METHOD 502.2

VOLATILE ORGANIC COMPOUNDS IN WATER BY PURGE AND TRAP CAPILLARY COLUMN GAS CHROMATOGRAPHY WITH PHOTOIONIZATION AND ELECTROLYTIC CONDUCTIVITY DETECTORS IN SERIES

Revision 2.1

Edited by J.W. Munch (1995)

R.W. Slater, Jr. and J.S. Ho - Method 502.2, Revision 1.0 (1986)

J.S. Ho - Method 502.2, Revision 2.0 (1989)

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VOLATILE ORGANIC COMPOUNDS IN WATER BY PURGE AND TRAP CAPILLARY COLUMN GAS CHROMATOGRAPHY WITH PHOTOIONIZATION AND ELECTROLYTIC CONDUCTIVITY DETECTORS IN SERIES

1.0 SCOPE AND APPLICATION

1.1 This is a general purpose method for the identification and simultaneous measurement of purgeable volatile organic compounds in finished drinking water, raw source water, or drinking water in any treatment stage[1-3]. 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 efficiently removed from water samples with purge and trap procedures. The following compounds can be determined by this method.

Analyte	Chemical Abstract Services Registry Number
Benzene	71-43-2
Bromobenzene	108-86-1
Bromochloromethane	74-97-5
Bromodichloromethane	75-27-4
Bromoform	75-25-2
Bromomethane	74-83-9
n-Butylbenzene	104-51-8
sec-Butylbenzene	135-98-8
tert-Butylbenzene	98-06-6
Carbon Tetrachloride	56-23-5
Chlorobenzene	108-90-7
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
Dichlorodifluoromethane	75-71-8

Analyte	Chemical Abstract Services Registry Number
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
cis-1,3-Dichloropropene	10061-01-5
trans-1,3-Dichloropropene	10061-02-6
Ethylbenzene	100-41-4
Hexachlorobutadiene	87-68-3
Isopropylbenzene	98-82-8
4-Isopropylbenzene	99-87-6
Methylene Chloride	75-09-2
Naphthalene	91-20-3
Propylbenzene	103-65-1
Styrene	100-42-5
1,1,2,2-Tetrachloroethane	630-20-6
1,1,1,2-Tetrachloroethane	79-34-5
Tetrachloroethene	127-18-4
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
Trichlorofluormethane	75-69-4
1,2,3-Trichloropropane	96-18-4
1,2,4-Trimethylbenene	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

1.2 This method is applicable to the determination of total trihalomethanes and other volatile organic compounds (VOCs). Method detection limits (MDLs)[4] are compound and instrument dependent and vary from approximately 0.01-3.0 µg/L. The applicable concentration range of this method is also compound and

instrument dependent and is approximately 0.02-200 µg/L. Analytes that are inefficiently purged from water will not be detected when present at low concentrations, but they can be measured with acceptable accuracy and precision when present in sufficient amounts.

1.3 Two of the three isomeric xylenes may not be resolved on the capillary column, and if not, must be reported as isomeric pairs.

2.0 SUMMARY OF METHOD

2.1 Highly volatile organic compounds with low water solubility are extracted (purged) from the sample matrix by bubbling an inert gas through a 5 mL 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 thermally desorb trapped sample components onto a capillary gas chromatography (GC) column. The column is temperature programmed to separate the method analytes which are then detected with a photoionization detector (PID) and an electrolytic conductivity detector (ELCD) placed in series. Analytes are quantitated by procedural standard calibration (Section 3.14).

2.2 Identifications are made by comparison of the retention times of unknown peaks to the retention times of standards analyzed under the same conditions used for samples. Additional confirmatory information can be gained by comparing the relative response from the two detectors. For absolute confirmation, a gas chromatography/ mass spectrometry (GC/MS) determination according to USEPA Method 524.2 is recommended.

2.3 This method requires the use of a PID to measure target analytes that cannot be measured with an electrolytic conductivity detector. If only halogenated analytes, such as the trihalomethanes are to be measured, a PID is not needed.

3.0 DEFINITIONS

3.1 Internal Standard (IS) -- A pure analyte(s) added to a 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 and is measured with the same procedures used to measure other sample components. The purpose of a surrogate analyte is to monitor method performance with each sample.

3.3 Laboratory Duplicates (LD1 and LD2) -- Two sample aliquots taken in the analytical laboratory and analyzed separately with identical procedures. Analyses of LD1 and LD2 give a measure of the 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 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) -- Reagent water placed in a sample container in the laboratory and treated as a sample in all respects, including 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 method analytes, surrogate compounds, and internal standards 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 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 at the required method detection limit.

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 -- A concentrated solution containing a single certified standard that is a method analyte, or a concentrated solution of a single analyte

prepared in the laboratory with an assayed reference compound. Stock standard solutions are used to prepare primary dilution standards.

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 and stock standard solutions of 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 sample matrix containing method analytes or a solution of method analytes in a water miscible solvent which is used to fortify reagent water or environmental samples. The QCS is obtained from a source external to the laboratory, and 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.

4.0 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 non-polytetrafluoroethylene (PTFE) plastic tubing, non-PTFE 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 (Section 9.2) 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 analyze for 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 through PTFE tubing, all gas chromatography carrier gas lines and purge gas plumbing should be constructed from stainless steel or copper tubing. Laboratory clothing worn by the analyst should be clean since clothing previously exposed to methylene chloride fumes during common liquid/liquid extraction procedures can contribute to sample contamination.

4.4 When traps containing combinations of silica gel and coconut charcoal are used, residual water from previous analyses collects in the trap and can be randomly released into the analytical column. To minimize the possibility of this occurring, the trap is reconditioned after each use as described in Section 11.4.

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 available[5-7] 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.

6.0 EQUIPMENT AND SUPPLIES (All specifications are suggested. Catalog numbers are included for illustration only.)

6.1 Sample Containers -- 40-120 mL screw cap vials each equipped with a PTFE-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 one hour, 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) must be designed to accept 5 mL samples with a water column at least 5 cm deep. 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 that 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 ≤5 mm from the base of the water column.

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 must contain the following amounts of adsorbents: ⅓ of 2,6-diphenylene oxide polymer, ⅓ of silica gel, and ⅓ of coconut charcoal. It is recommended that 1.0 cm of methyl silicone coated packing be inserted at the inlet to extend the life of the trap. If it is not necessary to analyze for dichlorodifluoromethane, the charcoal can be eliminated and the polymer increased to fill ⅔ of the trap. If only compounds boiling above 35°C are to be analyzed, both the silica gel and charcoal can be eliminated and the polymer increased to fill the entire 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 minutes 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 9.0, and provided the purge and desorption procedures specified in Section 11.0 of the method are not changed. 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 11.0. 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 adsorbent from aerosols, and also of insuring that the adsorbent 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. The polymer section of the trap described in Section 6.2.2 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 lbs. per square inch across the trap during purging or by poor bromoform sensitivities.

