

**METHODS OF ANALYSIS BY THE U.S. GEOLOGICAL SURVEY
NATIONAL WATER QUALITY LABORATORY--DETERMINATION OF
VOLATILE ORGANIC COMPOUNDS IN WATER BY PURGE AND TRAP
CAPILLARY GAS CHROMATOGRAPHY/MASS SPECTROMETRY**

By Donna L. Rose and Michael P. Schroeder

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Gordon P. Eaton, Director

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For additional information
write to:

U.S. Geological Survey
Chief, National Water Quality Laboratory
Box 25046, Mail Stop 407
Federal Center
Denver, CO 80225

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CONVERSION FACTORS AND RELATED INFORMATION

<u>Multiply</u>	<u>By</u>	<u>To Obtain</u>
centimeter (cm)	3.94×10^{-1}	inch
kilopascal (kPa)	1.45×10^{-1}	pounds per square inch
meter (m)	3.281	foot
microliter (μL)	33.8×10^{-6}	ounce, fluid
micrometer (μm)	3.94×10^{-5}	inch
milligram (mg)	34.27×10^{-5}	ounce, avoirdupois
milliliter (mL)	0.0338	ounce, fluid
millimeter (mm)	0.03937	inch

Temperature can be converted from degree Celsius ($^{\circ}\text{C}$) to degree Fahrenheit ($^{\circ}\text{F}$) by using the following equation:

$$^{\circ}\text{F} = 9/5 (^{\circ}\text{C}) + 32.$$

The following water-quality terms also are used in this report:

microgram per liter ($\mu\text{g/L}$)
microgram per milliliter ($\mu\text{g/mL}$)
milliliter per minute (mL/min)

Other abbreviations are as follows:

ALS	Automated Liquid Sampler
amu	atomic mass units
BFB	bromofluorobenzene
CCV	continuing calibration verification standard
eV	electron volt
GC	gas chromatograph
IS	internal standards
LOQ	limit of quantitation standard
<i>M</i>	molarity (moles per liter)
MDL	method detection limit
MS	mass spectrometer
MTBE	methyl <i>tert</i> butyl ether
NIST	National Institute for Standards and Technology
NWQL	National Water Quality Laboratory
PTFE	polytetrafluoroethene
PT/GC/MS	purge and trap capillary gas chromatography/mass spectrometry
QCC	quality-control check standard
RRT	relative retention time
RSD	relative standard deviation
RT	retention time
s	second
SURRIS	surrogate/internal standard solution
USEPA	U.S. Environmental Protection Agency
USGS	U.S. Geological Survey
VOC	volatile organic compound
VOFW	volatile organic-free water

**METHODS OF ANALYSIS BY THE U.S. GEOLOGICAL SURVEY
NATIONAL WATER QUALITY LABORATORY--
DETERMINATION OF VOLATILE ORGANIC COMPOUNDS
IN WATER BY PURGE AND TRAP CAPILLARY
GAS CHROMATOGRAPHY/MASS SPECTROMETRY**

By Donna L. Rose and Michael P. Schroeder

ABSTRACT

Purge and trap capillary gas chromatography/mass spectrometry is a rapid, precise, and accurate method for determining volatile organic compounds in samples of surface water and ground water. The method can be used to determine 59 selected compounds, including chlorofluorohydrocarbons, aromatic hydrocarbons, and halogenated hydrocarbons. The volatile organic compounds are removed from the sample matrix by actively purging the sample with helium. The volatile organic compounds are collected onto a sorbant trap, thermally desorbed, separated by a Megabore gas chromatographic capillary column, and determined by a full-scan quadrupole mass spectrometer. Compound identification is confirmed by the gas chromatographic retention time and by the resultant mass spectrum. Unknown compounds detected in a sample can be tentatively identified by comparing the unknown mass spectrum to reference spectra in the mass-spectra computer-data system library compiled by the National Institute of Standards and Technology. Method detection limits for the selected compounds range from 0.05 to 0.2 microgram per liter. Recoveries for the majority of the selected compounds ranged from 80 to 120 percent, with relative standard deviations of less than 10 percent.

