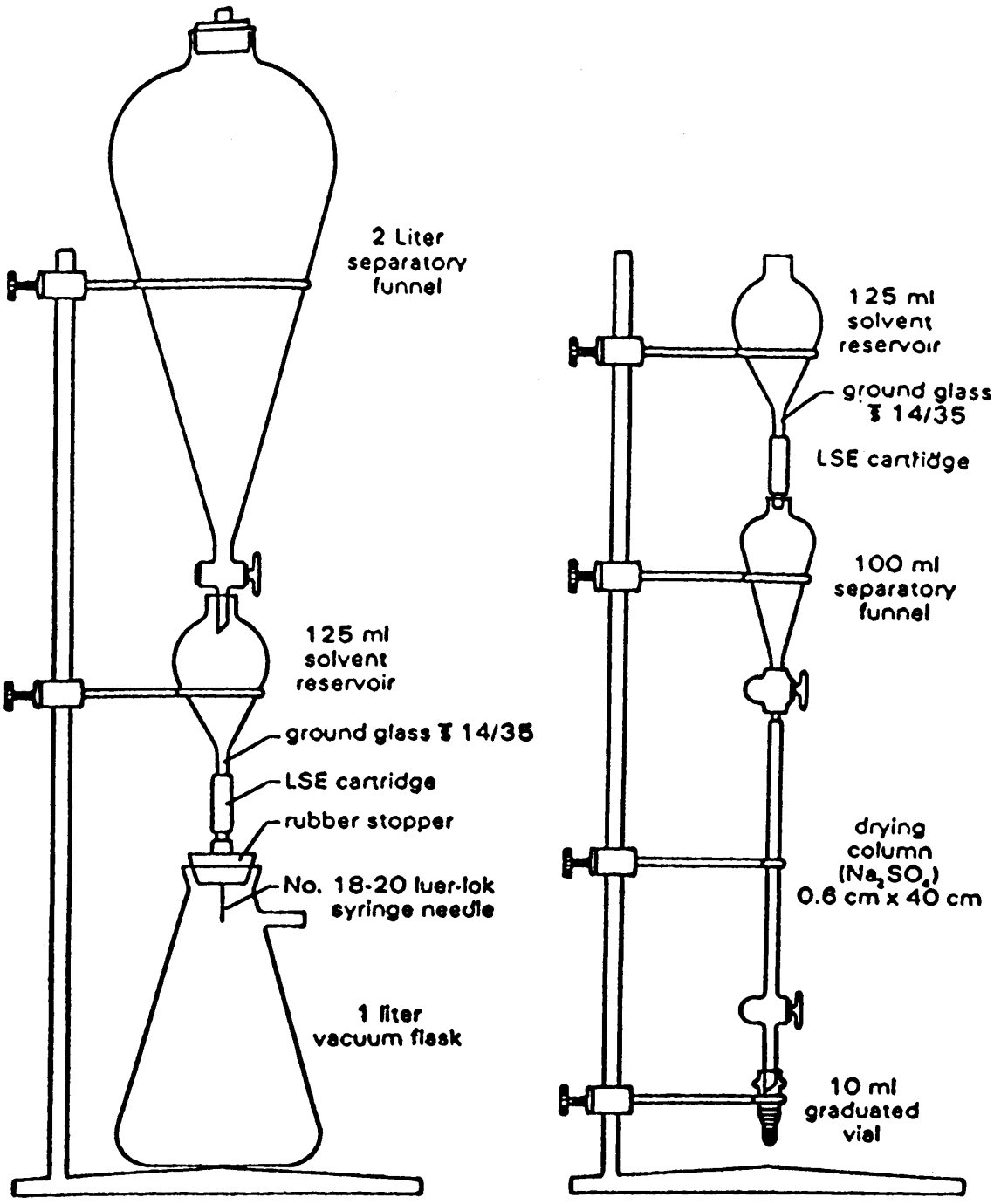
TABLE 8. ACCURACY AND PRECISION DATA FROM SEVEN DETERMINATIONS OF THE METHOD ANALYTES IN TAP WATER USING LIQUID-SOLID C-18 CARTRIDGE EXTRACTION AND THE ION TRAP MASS SPECTROMETER