6.3 Gas Chromatography System

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. The column oven may need to be cooled to <10°C (Section 6.3.3), and therefore, a subambient oven controller may be required.

6.3.2 Capillary Gas Chromatography Columns -- Any gas chromatography column that meets the performance specifications of this method may be used. Separations of the calibration mixture must be equivalent or better than those described in this method. If other GC columns or temperature programs are used, or whenever these procedures are changed, the method performance data in Section 9.3 must be repeated. Three useful columns have been identified: Column 1 (Section 6.3.3) and Column 2 (Section 6.3.4) both provide satisfied separations for sixty organic compounds. Column 3 (Section 6.3.5), which has been satisfactorily demonstrated for the GC/MS method 524.2, may also be used.

6.3.3 Column 1 - 60m long x 0.75 mm ID VOCOL (Supelco, Inc.) wide-bore capillary column with 1.5 µm film thickness, or equivalent. The flow rate of helium carrier gas is adjusted to about 6 mL/min. The column temperature is held for eight minutes at 10°C, then programmed to 180°C at 4°C/min., and held until all expected compounds have eluted. A sample chromatogram obtained with this column is presented in Figure 3. Retention times that may be anticipated with this column are listed in Table 1. Data obtained with this column is presented in Sections 13.0 and 17.0.

6.3.4 Column 2 - 105m long x 0.53mm ID, RTX-502.2 (O.I Corporation/RESTEK Corporation) mega-bore capillary column, with 3.0 µm film thickness, or equivalent. The flow rate of helium carrier gas is adjusted to about 8 mL/min. The column temperature is held for 10 minutes at 35°C, then programmed to 200°C at 4°C/min., and held until all expected compounds have eluted. A sample chromatogram obtained with this column is presented in Figure 4. Retention times that may be

anticipated with this column are listed in Table 3. Data obtained with this column is presented in Sections 13.0 and 17.0.

6.3.5 Column 3 - 30 m long x 0.53 mm ID DB-624 mega-bore (J&W Scientific, Inc.) column with 3 µm film thickness.

6.3.6 A series configuration of a high temperature photoionization detector (PID) equipped with 10 eV (nominal) lamp and electroconductivity detector (ELCD) is required. This allows the simultaneous analysis of VOCs that are aromatic or unsaturated by photoionization detector and organohalide by an electrolytic conductivity detector.

6.3.7 A Tracor 703 photoionization detector and a Tracor Hall model 700-A detector connected in series with a short piece of uncoated capillary tube, 0.32 mm ID was used to develop the single laboratory method performance data described in Section 13.0. The system and operating conditions used to collect these data are as follows:

Column:	Column 1 (Section 6.3.3)
The purge-and-trap Unit:	Tekmar LSC-2
PID detector base temperature:	250°C
Reactor tube:	Nickel 1/16 in. OD
Reactor temperature:	810°C
Reactor base temperature:	250°C
Electrolyte:	100% n-propyl alcohol
Electrolyte flow rate:	0.8 mL/min.
Reaction gas:	Hydrogen at 40 mL/min.
Carrier gas plus make-up gas:	Helium at 30 mL/min.

6.3.8 An O.I. Model 4430 photoionization detector mounting together with the model 4420 electrolytic conductivity detector (ELCD) as a dual detector set was used to develop the single laboratory method performance data for Column 2 described in Section 13.0. The system and the operating conditions used to collect these data are as follows:

Column:	Column 2 (Section 6.3.4)
The purge-and-trap unit:	O.I. 4460A
Reactor tube:	Nickel 1/16 in. OD & .02in.ID
Reactor temperature:	950°C
Reactor base temperature:	250°C
Electrolyte:	100 % n-propyl alcohol
Electrolyte flow rate:	0.050 mL/min.
Reaction gas:	Hydrogen at 100 mL/min.

Carrier gas plus make-up gas: Helium at 30 mL/min.

6.4 Syringe and Syringe Valves

6.4.1 Two 5 mL glass hypodermic syringes with Luer-Lok tip.

6.4.2 Three two-way syringe valves with Luer ends.

6.4.3 One 25 µL micro syringe with a 2 in x 0.006 in ID, 22° bevel needle (Hamilton #702N or equivalent).

6.4.4 Micro Syringes -- 10, 100 µL.

6.4.5 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 PTFE-lined screw caps.

7.0 REAGENT 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 Ascorbic Acid, ACS Reagent Grade -- Granular.

7.2.2 Sodium Thiosulfate, ACS Reagent Grade -- Granular.

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

7.2.4 Reagent Water -- It should be demonstrated to be free of interferences. 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 minutes followed by a one-hour purge with inert gas while the water temperature is held at 90°C. Store in clean, narrow-mouth bottles with PTFE-lined septa and screw caps.

7.2.5 Methanol -- Demonstrated to be free of analytes.

7.2.6 Vinyl Chloride -- 99.9% pure vinyl chloride is available from Ideal Gas Products, Inc., Edison, New Jersey and from Matheson, East Rutherford, New Jersey. Certified mixtures of vinyl chloride in nitrogen at 1.0 and 10.0 ppm (v/v) are available from several sources.

7.3 Stock Standard Solutions (SSS) -- These solutions may be purchased as certified solutions or prepared from pure standard materials using the following procedures:

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 minutes or until all alcohol-wetted surfaces have dried. 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 micrograms per microliter 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 PTFE-lined screw caps. Methanol solutions prepared from liquid analytes are stable for at least four weeks when stored at 4°C. Methanol solutions prepared from gaseous analytes are not stable for more than one week when stored at <0°C; at room temperature, they must be discarded after one day. Storage time may be extended only if the analyte proves their validity by analyzing quality control samples.

7.4 Primary Dilution Standard Solution (PDS) -- Use stock standard solutions to prepare primary dilution standard solutions that contain the analytes in methanol. The primary dilution standards should be prepared at concentrations that can be easily diluted to prepare aqueous calibration standard solutions (Section 9.2) 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 standard solutions from them. Storage times described for stock standard solutions in Section 7.3.4 also apply to primary dilution standard solutions.

7.5 Internal Standard Solution -- Prepare a fortified solution containing 1-chloro-2-fluorobenze or fluorobenzene and 2-bromo-1-chloropropane in methanol using the procedures described in Sections 7.3 and 7.4. It is recommended that the primary dilution standard be prepared at a concentration of 5 µg/mL of each internal standard compound. The addition of 10 µL of such a standard to 5.0 mL of sample or calibration standard would be equivalent to 10 µg/L.