INTRODUCTION

Purge and trap capillary gas chromatography/mass spectrometry (PT/GC/MS) has been used since the 1980s for the determination of volatile organic compounds (VOCs). Initially, a packed GC column was used for determining VOCs in the U.S. Environmental Protection Agency's (USEPA) Method 624 (U.S. Environmental Protection Agency, 1984). The USEPA Method 624 is suitable for determining VOCs in municipal and industrial discharges, while USEPA Method 524.2 (Slater, 1986) is suitable for determining VOCs in drinking-water samples. In Method 624, samples containing 31 volatile organic compounds are analyzed, with method detection limits (MDLs) ranging from 1.6 to 7.2 $\mu\text{g/L}$ from a 5-mL sample. In Method 524.2, the 30-m Megabore capillary column and 25-mL sample volume resulted in lower detection limits than in Method 624, ranging from 0.03 to 0.35 $\mu\text{g/L}$, as well as baseline separation of many isomers, and allowed the addition of 30 selected compounds.

The U.S. Geological Survey (USGS) National Water Quality Laboratory's (NWQL) method described below is essentially the same as the USEPA Method 524.2 (Eichelberger and Budde, 1989), with a few minor adjustments.

Some of the PT/GC/MS operating conditions have been adjusted to optimize analytical performance. The USEPA Method 524.2 (Slater, 1986) has only one internal standard and two surrogate standards. The USGS method has two internal standards and three surrogate standards. A few of the quantitation ions have been changed because of interferences from coeluting analytes.

This report provides a detailed description of all aspects of the method from sampling protocol through calibration and reporting of results. Accuracy and precision data and method detection limits for 59 VOCs are presented.

The NWQL method supplements other methods of the USGS for determination of organic substances in water that are described by Wershaw and others (1987). This method was implemented at the NWQL in May 1988.

ANALYTICAL METHOD

Organic Compounds and Parameter Codes: Volatile organic compounds, whole water, gas chromatography/mass spectrometry, purge and trap, O-3127-94 (see table 1)

1. Scope and application

This method is suitable for determining purgeable VOCs (table 1). The method may be applied to surface- or ground-water samples, or both. Method detection limits, as well as the linear range of measurement, are dependent on the chemical characteristics of the compound and the ability of the analytical technique to detect and measure the compound. Method detection limits range from 0.05 to 0.2 µg/L using this method. The linear calibration range for most of the compounds in undiluted samples is 0.2 to 25 µg/L. Samples containing VOC concentrations greater than 25 µg/L need to be diluted accordingly.

Table 1.--*Purgeable volatile organic compounds*
[CAS, Chemical Abstracts Service; WATSTORE, Water Data Storage and Retrieval System]

Compound	CAS number	WATSTORE code
Benzene	71-43-2	34030
Bromobenzene	108-86-1	81555
Bromochloromethane	74-97-5	77297
Bromodichloromethane	75-27-4	32101
Bromoform	75-25-2	32104
Bromomethane	74-83-9	34413
<i>n</i> -Butylbenzene	104-51-8	77342
<i>sec</i> -Butylbenzene	135-98-8	77350
<i>tert</i> -Butylbenzene	98-06-6	77353
Carbon tetrachloride	56-23-5	32102
Chlorobenzene	108-90-7	34301
Chloroethane	75-00-3	34311
2-Chloroethyl vinyl ether	110-75-8	34576
Chloroform	67-66-3	32106
Chloromethane	74-87-3	34418
2-Chlorotoluene	95-49-8	77275
4-Chlorotoluene	106-43-4	77277
Dibromochloromethane	124-48-1	32105
1,2-Dibromo-3-chloropropane	96-12-8	38437
1,2-Dibromoethane	106-93-4	77651
Dibromomethane	74-95-3	30217
1,2-Dichlorobenzene	95-50-1	34536
1,3-Dichlorobenzene	541-73-1	34566
1,4-Dichlorobenzene	106-46-7	34571