Compound	True Conc.	Mean	% RSD	% REC
diethylphthalate	5.0	6.4	7.4	127
dimethylphthalate	5.0	5.8	7.1	116
2,4-dinitrotoluene	5.0	4.2	8.7	84
2,6-dinitrotoluene	5.0	4.1	8.5	82
diphenamid	5.0	5.2	7.7	104
disulfoton	5.0	2.5	33	50
disulfoton sulfone	5.0	5.5	7.4	110
disulfoton sulfoxide	5.0	9.4	11	188
endosulfan I	5.0	5.5	11	109
endosulfan II	5.0	5.3	9.6	106
endosulfan sulfate	5.0	5.3	7.8	106
endrin	5.0	6.1	3.9	121
endrin aldehyde	5.0	5.1	9.1	102
EPTC	5.0	5.1	2.1	102
ethoprop	5.0	6.3	4.2	125
etridiazole	5.0	5.8	7.5	117
fenamiphos	5.0	5.9	22	119
fenarimol	5.0	7.1	3.3	141
fluorene	5.0	5.7	5.2	114
fluridone	5.0	6.2	9.0	125
HCH, alpha	5.0	5.9	2.6	118
HCH, beta	5.0	5.3	8.4	106
HCH, delta	5.0	5.3	5.2	106
HCH, gamma (Lindane)	5.0	5.3	6.9	107
heptachlor	5.0	4.7	8.7	93
heptachlor epoxide	5.0	5.2	7.7	105
2,2',3,3',4,4',6-heptachlorobiphenyl	5.0	5.1	6.9	103
hexachlorobenzene	5.0	4.6	7.4	93
2,2',4,4',5,6'-hexachlorobiphenyl	5.0	5.6	8.1	112
hexachlorocyclopentadiene	5.0	6.0	4.8	120
hexazinone	5.0	6.9	6.3	138
indeno[1,2,3,c,d]pyrene	5.0	6.8	7.7	135
isophorone	5.0	4.9	12	99
methoxychlor	5.0	5.6	4.9	112
methyl paraoxon	5.0	5.6	11	111
metolachlor	5.0	5.6	7.7	111
metribuzin	5.0	2.1	5.8	42
mevinphos	5.0	3.3	1.6	67
MGK 264 - isomer a	3.3	3.6	6.2	107
MGK 264 - isomer b	1.7	1.8	7.6	110
molinate	5.0	5.5	1.5	110

TABLE 8. ACCURACY AND PRECISION DATA FROM SEVEN DETERMINATIONS OF THE METHOD ANALYTES IN TAP WATER USING LIQUID-SOLID C-18 CARTRIDGE EXTRACTION AND THE ION TRAP MASS SPECTROMETER

Compound	True Conc.	Mean	% RSD	% REC
napropamide	5.0	5.3	8.9	106
norflurazon	5.0	6.7	7.2	135
2,2',3',4,6-octaclorobiphenyl	5.0	4.9	6.9	97
pebulate	5.0	5.3	3.1	106
2,2',3',4,6-pentachlorobiphenyl	5.0	5.3	8.1	107
pentachlorophenol	20	33	4.9	162
permethrin, cis	5.0	3.3	3.5	130
permethrin, trans	5.0	8.5	2.2	113
phenanthrene	5.0	5.5	4.0	109
prometon	5.0	2.0	25	40
prometryn	5.0	4.5	4.3	89
pronamide	5.0	5.7	5.3	115
propachlor	5.0	6.2	4.0	124
propazine	5.0	5.6	4.9	113
pyrene	5.0	5.2	6.7	104
simazine	5.0	6.0	9.0	120
simetryn	5.0	3.9	7.0	78
stirofos	5.0	6.1	12	121
tebuthiuron	5.0	6.5	9.7	130
terbacil	5.0	4.0	5.5	79
terbufos	5.0	4.5	8.4	90
terbutryn	5.0	4.3	6.5	86
2,2',4,4'-tetrachlorobiphenyl	5.0	5.3	4.3	106
triademefon	5.0	6.0	12	121
2,4,5-trichlorobiphenyl	5.0	5.2	5.1	103
tricyclazole	5.0	4.8	5.2	96
trifluralin	5.0	5.9	7.8	119
vernolate	5.0	5.4	3.3	108

[a]Data from samples extracted at pH 2 - for accurate determination of this analyte, a separate sample must be extracted at ambient pH.