8.0 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 a dechlorinating agent the bottle. The preferred dechlorinating agent is sodium thiosulfate, but ascorbic acid may also be used. Add 3 mg of sodium thiosulfate or 25 mg of ascorbic acid per 40 mL of sample to the sample bottle before filling.

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 3 mg of sodium thiosulfate or 25 mg of ascorbic acid 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 minutes). 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 one minute. 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 hours 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.

8.3 Sample Storage

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

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

8.4 Field Reagent Blanks (FRB)

8.4.1 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.

8.4.2 Use the same procedures used for samples to add sodium thiosulfate or ascorbic acid and HCl to blanks (Section 8.1.1). The same batch of ascorbic acid and HCl should be used for the field reagent blanks in the field.

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, field reagent blanks, and laboratory fortified blanks. A method detection limit (MDL) must also be determined for each analyte. 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 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 Capability

9.3.1 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 0.1-5 µg/L. This concentration should represent a concentration of ten times the MDL or a concentration near the middle of the calibration range demonstrated (Section 10.0). 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 they are being used. If it is expected that field samples will contain a

dechlorinating agent and HCl, then add these to the LFBs in the same amounts prescribed in Section 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 11.0.

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 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. 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 To determine the MDL, analyze a minimum of seven LFBs prepared at a low concentration. MDLs in Tables 2 and 4 were calculated from samples fortified at 0.1 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 three to five signal to noise ratio. Analyze the seven replicates as described in Section 11.0, 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 procedures described in Reference 4. The equation for this calculation is also in Section 13.3.

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 Laboratory Reagent Blanks (LRBs) -- With each batch of samples processed as a group within a work shift, analyze a laboratory reagent blank to determine the background system contamination. LRBs should contain the same additives (dechlorinating agent and HCl) as field samples.

9.5 Assessing Laboratory Performance -- 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 9.3.1. LFBs should contain a dechlorination agent and/or HCl as appropriate to match the field samples being analyzed. The minimum frequency of LFB analysis is once every twelve hours. Use the criteria described in

Section 9.3.3 to evaluate the accuracy of the measurements, and to estimate whether the method detection limits can be obtained. If acceptable accuracy and method detection limits cannot be achieved, the problem must be located and corrected before further samples are analyzed. Data from all field samples analyzed since the last acceptable LFB should be considered suspect, and duplicate samples should be analyzed, if they are available, after the problem has been corrected. LFB results should be added to the on-going control charts to document data quality.

Since the calibration check sample in Section 10.3.2 and the LFB are made the same way and since procedural standards are used, the sample analyzed here may also be used as the calibration check in Section 10.3.2.

9.6 Assessing the Internal Standard -- If internal standard calibration is used, the analyst must assess the response of the internal standard in every LRB, FRB, LFB, CAL, and field sample. The IS response (peak height or peak area units) must be within 20% of the mean peak response of the IS in the CAL standards used to develop the calibration. If this criteria cannot be met, take remedial action. If there are interferences in field samples that affect the measurement of the internal standard, external standard calibration should be used (Section 10.3.2).

9.7 Assessing the Surrogate Analyte -- Calculate the amount of the surrogate analyte recovered in each LRB, LFB, FRB, CAL, and field sample (Section 10.0). If the surrogate recovery in blanks or calibration standards does not meet the criteria in Section 9.3.3., take remedial action. If the surrogate recovery in a field sample does not meet the criteria in Section 9.3.3., and data from LFBs shows the laboratory to be in control, reanalyze the sample.

9.8 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.

9.9 At least quarterly, replicates of laboratory fortified blanks should be evaluated to determine the precision of the laboratory measurements. Add these results to the on-going control charts to document data quality.

9.10 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.

9.11 Sample matrix effects have not been observed when this method is used with distilled water, reagent water, drinking water, and ground water. Therefore, analysis of a laboratory fortified sample matrix (LFM) is not required.

9.12 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. 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. Since this method uses procedural standards, the analysis of the laboratory fortified blank, which is required in Section 9.5, may be used here as a calibration check sample.

10.2 Preparation of Calibration Standards

10.2.1 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 two to 10 times greater than the method detection limit (Tables 2 and 4) for that compound. The other CAL standards should contain each analyte of concern at concentrations that define the range of the sample analyte concentrations. When internal standard calibration is being used, every CAL solution contains the internal standard at same concentration (10 µg/L).

10.2.2 To prepare a calibration standard, add an appropriate volume of a primary dilution standard solution to an aliquot of reagent water in a volumetric container or sample syringe. The reagent water used should also contain the appropriate dechlorinating agent and/or HCl so as to match the field samples to be analyzed. Use a microsyringe and rapidly inject the alcoholic standard into the water. Remove the needle as quickly as possible after injection. Accurate calibration standards can be prepared by injecting 20 µL of the primary dilution standards to 25 mL or more of reagent water using the syringe described in Section 6.4.3. Aqueous standards are not stable in volumetric container and should be discarded after one hour unless transferred to sample bottle and sealed immediately as described in Section 8.1.2.

10.3 Calibration

10.3.1 External standard calibration -- Starting with the standard of lowest concentration, analyze each calibration standard according to Section 11.0 and tabulate peak height or area response versus the concentration in the standard. The results can be used to prepare a calibration curve for each compound. Alternatively, if the ratio of response to concentration (calibration factor) is a constant over the working range (< 10% relative standard deviation), linearity through the origin can be assumed and the average ratio or calibration factor can be used in place of a calibration curve.

10.3.2 Internal standard calibration -- The organohalides recommended as internal standards are: 1-chloro-2-fluorobenze or 2-bromo-1-chloropropane and fluorobenzene. The internal standard is added to the sample just before purging. Check the validity of the internal standard response factors daily by analyzing a calibration standard.

Note: Since the calculated concentrations can be strongly biased by inaccurate detector response measurements for the internal standard or by coelution of an unknown with the internal standard, it is required that the area measurement of the internal standard of each sample be within ± 3 standard deviations of those obtained from calibration standards, or ± 20% of the mean response obtained from calibration standards, whichever is greater. If they do not, then internal standards can not be used.

10.3.3 Following analysis, tabulate peak height or area responses against concentration for each compound and the internal standard. Calculate the response factor (RF) for each compound using the following equation:

$$RF = \frac{(A_s)\ (C_{is})}{(A_{is})\ (C_s)}$$

where:

A_s = Response for the analyte to be measured
A_{is} = Response for the internal standard
C_{is} = Concentration of the internal standard (µg/L)
C_s = Concentration of the analyte to be measured (µg/L)

If RF value over the working range is constant (< 10% RSD), the average RF can be used for calculations. Alternatively, the results can be used to plot a calibration curve of response versus analyte ratios, A_s/A_{is} vs. C_s/C_{is}.

