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

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

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

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

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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.

Analyte	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	156-59-2
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. Analytes are quantitated using procedural standard calibration (Sect. 3.14). 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.

3.14 PROCEDURAL STANDARD CALIBRATION -- A calibration method where aqueous calibration standards are prepared and processed (e.g. purged,extracted, and/or derivatized) in exactly the same manner as a sample. All steps in the process from addition of sampling preservatives through instrumental analyses are included in the calibration. Using procedural standard calibration compensates for any inefficiencies in the processing procedure.

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 (All specifications are suggested. Catalog numbers are included for illustration only.)

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 provided the data acquired meets all quality control criteria described in Section 9, and <u>provided the purge and desorption procedures specified in Section 11 of the method are not changed</u>. Specifically, the purging time, the purge gas flow rate, and the desorption time may not be changed. Since many of the potential alternate sorbents may be thermally stable above 180°C, alternate traps may be desorbed and baked out at higher temperatures than those described in Section 11. If higher temperatures are used, the analyst should monitor the data for possible analyte and/or trap decomposition.

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 Scien-tific, 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 Scien-tific, 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 (or equivalent) 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. Alternately, aqueous calibration standards may be prepared in a gas tight, 5 mL or 25 mL syringe. **NOTE:** If unacidified samples are being analyzed for THMs only, calibration standards should be prepared without acid.

8. SAMPLE COLLECTION, PRESERVATION, AND STORAGE

8.1 SAMPLE COLLECTION AND DECHLORINATION

8.1.1 Collect all samples in duplicate. If samples, such as finished drinking 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 analytes that are gases at room temperature (such as vinyl chloride), or analytes in Table 7 are not to be determined, sodium thiosulfate is recommended to reduce the residual chlorine. Three milligrams of sodium thiosulfate should be added for each 40 mL of water sample.
NOTE: 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 or 3 mg of sodium thiosulfate per each 5 mg/L of residual chlorine.

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 containing the desired dechlorinating agent from the flowing stream.

8.1.3 When sampling from an open body of water, partially fill a 1-quart wide-mouth bottle or 1-L beaker with sample from a representative area. Fill duplicate sample bottles containing the desired dechlorinating agent with sample from the larger container.

8.1.4 Fill sample bottles to overflowing, but take care not to flush out the rapidly dissolving dechlorinating agent. No air bubbles should pass through the sample as the bottle is filled, or be trapped in the sample when the bottle is sealed.

8.2 SAMPLE PRESERVATION

8.2.1 Adjust the pH of all samples to < 2 at the time of collection, but after dechlorination, by carefully adding two drops of 1:1 HCl for each 40 mL of sample. Seal the sample bottles, Teflon face down, and mix for 1 min. Exceptions to the acidification requirement are detailed in Sections 8.2.2 and 8.2.3. **NOTE:** Do not mix the ascorbic acid or sodium thiosulfate with the HCl in the sample bottle prior to sampling.

8.2.2 **When sampling for THM analysis only**, acidification may be omitted if sodium thiosulfate is used to dechlorinate the sample. This exception to acidification does not apply if ascorbic acid is used for dechlorination.

8.2.3 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 if they are to be analyzed for any compounds other than THMs.

8.2.4 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.

8.2 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 as for the field samples.

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. A MDL for each analyte must also be determined. 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, reagent water, 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 four to seven replicates of a laboratory fortified blank containing each analyte of concern at a concentration in the range of 2-5 µg/L depending upon the calibration range of the instrumentation.

9.3.1 Prepare each replicate by adding an appropriate aliquot of a quality control sample to reagent water. It is recommended that a QCS from a source different than the calibration standards be used for this set of LFBs, since it will serve as a check to verify the accuracy of the standards used to generate the calibration curve. This is particularly useful if the laboratory is using the method for the first time, and has no historical data base for standards. Prepare each replicate by adding an appropriate aliquot of a quality control sample to reagent water. Also add the appropriate amounts of internal standard and surrogates. If it is expected that field samples will contain a dechlorinating agent and HCl, then add these to the LFBs in the same amounts proscribed in Sect. 8.1.1. If only THMs are to be determined and field samples do not contain HCl, then do not acidify LFBs. Analyze each replicate according to the procedures described in Section 11.