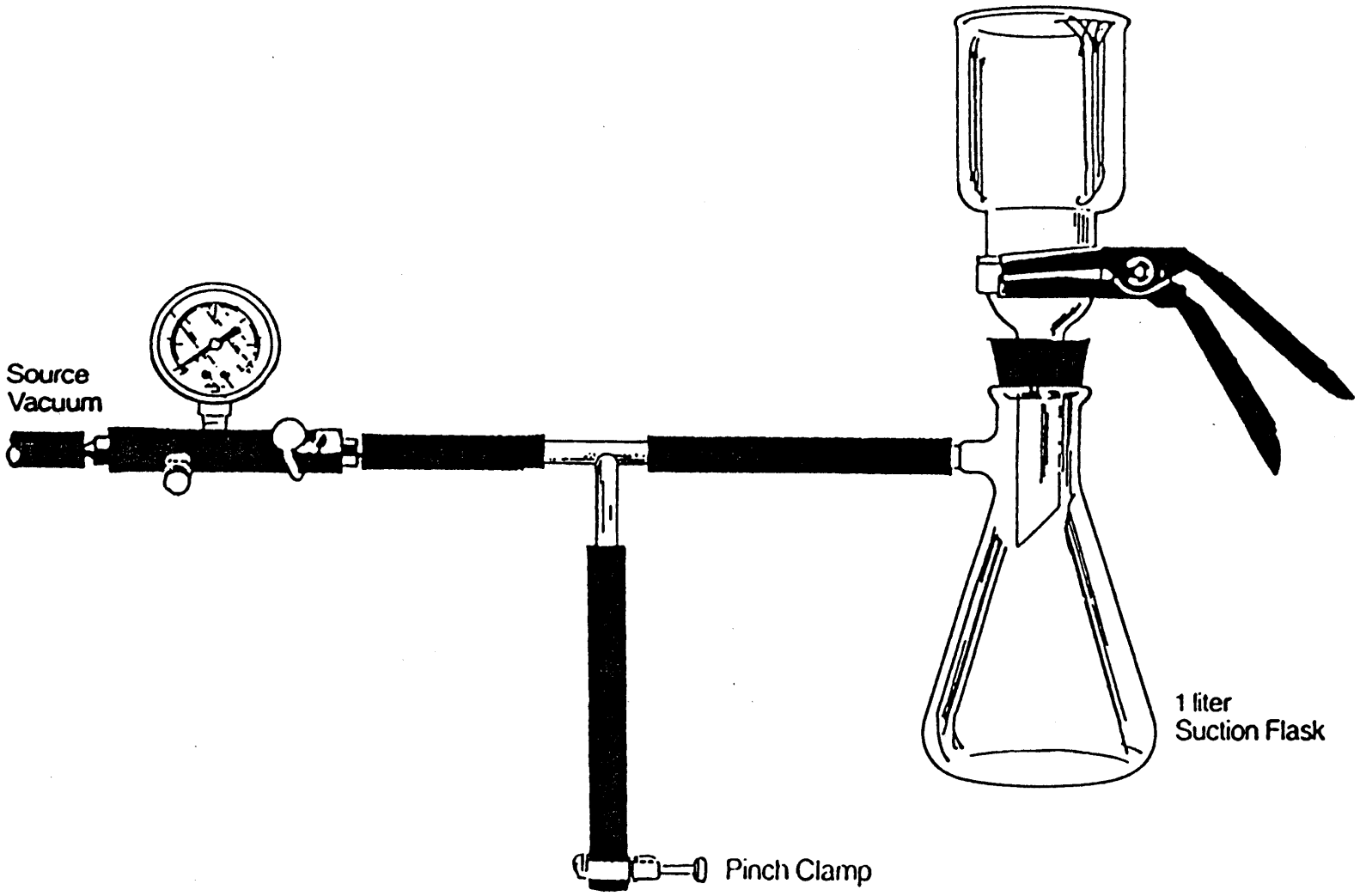


A. Extraction apparatus

B. Elution apparatus

FIGURE 1. CARTRIDGE EXTRACTION APPARATUS

FIGURE 2. DISK EXTRACTION APPARATUS



525.2-55