10.3.4 The working calibration curve or calibration factor must be verified by the measurement of one or more calibration standards. This must be done at

least once each work shift, but no less than once 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. It is also recommended that more that one concentration of continuing calibration standard be analyzed, in order to evaluate the accuracy of the calibration at more than one point. If the response for any analyte varies from the predicted response by more than ±20%, the test must be repeated using a fresh calibration standard. If the results still do not agree, generate a new calibration curve. Any field samples analyzed since the last acceptable calibration check should be considered suspect, and should be reanalyzed if they are available.

10.4 Calibration for Vinyl Chloride Using a Certified Gaseous Mixture (Optional)

10.4.1 Fill the purging device with 5.0 mL of reagent water or aqueous calibration standard, and add internal standards.

10.4.2 Start to purge the aqueous mixture (Section 7.2.6). 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 the aqueous sample inlet needle. After completion, inject 2 mL of clean room air to sweep the gases from the inlet needle into the purging device. Inject the gaseous standard before five min of the 11 minutes purge time have elapsed.

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

$$S = 0.51\ (C)\ (V)$$

where:

S = Aqueous equivalent concentration of vinyl chloride standardin µg/L;
C = Concentration of gaseous standard in ppm (v/v);
V = Volume of standard injected in milliliter

11.0 PROCEDURE

11.1 Initial Conditions

11.1.1 Recommended chromatographic conditions are summarized in Section 6.3. Other columns or GC conditions may be used if the requirements of Section 9.3 are met.

11.1.2 Calibrate the system daily as described in Section 10.0.

11.1.3 Adjust the purge gas (nitrogen or helium) flow rate to 40 mL/min. Attach the trap inlet to the purging device and open the syringe valve on the purging device.

11.2 Sample Introduction and Purging

11.2.1 To generate accurate data, samples and calibration standards must be analyzed under identical conditions. Remove the plungers from two 5 mL syringes and attach a closed syringe valve to each. Allow the sample to come to room temperature, open the sample (or standard) 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 5.0 mL. Add 10 µL of the internal calibration standard 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.

11.2.2 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 ± 0.1 minute at ambient temperature.

Note: Ambient room temperature must be relatively constant. If it varies by more than 10°C during an analysis day, or between calibration and sample analysis, precision and accuracy of some analytes will be affected.

11.3 Sample Desorption -- After the 11-minute purge, couple the trap to the chromatograph by switching the purge and trap system to the desorb mode, initiate the temperature program sequence of the gas chromatograph and start data acquisition. Introduce the trapped materials to the GC column by rapidly heating the trap to 180°C while backflushing the trap with an appropriate inert gas flow for 4.0 ± 0.1 minute. While the extracted sample is being introduced into the gas chromatograph, empty the purging device using the sample syringe and wash the chamber with two 5 mL flushes of reagent water.

11.4 Trap Reconditioning -- After desorbing the sample for four min, recondition the trap by returning the purge and trap system to the purge mode. Maintain the trap temperature at 180°C. After approximately seven minutes, 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.

12.0 DATA ANALYSIS AND CALCULATIONS

12.1 Identify each analyte in the sample chromatogram by comparing the retention time of the suspect peak to retention times generated by the calibration standards, the LFB and other fortified quality control samples. If the retention time of the suspect peak agrees within ±3 standard deviations of the retention times of those generated by known standards (Tables 1 and 3) then the identification may be considered as positive. If the suspect peak falls outside this range or coelutes with other compounds (Tables 1 and 3), then the sample should be reanalyzed. When applicable, determine the relative response of the alternate detector to the analyte. The relative response should agree to within 20% of the relative response determined from standards.

12.2 Xylenes and other structural isomers 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 isomer peaks is less than 25% of the sum of the two peak heights. Otherwise, structural isomers are identified as isomeric pairs.

12.3 When both detectors respond to an analyte, quantitation is usually performed on the detector which exhibits the greater response. However, in cases where greater specificity or precision would result, the analyst may choose the alternate detector. Do not extrapolate beyond the calibration range established in Section 10.0. If peak response exceeds the highest calibration standard, a duplicate sample must be diluted and reanalyzed. Use only the multi-point calibration data obtained in Section 10.0 for all calculations. Do not use the daily calibration verification standard to quantitate method analyte in samples.

12.4 Determine the concentration of the unknowns when external standards are used, by using the calibration curve or by comparing the peak height or area of the unknowns to the peak height or area of the standards as follows:

Concentration of unknown (µg/L) = (Peak height sample/Peak height standard) x Concentration of standard (µg/L).

12.5 Calculate analyte and surrogate concentrations when internal standards are used with the equation in Section 10.3.3.

12.6 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 1 significant figure for lower concentrations.

12.7 Calculate the total trihalomethane concentrations by summing the four individual trihalomethane concentrations in µg/L.

13.0 METHOD PERFORMANCE

13.1 This method was tested in a single laboratory using reagent water fortified at 10 µg/L (1). Single laboratory precision and accuracy data for each detector are presented for the method analytes in Tables 2 and 4.

13.2 Method detection limits for these analytes have been calculated from data collected by fortifying reagent water at 0.1 µg/L.[1] These data are presented in Tables 2 and 4.

13.3 Method detection limits 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 = the standard deviation of the replicate analyses.

14.0 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.

15.0 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.

16.0 REFERENCES

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17.0 TABLES, DIAGRAMS, FLOWCHARTS, AND VALIDATION DATA

TABLE 1. RETENTION TIMES FOR VOLATILE ORGANIC COMPOUNDS ON PHOTOIONIZATION DETECTOR (PID) AND ELECTROLYTIC CONDUCTIVITY DETECTOR (ELCD) FOR COLUMN 1