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 Some analytes, particularly early eluting gases and late eluting higher molecular weight compounds, will be measured with less accuracy and precision than other analytes. However, the accuracy and precision for all analytes must fall within the limits expressed below. If these criteria are not met for an analyte of interest, take remedial action and repeat the measurements for that analyte until satisfactory performance is achieved. For each analyte, the mean accuracy must be 80-120% (i.e. an accuracy of ± 20%). The preci-

sion of the recovery (accuracy) for each analyte must be less than twenty percent (<20%). These criteria are different than the ± 30% response factor criteria specified in Sect. 10.3.5. The criteria differ, because the measurements in Sect. 9.3.3 as part of the initial demonstration of capability are meant to be more stringent than the continuing calibration measurements in Sect. 10.3.5.

9.3.4 To determine the MDL, analyze a minimum of 7 LFBs prepared at a low concentration. MDLs in Table 5 were calculated from samples fortified from 0.1-0.5 µg/L, which can be used as a guide, or use calibration data to estimate a concentration for each analyte that will yield a peak with a 3-5 signal to noise response. Analyze the 7 replicates as described in Sect.11, and on a schedule that results in the analyses being conducted over several days. Calculate the mean accuracy and standard deviation for each analyte. Calculate the MDL using the equation in Sect. 13.

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 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.

9.6 Assessing Laboratory Performance. Use the procedures and criteria in Sects. 10.3.4 and 10.3.5 to evaluate the accuracy of the measurement of the laboratory fortified blank (LFB), which must be analyzed with each batch of samples that is processed as a group within a work shift. If more than 20 samples are in a work shift batch, analyze one LFB per 20 samples. Prepare the LFB with the concentration of each analyte that was used in the Sect. 9.3.3 analysis. If the acceptable accuracy for this measurement (±30%) is not achieved, the problem must be solved before additional samples may be reliably analyzed. Acceptance criteria for the IS and surrogate given in Sect.10.3.4 also applies to this LFB.

Since the calibration check sample in Sect. 10.3.5 and the LFB are made the same way and since procedural standards are used, the sample analyzed here may also be

used as a calibration check in Sect. 10.3.5. Add the results of the LFB analysis to the control charts to document data quality.

9.7 If a water sample is contaminated with an analyte, verify that it is not a sampling error by analyzing a field reagent blank. The results of these analyses will help define contamination resulting from field sampling, storage and transportation activities. If the field reagent blank shows unacceptable contamination, the analyst should identify and eliminate the contamination.

9.8 At least quarterly, replicate LFB data should be evaluated 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. In addition, acceptable performance must be confirmed intermittently throughout analysis of samples by performing continuing calibration checks. These checks are required at the beginning of each work shift, but no less than every 12 hours. Additional periodic calibration checks are good laboratory practice. It is highly recommended that an additional calibration check be performed at the end of any cycle of continuous instrument operation, so that each set of field samples is bracketed by calibration check standards. **NOTE:** Since this method uses procedural standards, the analysis of the laboratory fortified blank, which is required in Sect. 9.6, may be used here as a calibration check sample.

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 returned 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 calibration standards. 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 there is poor resolution between peaks, 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, by plotting A/A_{is} vs. Q_x.

10.3 CONTINUING CALIBRATION CHECK -- Verify the MS tune and initial calibration at the beginning of each 12-hr work shift during which analyses are performed using the following procedure. Additional periodic calibration checks are good laboratory practice. It is highly recommended that an additional calibration check be performed at the end of any cycle of continuous instrument operation, so that each set of field samples is bracketed by calibration check standards.

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 returned and adjusted to meet all criteria before proceeding with the continuing calibration check.

10.3.2 Purge a CAL solution and analyze with the same conditions used during the initial calibration. Selection of the concentration level of the calibration check standard should be varied so that the calibration is verified at more than one point over the course of several days.

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 calibration solution. If these conditions do not exist, remedial action must be taken which may require recalibration. All data from field samples obtained after the last successful calibration check standard, should be considered suspect. After remedial action has been taken, duplicate samples should be analyzed if they are available.

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 success-

fully. 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 one of the following equations:

$$\text{5 mL samples, } S = 0.51\,(C)(V)$$
$$\text{25 mL samples, } S = 0.102\,(C)(V)$$

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 or 5-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 must be reasonably constant, and changes in excess of 10°F will 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, recon-dition 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. If the response for any analyte exceeds the linear range of the calibration established in Section 10, obtain and dilute a duplicate a duplicate sample. Do not extrapolate beyond the calibration range.