Table 1.--*Purgeable volatile organic compounds*--Continued

Compound	CAS number	WATSTORE code
Dichlorodifluoromethane	75-71-8	34668
1,1-Dichloroethane	75-34-3	34496
1,2-Dichloroethane	107-06-2	32103
1,1-Dichloroethene	75-35-4	34501
<i>cis</i> -1,2-Dichloroethene	156-59-4	77093
<i>trans</i> -1,2-Dichloroethene	156-60-5	34546
1,2-Dichloropropane	78-87-5	34541
1,3-Dichloropropane	142-28-9	77173
2,2-Dichloropropane	590-20-7	77170
1,1-Dichloropropene	563-58-6	77168
<i>cis</i> -1,3-Dichloropropene	10061-01-5	34704
<i>trans</i> -1,3-Dichloropropene	10061-02-6	34699
Ethylbenzene	100-41-4	34371
Hexachlorobutadiene	87-68-3	39702
Isopropylbenzene	98-82-8	77223
<i>p</i> -Isopropyltoluene	99-87-6	77356
Methylene chloride	75-09-2	34423
Naphthalene	91-20-3	34696
<i>n</i> -Propylbenzene	103-65-1	77224
Styrene	100-42-5	77128
1,1,1,2-Tetrachloroethane	630-20-6	77562
1,1,2,2-Tetrachloroethane	79-34-5	34516
Tetrachloroethene	127-18-4	34475
Toluene	108-88-3	34010
1,2,3-Trichlorobenzene	87-61-6	77613
1,2,4-Trichlorobenzene	120-82-1	34551
1,1,1-Trichloroethane	71-55-6	34506
1,1,2-Trichloroethane	79-00-5	34511
Trichloroethene	79-01-6	39180
Trichlorofluoromethane	75-69-4	34488
1,2,3-Trichloropropane	96-18-4	77443
1,2,4-Trimethylbenzene	95-63-6	77222
1,3,5-Trimethylbenzene	108-67-8	77226
Vinyl chloride	75-01-4	39175
Xylenes (dimethyl- benzenes), total	(<i>meta</i> -) 108-38-3 (<i>para</i> -) 106-42-3 (<i>ortho</i> -) 95-47-6	81551

2. Summary of method

2.1 Volatile organic compounds are purged from the sample matrix by bubbling helium through a 25-mL aqueous sample. The compounds are trapped in a tube containing suitable sorbent materials and then thermally desorbed onto a Megabore capillary column. The gas chromatograph is temperature programmed to separate the compounds, which then are detected by the mass spectrometer.

2.2 Determination of selected compounds is confirmed by analyzing standard reference materials under the same conditions as the samples, comparing retention times and mass spectra.

3. Interferences

3.1 The main sources of contamination in volatile analysis will be from volatile compounds present in the laboratory atmosphere, impurities in the helium, or impurities in the trap. Common laboratory contaminants include solvents such as methylene chloride and toluene, and refrigerants such as dichlorodifluoromethane. Polytetrafluoroethene (PTFE) plastic tubing in the purging device is not used because organic compounds might permeate the tubing, resulting in concentration of the contaminants on the trap.

3.2 Take special care to eliminate all potential organic contaminants. Wear laboratory clothing that has not been exposed to methylene chloride vapors. Avoid dichlorodifluoromethane when checking for leaks in the mass spectrometer. To minimize this problem, analyze daily a laboratory blank to quantify any contaminants and to determine if corrective actions are required. Also, the analytical laboratory for volatiles needs to be located far from other laboratories where extractions using organic solvents (particularly, methylene chloride) are conducted. To reduce the possibility of contaminating samples, store laboratory solvents, with the exception of methanol, outside of the VOC laboratory. Moreover, do not store stock VOC solutions near samples.

3.3 Cross contamination can interfere when a sample containing small concentrations of VOCs is analyzed after a sample containing large concentrations of VOCs. In this event, reanalyze the subsequent samples suspected of contamination to verify the results. Replace the purge vessel containing the contaminated sample.

4. Instrumentation

4.1 *Purge and trap unit*, Tekmar Model LSC2000 concentrator with a model 2016 or 2032 Automated Liquid Sampler (ALS) or equivalent. The ALS is equipped with fritted purge vessels that will hold 25 mL of sample. Suggested configurations follow:

4.1.1 *Purge cycle*, 11 minutes with a flow of 40 mL/min of helium, measured at the vent of the purge and trap unit.

4.1.2 *Purge pressure*, 138 kPa (20 lb/in²).