		Retention Time (min)[a]	
	Analyte[b]	PID	ELCD
1	Dichlorodifluoromethane	–[c]	8.47
2	Chloromethane	–	9.47
3	Vinyl Chloride	9.88	9.93
4	Bromomethane	–	11.95
5	Chloroethane	–	12.37
6	Trichlorofluoromethane	–	13.49
7	1,1-Dichloroethene	6.14	16.18
8	Methylene Chloride	–	18.39
9	trans-1,2-Dichloroethene	19.30	19.33
10	1,1-Dichloroethane	–	20.99
11	2,2-Dichloropropane	–	22.88
12	cis-1,2-Dichloroethene	23.11	23.14
13	Chloroform	–	23.64
14	Bromochloromethane	–	24.16
15	1,1,1-Trichloroethane	–	24.77
16	1,1-Dichloropropane	25.21	25.24
17	Carbon Tetrachloride	–	25.47
18	Benzene	26.10	–
19	1,2-Dichloroethane	–	26.27
20	Trichloroethene	27.99	28.02
21	1,2-Dichloropropane	–	28.66
22	Bromodichloromethane	–	29.43
23	Dibromomethane	–	29.59
24	cis-1,3-Dichloropropene	31.38	31.41
25	Toluene	31.95	–
26	trans-1,3-Dichloropropene	33.01	33.04
27	1,1,2-Trichloroethane	–	33.21
28	Tetrachloroethene	33.88	33.90
29	1,3-Dichloropropane	–	34.00
30	Dibromochloromethane	–	34.73
31	1,2-Dibromoethane	–	35.34
32	Chlorobenzene	36.56	36.59
33	Ethylbenzene	36.72	–
34	1,1,1,2-Tetrachloroethane	–	36.80

TABLE 1. RETENTION TIMES FOR VOLATILE ORGANIC COMPOUNDS ON PHOTOIONIZATION DETECTOR (PID) AND ELECTROLYTIC CONDUCTIVITY DETECTOR (ELCD) FOR COLUMN 1

		Retention Time (min)[a]	
	Analyte[b]	**PID**	**ELCD**
35	m-Xylene	36.98	–
36	p-Xylene	36.98	–
37	o-Xylene	38.39	–
38	Styrene	38.57	–
39	Isopropylbenzene	39.58	–
40	Bromoform	–	39.75
41	1,1,2,2-Tetrachloroethane	–	40.35
42	1,2,3-Trichloropropane	–	40.81
43	n-Propylbenzene	40.87	–
44	Bromobenzene	40.99	41.03
45	1,3,5-Trmethylbenzene	41.41	–
46	2-Chlorotoluene	41.41	41.45
47	4-Chlorotoluene	41.60	41.63
48	tert-Butylbenzene	42.71	
49	1,2,4-Trimethylbenzene	42.92	–
50	sec-Butylbenzene	43.31	–
51	p-Isopropyltoluene	43.81	–
52	1,3-Dichlorobenzene	44.08	44.11
53	1,4-Dichlorobenzene	44.43	44.47
54	n-Butylbenzene	45.20	–
55	1,2-Dichlorobenzene	45.71	45.74
56	1,2-Dibromo-3-Chloropropane	–	48.57
57	1,2,4-Trichlorobenzene	51.43	51.46
58	Hexachlorobutadiene	51.92	51.96
59	Napthalene	52.38	–
60	1,2,3-Trichlorobenzene	53.34	53.37
Internal Standards			
	Fluorobenzene	26.84	–
	2-Bromo-1-chloropropane[d]	–	33.08

[a]Column and analytical conditions are described in Section 6.3.
[b]Number refers to peaks in Figure 502.2-1.
[c]Dash inidicates detector does not respond.
[d]Interferes with trans-1,3-dichloropropene and 1,1,2-trichloroethane on the column. Use with care.

TABLE 2. SINGLE LABORATORY ACCURACY, PRECISION, AND METHOD DETECTION LIMITS FOR VOLATILE ORGANIC COMPOUNDS IN REAGENT WATER FOR COLUMN 1[a]

	Photoionization Detector			Electrolytic Conductivity Detector		
Analyte	Average Recovery (µg/L)	Rel. Std. Deviation (%)	MDL (µg/L)	Average Recovery (µg/L)	Rel. Std. Deviation (%)	MDL (µg/L)

TABLE 2. SINGLE LABORATORY ACCURACY, PRECISION, AND METHOD DETECTION LIMITS FOR VOLATILE ORGANIC COMPOUNDS IN REAGENT WATER FOR COLUMN 1[a]

	Photoionization Detector			Electrolytic Conductivity Detector		
Analyte	Average Recovery (µg/L)	Rel. Std. Deviation (%)	MDL (µg/L)	Average Recovery (µg/L)	Rel. Std. Deviation (%)	MDL (µg/L)
2,2-Dichloropropane	–	–	–	105	3.4	0.05
1,1-Dichloropropene	103	3.5	0.02	103	3.3	0.02
Ethylbenzene	101	1.4	0.01	–	–	–
Hexachlorobutadiene	99	9.5	0.06	98	8.3	0.02
Isopropylbenzene	98	0.9	0.05	–	–	–
p-Isopropyltoluene	98	2.4	0.01	–	–	–
Methylene chloride	–	–	–	97	2.9	0.02
Napthalene	102	6.2	0.06	–	–	–
n-Propylbenzene	103	2.0	0.01	–	–	–
Styrene	104	1.3	0.01	–	–	–
1,1,1,2-Tetrachloroethane	–	–	–	99	2.3	0.01
1,1,2,2-Tetrachloroethane	–	–	–	99	6.8	0.01
Tetrachloroethene	101	1.8	0.05	97	2.5	0.04
Toluene	99	0.8	0.01	–	–	–
1,2,3-Trichlorobenzene	106	1.8	N.D.	98	3.1	0.03
1,2,4-Trichlorobenzene	104	2.2	0.02	102	2.1	0.03
1,1,1-Trichloroethane	–	–	–	104	3.3	0.03
1,1,2-Trichloroethane	–	–	–	109	5.6	N.D.
Trichloroethene	100	0.78	0.02	96	3.6	0.01
Trichlorofluoromethane	–	–	–	96	3.5	0.03
1,2,3-Trichloropropane	–	–	–	99	2.3	0.4
1,2,4-Trimethylbenzene	99	1.2	0.05	–	–	–
1,3,5-Trimethylbenzene	101	1.4	0.01	–	–	–
Vinyl chloride	109	5.0	0.02	95	5.9	0.04
o-Xylene	99	0.8	0.02	–	–	–
m-Xylene	100	1.4	0.01	–	–	–
p-Xylene	99	0.9	0.01	–	–	–

TABLE 3. RETENTION TIMES FOR VOLATILE ORGANIC COMPOUNDS ON PHOTOIONIZATION DETECTOR (PID) AND ELECTROLYTIC CONDUCTIVITY DETECTOR (ELCD) FOR COLUMN 2