12.1.1 Calculate analyte and surrogate concentrations, using the multi-point calibration established in Section 10. Do not use the daily calibration verification data to quantitate analytes in samples.

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

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 curve established in Section 10. Do not use the daily calibration verification data to quantitate analytes in samples.

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 0.1 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):

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

where:

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

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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[a]	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,l32
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) Col. 1[b]	Col. 2[b]	Col. 2[c]	Col. 3[d]	Col. 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) Col. 1[b]	Col. 2[b]	Col. 2[c]	Col. 3[d]	Col. 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) Col. 1[b]	Col. 2[b]	Col. 2[c]	Col. 3[d]	Col. 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

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)
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
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 (Section 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 THE 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 Det. 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-1,2-Dichloropropene				
trans-1,2-Dichloropropene				
Ethylbenzene	0.1	99	5.2	0.03
Hexachlorobutadiene	0.1	100	6.7	0.04

TABLE 5. ACCURACY AND PRECISION DATA FROM SEVEN DETERMINATIONS OF THE 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 Det. Limit (µg/L)
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
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	0.1	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 (Section 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-Bromofluorobenze	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

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 (%)
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
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-1,2-Dichloropropene[c]					
trans-1,2-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.

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 (%)
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 (Section 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[a]

Compound	True Conc. (µg/L)	Mean Conc. Detected (µg/L)	Rel. Std. Dev. (%)	Method Detect. 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
trans-Dichloro-2-Butene	1.0	1.3	8.7	0.36
1,1-Dichloropropanone	5.0	4.2	7.7	1.0
cis-1,3-Dichloropropene	0.20	0.20	3.1	0.020
trans-1,3-Dichloropropene	0.10	0.11	14	0.048
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-Nitrobenzene	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

[a]Data obtained using Column 4 with the open split interface and an ion trap mass spectrometer.

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

	REAGENT WATER			RAW WATER			TAP WATER		
Compound	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. ACCURACY AND PRECISION FROM FOUR DETERMINATIONS OF METHOD ANALYTES IN THREE WATER MATRICES FORTIFIED AT 20 µG/L[a]

	Reagent Water			Raw Water			Tap Water		
Compound	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%

[a]Data obtained using Column 4 with the open-split interface and an ion trap mass spectrometer with all Table 8 analyses in the same reagent water solution (1).