4.1.3 *Six-port valve temperature*, 100°C.

4.1.4 *Desorb preheat temperature*, 175°C.

4.1.5 *Desorb temperature*, 180°C for 4 minutes.

4.1.6 *Trap*, Tekmar #5 or equivalent, 25-cm x 0.27-cm inside diameter (ID). Starting from the purge inlet, the trap contains 1 cm of 3 percent OV-1 packing with 60/80 mesh and the following adsorbents: one-third Tenax, one-third silica gel, and one-third activated charcoal. Use silanized glass wool as a spacer at the trap inlet and outlet. A new trap needs to be conditioned in the bake cycle for 30 minutes. Condition the trap for at least 10 minutes prior to daily use. Indications of trap degradation include the presence of trace quantities of benzene, lack of response, and a decrease in bromoform sensitivity. Do not heat the trap to a temperature greater than 225°C.

4.1.7 *Bake cycle*, 10 minutes at 205°C.

4.1.8 *ALS transfer line*, aluminized fused silica, 0.32 mm ID.

4.1.9 *ALS transfer line temperature to GC inlet*, 100°C.

4.2 *Gas chromatograph/mass spectrometer (GC/MS)*: Hewlett-Packard model 5996, Finnigan Incos model 50 or equivalent, equipped with subambient GC oven-cooling capability, and a jet separator. Suggested gas chromatographic configurations follow:

4.2.1 *Column*, fused-silica Megabore[®], 30-m x 0.53-mm ID, 3.0-μm film thickness, J&W DB-624 or equivalent.

4.2.2 *Carrier gas*, helium, 15 mL/min flow at 22°C.

4.2.3 *GC/MS interface temperature*, 200°C.

4.2.4 *Oven temperature program*, initial temperature 10°C, hold 5 minutes, program at 6°C/min to 160°C and hold at 160°C to allow all selected compounds to elute.

4.2.5 Remove the injection port, and plumb the ALS aluminized fused silica transfer line directly into the Megabore column.

4.3 *Mass spectrometer conditions*:

4.3.1 *Ionization mode*, electron impact at 70-eV (electron volts).

4.3.2 *Scan Range*, 45 to 300 amu.

4.3.3 *Scan Rate*, 1 scan/s

4.3.4 Adjust the instrument to meet the bromofluorobenzene (BFB) performance criteria listed in table 3.

4.4 The aforementioned operating conditions are listed in table 2.

Table 2.--Summary of purge and trap capillary gas chromatography/mass spectrometry operating conditions

[GC/MS, gas chromatography/mass spectrometry; mL/min, milliliters per minute; °C, degrees Celsius; kPa, kilopascal; lb/in², pounds per square inch; m, meter; mm, millimeter; ID, inside diameter; eV, electron volt; amu, atomic mass units; scan/s, scan per second; USEPA, U.S. Environmental Protection Agency]

<u>Purge and trap configurations</u>	
Purge cycle	11 minutes
Carrier gas	Helium, 40-mL/min flow at 22°C
Desorb preheat temperature	175°C
Desorb temperature	180°C for 4 minutes
Bake cycle	10 minutes at 205°C
Transfer line temperature to GC inlet	100°C
Six-port valve temperature	100°C
Purge pressure	138 kPa (20 lb/in ²)
Trap	Tekmar #5
<u>Gas chromatograph configurations</u>	
Column	DB-624 30-m x 0.53-mm ID
Carrier gas	Helium, 15 mL/min flow at 22°C
GC/MS interface temperature	200°C
<u>Mass spectrometer configurations</u>	
Ionization mode	Electron impact, 70-eV
Scan range	45 to 300 amu
Scan rate	1 scan/s
Bromofluorobenzene criteria	Meets USEPA specifications

Table 3.--Gas chromatograph/mass spectrometer performance evaluation using bromofluorobenzene (Eichelberger and Budde, 1989) [m/z, mass to charge ratio]

Mass to charge ratio	Ion abundance criteria
50	15 to 40 percent of m/z 95
75	30 to 80 percent of m/z 95
95	Base peak, 100 percent relative abundance
96	5 to 9 percent of m/z 95
173	Less than 2 percent of m/z 174
174	Greater than 50 percent of m/z 95
175	5 to 9 percent of m/z 174
176	Greater than 95 percent but less than 101 percent of m/z 174
177	5 to 9 percent of m/z 176