	Analyte[b]	PID		ELCD	
		RT (min)[a]	RSD	RT (min)[a]	RSD
1	Dichlorodifluoromethane	–[c]		7.36	0.06
2	Chloromethane	–		8.09	0.06
3	Vinyl Chloride	8.57	0.06	8.58	0.08
4	Bromomethane	–		10.39	0.06
5	Chloroethane	–		10.74	0.05
6	Trichlorofluoromethane	–		11.85	0.07
7	1,1-Dichloroethene	14.46	0.08	14.47	0.07
8	Methylene Chloride	–		16.46	0.04
9	trans-1,2-Dichloroethene	17.61	0.02	17.62	0.03
10	1,1-Dichloroethane	–		19.25	0.03
11	2,2-Dichloropropane	–		21.36	0.03
12	cis-1,2-Dichloroethene	21.52	0.02	21.52	0.02
13	Chloroform	–		22.08	0.02
14	Bromochloromethane	–		22.69	0.02
15	1,1,1-Trichloroethane	–		23.53	0.02
16	1,1-Dichloropropane	24.07	0.01	24.08	0.02
17	Carbon Tetrachloride	–		24.47	0.02
18	1,2-Dichloroethane	–		24.95	0.01
19	Benzene	25.06	0.01	–	
20	Trichloroethene	27.99	0.01	27.15	0.01
21	1,2-Dichloropropane	–		27.73	0.01
22	Bromodichloromethane	–		28.57	0.02
23	Dibromomethane	–		28.79	0.01
24	cis-1,3-Dichloropropene	30.40	0.01	30.41	0.02
25	Toluene	31.58	0.01	–	
26	trans-1,3-Dichloropropene	32.11	0.01	32.13	0.01
27	1,1,2-Trichloroethane	–		32.69	0.01
28	1,3-Dichloropropane	–		33.57	0.01
29	Tetrachloroethene	33.85	0.01	33.86	0.01
30	Dibromochloromethane	–		34.58	0.01
31	1,2-Dibromoethane	–		35.29	0.01
32	Chlorobenzene	36.76	0.01	36.87	0.01
33	1,1,1,2-Tetrachloroethane	–		36.87	0.01
34	Ethylbenzene	36.92	0.01	–	
35	m-Xylene	37.19	0.01	–	

TABLE 3. RETENTION TIMES FOR VOLATILE ORGANIC COMPOUNDS ON PHOTOIONIZATION DETECTOR (PID) AND ELECTROLYTIC CONDUCTIVITY DETECTOR (ELCD) FOR COLUMN 2

	Analyte[b]	PID		ELCD	
		RT (min)[a]	RSD	RT (min)[a]	RSD
43	n-Propylbenzene	41.51	0.01	–	
44	Bromobenzene	41.73	0.01	41.75	0.01
45	1,3,5-Trmethylbenzene	42.08	0.01	–	
46	2-Chlorotoluene	42.20	0.01	42.21	0.01
47	4-Chlorotoluene	42.36	0.01	42.36	0.01
48	tert-Butylbenzene	43.40	0.01	–	
49	1,2,4-Trimethylbenzene	43.55	0.01	–	
50	sec-Butylbenzene	44.19	0.01	–	
51	p-Isopropyltoluene	44.69	0.01	–	
52	1,3-Dichlorobenzene	45.08	0.01	45.09	0.01
53	1,4-Dichlorobenzene	45.48	0.01	45.48	0.01
54	n-Butylbenzene	46.22	0.01	–	
55	1,2-Dichlorobenzene	46.88	0.01	46.89	0.01
56	1,2-Dibromo-3-Chloropropane		–	49.84	0.01
57	1,2,4-Trichlorobenzene	53.26	0.01	53.26	0.01
58	Hexachlorobutadiene	53.86	0.01	53.87	0.01
59	Napthalene	54.45	0.01	–	
60	1,2,3-Trichlorobenzene	55.54	0.01	55.54	0.01
Internal Standards					
	1-Chloro-2-Fluorobenzene	37.55	0.01	37.56	0.01

[a]Column and analytical conditions are described in Section 6.3.4.
[b]Number refers to peaks in Figure 502.2-2.
[c]Dash inidicates detector does not respond.

TABLE 4. SINGLE LABORATORY ACCURACY, PRECISION, AND METHOD DETECTION LIMITS FOR VOLATILE ORGANIC COMPOUNDS IN REAGENT WATER FOR COLUMN 2[a]

	Photoionization Detector			Electrolytic Conductivity Detector		
Analyte	Average Recovery (µg/L)	Rel. Std. Deviation (%)	MDL (µg/L)	Average Recovery (µg/L)	Rel. Std. Deviation (%)	MDL (µg/L)

TABLE 4. SINGLE LABORATORY ACCURACY, PRECISION, AND METHOD DETECTION LIMITS FOR VOLATILE ORGANIC COMPOUNDS IN REAGENT WATER FOR COLUMN 2[a]

	Photoionization Detector			Electrolytic Conductivity Detector		
Analyte	Average Recovery (µg/L)	Rel. Std. Deviation (%)	MDL (µg/L)	Average Recovery (µg/L)	Rel. Std. Deviation (%)	MDL (µg/L)
2,2-Dichloropropane	–	–	–	95	14.2	N.D.
1,1-Dichloropropene	103	3.5	0.02	103	3.3	0.02
cis-1,3-Dichloropropene	101	1.4	0.01	–	–	–
trans-1,3-Dichloropropene	99	9.5	0.06	98	8.3	0.02
Ethylbenzene	98	0.9	0.05	–	–	–
Hexachlorobutadiene	98	2.4	0.01	–	–	–
Isopropylbenzene	–	–	–	97	2.9	0.02
p-Isopropyltoluene	102	6.2	0.06	–	–	–
Methylene chloride	103	2.0	0.01	–	–	–
Napthalene	104	1.3	0.01	–	–	–
n-Propylbenzene	–	–	–	99	2.3	0.01
Styrene	–	–	–	99	6.8	0.01
1,1,1,2-Tetrachloroethane	101	1.8	0.05	97	2.5	0.04
1,1,2,2-Tetrachloroethane	99	0.8	0.01	–	–	–
Tetrachloroethene	106	1.8	N.D.	98	3.1	0.03
Toluene	104	2.2	0.02	102	2.1	0.03
1,2,3-Trichlorobenzene	–	–	–	104	3.3	0.03
1,2,4-Trichlorobenzene	–	–	–	109	5.6	N.D.
1,1,1-Trichloroethane	100	0.78	0.02	96	3.6	0.01
1,1,2-Trichloroethane	–	–	–	96	3.5	0.03
Trichloroethene	–	–	–	99	2.3	0.4
Trichlorofluoromethane	99	1.2	0.05	–	–	–
1,2,3-Trichloropropane	101	1.4	0.01	–	–	–
1,2,4-Trimethylbenzene	109	5.0	0.02	95	5.9	0.04
1,3,5-Trimethylbenzene	99	0.8	0.02	–	–	–
Vinyl chloride	100	1.4	0.01	–	–	–
o-Xylene	99	0.9	0.01	–	–	–
m-Xylene						
p-Xylene						