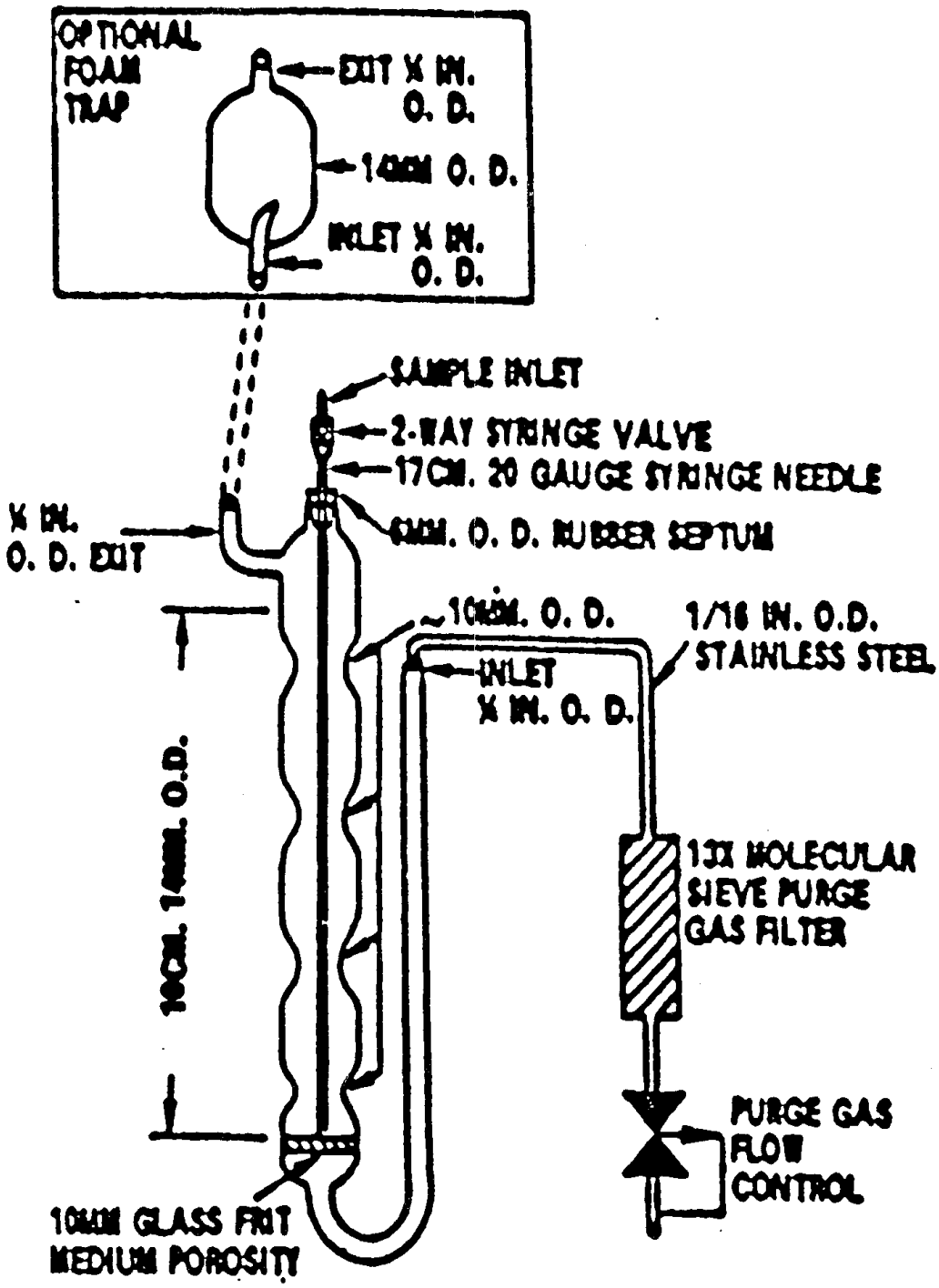

FIGURE 1. PURGING DEVICE

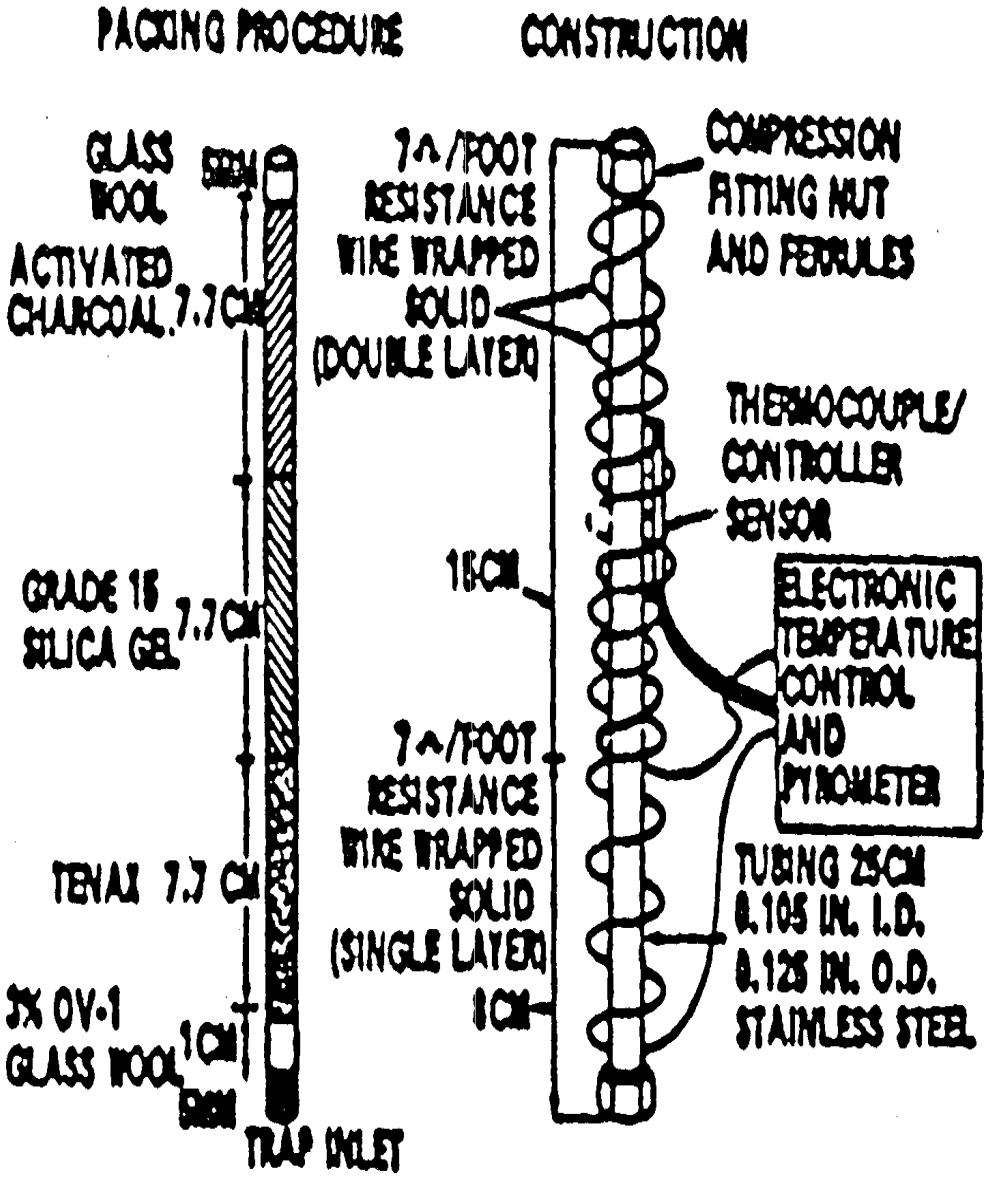

FIGURE 2. TRAP PACKINGS AND CONSTRUCTION TO INCLUDE DESORB CAPABILITY

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