5. Apparatus and equipment

5.1 Syringes, 25-mL, gas-tight, Teflon with Luer lock tip, or 30-mL syringe with glass barrel.

5.2 Gas-tight syringes ranging from 5 to 100 μ L for standard solution preparation.

5.3 Syringe, 10- μ L, for spiking surrogate standard and internal standard solutions.

5.4 Volumetric flask, 10-mL, baked at 105°C for at least 15 minutes.

5.5 Amber vials, 1- or 2-mL, to store working standard solutions.

5.6 Oven, capable of heating to 105°C.

5.7 Freezer for storing standard solutions at -10°C or lower.

5.8 Refrigerator for storing samples at about 4°C.

6. Reagents

6.1 Water, volatile organic-free (VOFW), deionized and distilled in glass, boiled for 1 hour, cooled and purged with ultrahigh purity grade nitrogen for a minimum of 1 hour. Prepare daily.

6.2 Methanol, distilled in glass, purge and trap grade, Burdick and Jackson or equivalent.

7. Standard solutions

The following purchased methanol solutions are used to prepare standard solutions by spiking the appropriate quantity into 25 mL of organic-free water contained in a gas-tight syringe. Store all purchased standard solutions and prepared standard solutions in darkness at 4°C or colder in 2-mL amber vials with minimum headspace. All standard solutions are stored separately from the samples.

7.1 Mass spectrometer performance evaluation standard solution, 1-bromo-4-fluorobenzene, Supelco, USEPA or equivalent. Prepare a 25- μ g/mL solution in methanol.

7.2 Internal standard/surrogate standard solution (SURRIS), fluorobenzene and 1,2-dichlorobenzene- d_4 , 1,2-dichloroethane- d_4 , toluene d_8 , and 1-bromo-4-fluorobenzene, Supelco, 2,000 μ g/mL of each component in methanol or equivalent. Prepare a solution in methanol to arrive at a final concentration of 25 μ g/mL.

7.3 Selected compound calibration standard solution, Supelco Volatile Organic Compound Mixtures I through VI, 2,000 μ g/mL in methanol or equivalent. Prepare a solution, in methanol, containing mixtures I through VI, to arrive at a final concentration of 5 μ g/mL. Prepare the calibration standards at least once every 2 weeks, or more frequently if the calculated concentrations do not meet the criteria in paragraph 11.3.2.

7.4 *Quality control (QC) check solution*, Supelco, USEPA or equivalent. Prepare a solution in methanol containing 5 µg/mL of each compound being reported. Prepare the QC check solution from a source other than that used for the calibration standards in paragraph 7.3.

7.5 *Matrix spike solution*, 1,1,-dichloroethene, benzene, toluene, trichloroethene, and chlorobenzene, Supelco, USEPA or equivalent. Prepare the matrix spike solution from a different source than the one used to prepare the calibration standards in paragraph 7.3. Prepare a solution in methanol containing 25 µg/mL of each compound.

8. Sample collection, preservation, and storage

8.1 Sample collection

8.1.1 Sampling for VOCs requires special considerations. Samples easily can become contaminated if the protocol is not followed. Collect samples for VOC analysis in triplicate in clean 40-mL borosilicate amber vials with Teflon-faced silicone septa. Fill the vials to overflowing and cap immediately. Do not allow air to pass through the sample or to become trapped inside the vial. Headspace present inside the vial can result in substantial losses of VOCs, especially the more volatile compounds, such as dichlorodifluoromethane (Pankow, 1986).

8.1.2 Store the samples immediately at 4°C. Pack enough ice in each shipping container to ensure the samples remain chilled throughout transit. Do not use dry ice for shipping volatiles.

8.1.3 Do not wrap tape around the seal of the VOC vial because solvents in the glue might outgas to the sample, contaminating it with toluene, acetone, methyl ethyl ketone, or other common solvents used in glues. Do not use Freon-puffed Styrofoam pellets when packaging VOC samples for shipment. The samples might become contaminated with trichlorofluoromethane.