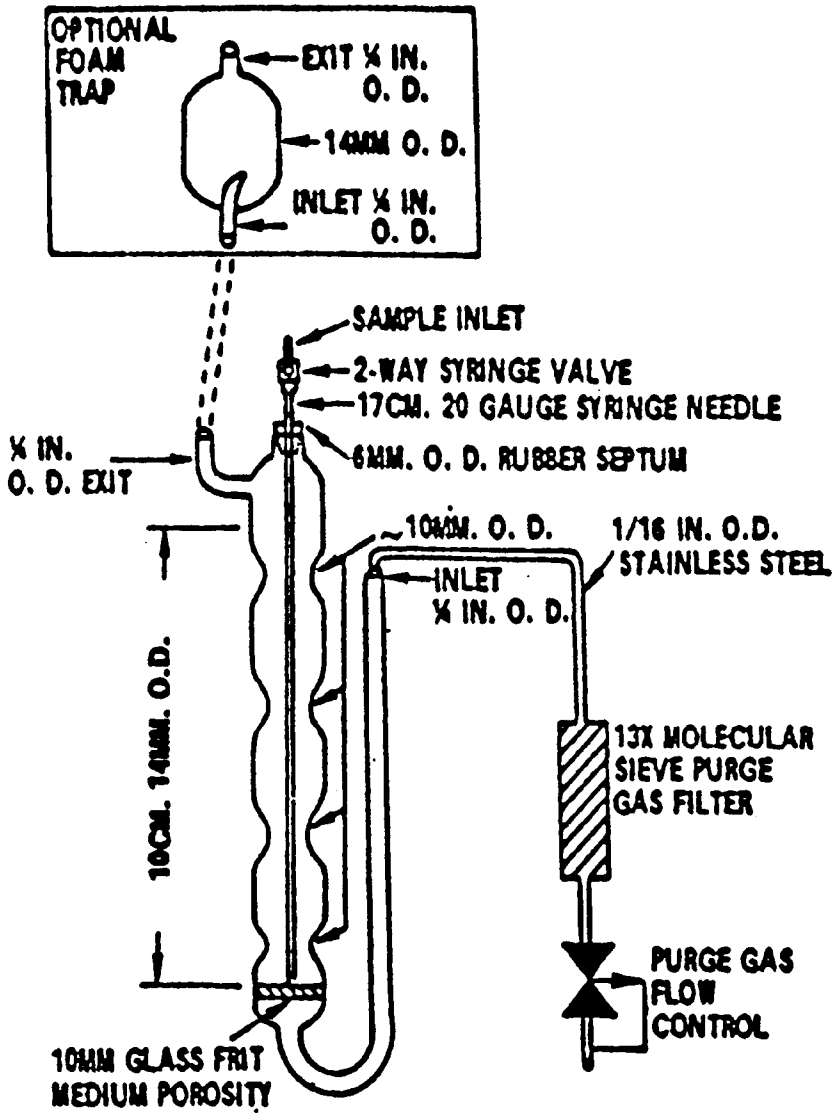

FIGURE 1. PURGING DEVICE

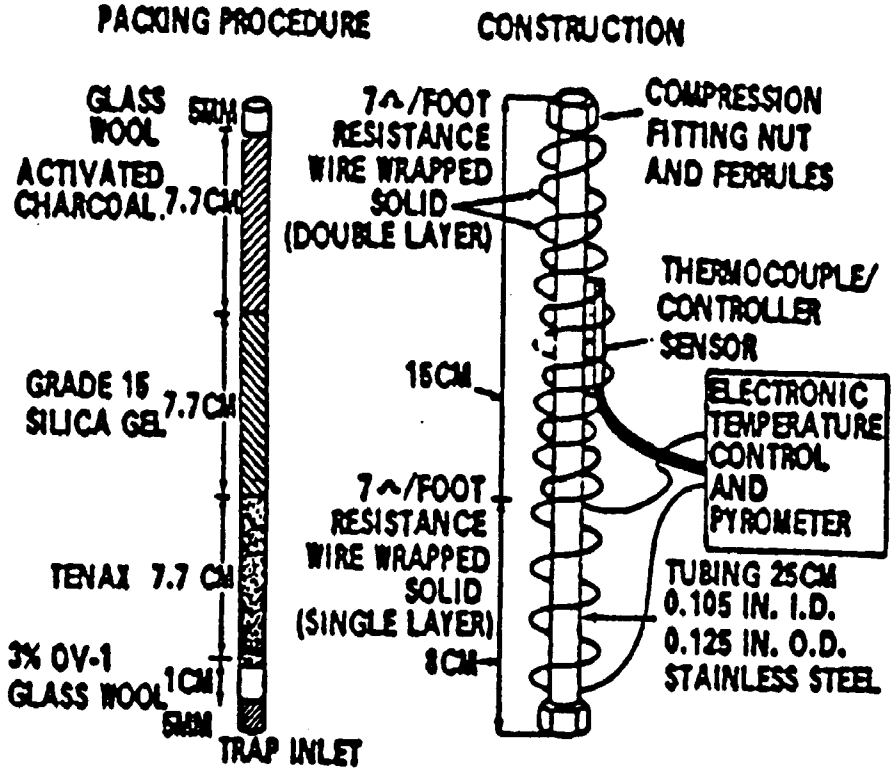

FIGURE 2. TRAP PACKINGS AND CONSTRUCTION TO INCLUDE DESORB CAPABILITY