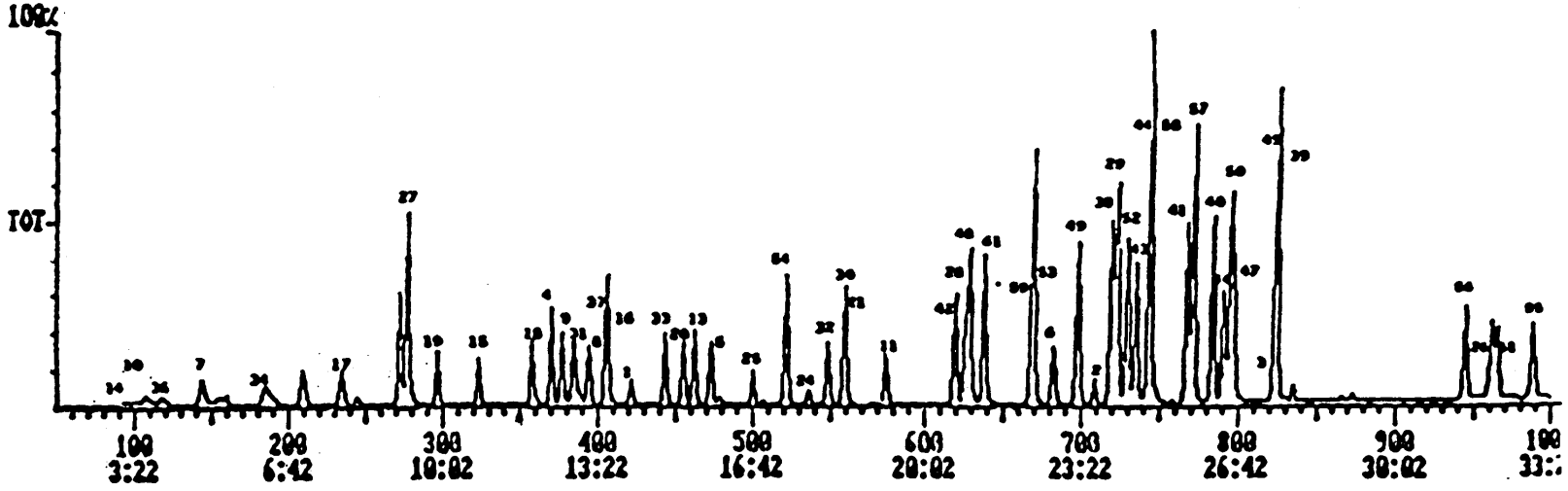

FIGURE 4. AMPLIFIED FIRST EIGHT MINUTES OF A TOTAL ION CURRENT CHROMATOGRAM FROM A VOLATILE COMPOUND CALIBRATION MIXTURE CONTAINING 25 ng (5 µg/L) OF EACH COMPONENT. THE COMPOUND IDENTIFICATION NUMBERS ARE GIVEN IN TABLE 6.