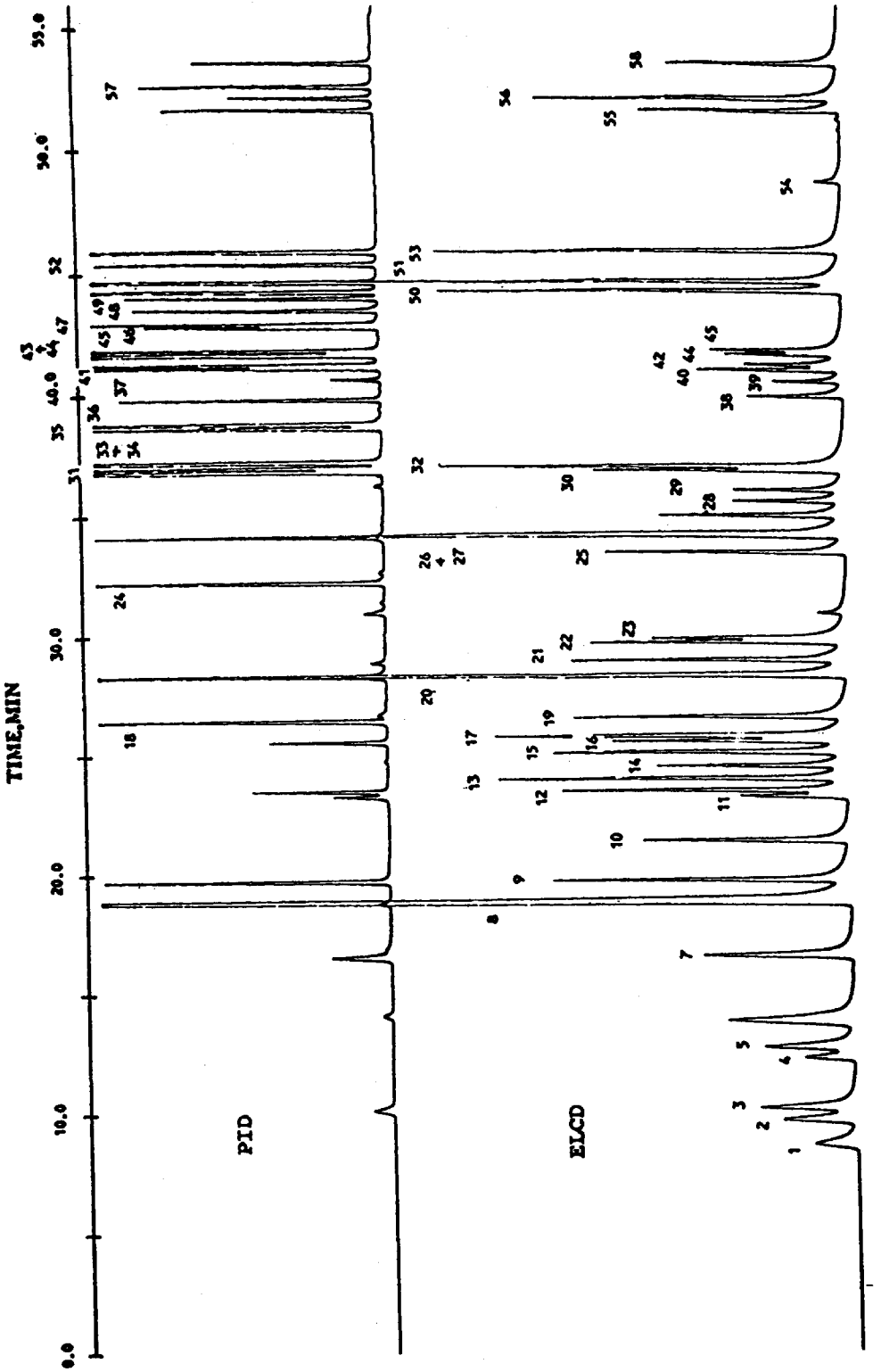

FIGURE 3. DUAL CHROMATOGRAM OF ORGANIC COMPOUNDS FOR COLUMN 1

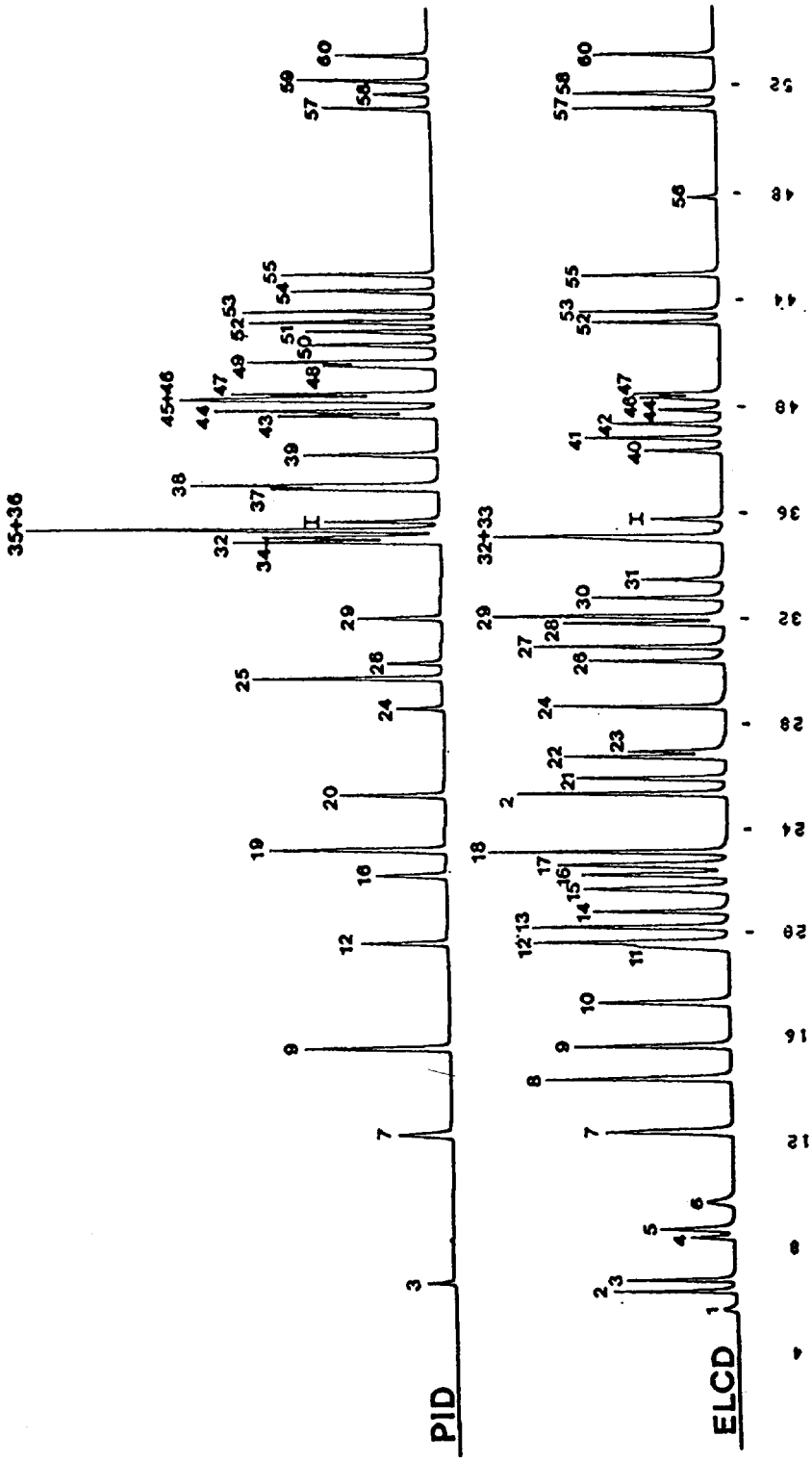

FIGURE 4. DUAL CHROMATOGRAM OF ORGANIC COMPOUNDS FOR COLUMN 2