8.1.4 The USEPA recommends preparing a field equipment blank when sampling. A field equipment blank goes through the same mechanical procedures as the samples. Use volatile organic-free water (VOFW) for field equipment blanks. Make VOFW by boiling distilled water for 1 hour, cooling, and using immediately. It is critical that the environment where the water is prepared is free of VOCs. For example, it would not be prudent to prepare VOFW near a laboratory for organic-sample preparation. The water might be contaminated by levels of methylene chloride, chloroform, toluene, benzene, acetone, and other solvents. Do not rinse the sampling equipment with any solvents, except for methanol. Solvents, such as hexane, acetone, and isopropyl alcohol, will contaminate the samples and result in interferences.

8.1.5 Prepare a trip blank, which accompanies the sample throughout the sampling and transit period, from VOFW. The trip blank is not opened until it is ready for analysis at the laboratory. The field equipment blank and trip blank are useful for determining sources of contamination caused by sampling and transportation.

8.2 Sample preservation

8.2.1 The USEPA recommends preserving volatiles with two drops of a 1:1 solution of concentrated hydrochloric acid and organic-free water for a 40-mL sample. Dispense the acid from a Teflon squeeze bottle equipped with a dropper to a full VOC vial. Do not use plastic pipettes to dispense the acid. The compound 1,2-dichloroethane has been detected in samples where plastic pipettes were used. If residual free chlorine is present in the samples, add 25 mg of ascorbic acid to an empty vial, fill with the sample, and then add two drops of 1:1 hydrochloric acid according to USEPA Method 524.2 (Slater, 1986).

8.2.2 Do not preserve samples with hydrochloric acid if analysis for 2-chloroethyl vinyl ether is needed. The 2-chloroethyl vinyl ether reacts with the acid and decomposes at a pH less than 5.

8.3 Sample receipt and storage

Store samples for VOC analysis on ice and ship immediately to preserve the integrity of the sample. The samples need to be analyzed within 14 days of collection.

9. Instrument performance

9.1 *Mass spectrometer performance evaluation.*

9.1.1 Prior to analyzing the samples, determine if the instrument performance meets the bromofluorobenzene (BFB) criteria listed in table 3 by analyzing a blank containing the SURRIS solution (paragraph 7.2) or by analyzing a direct injection of a BFB solution (paragraph 7.1). In addition, tune the MS to ensure that the established reporting level for each selected compound can be achieved.

9.1.2 Mass spectral peak-abundance averaging and background correction may be used to obtain a BFB spectrum for evaluation.

9.1.3 If the mass spectrum for BFB fails to meet the criteria specified in table 3, retune the mass spectrometer, and reanalyze BFB until the criteria are passed.

9.2 *Gas chromatograph performance evaluation.* The GC performance normally is evaluated by examining the variation of the selected compound-response factors, relative to response factors obtained using a new capillary column and freshly prepared standard solutions (paragraph 7.3).

10. Calibration

10.1 Prepare five to seven calibration standard solutions in organic-free water to arrive at concentrations ranging from 0.2 to 20 µg/L.

10.1.1 Fill a glass syringe with 25 mLs of organic-free water.

10.1.2 Add 5 µL of the SURRIS solution (paragraph 7.2) to the syringe.

10.1.3 Add 1 µL to 100 µL of the selected compound calibration standard solution (paragraph 7.3) to the syringe.

10.1.4 Acquire data for each selected compound by analyzing the calibration standard solution according the GC/MS conditions described in paragraphs 4.1, 4.2, and 4.3. Acquire initial calibration data using a new GC column and freshly prepared standard solutions. These data are used in subsequent evaluation of system performance.

10.2 Calculate the relative retention time (RRT) for each compound as follows:

$$RRT = \frac{RT_c}{RT_i}$$

where RT_c = uncorrected retention time of the selected compound or surrogate compound; and
 RT_i = uncorrected retention time of the internal standard for the compound in question.

10.3 Calculate the response factor (RF) for each selected compound and surrogate compound as follows:

$$RF = \frac{C_i \times A_c}{C_c \times A_i},$$

where C_i = concentration of the internal standard solution, in micrograms per liter;
 A_c = GC peak area of the quantitation ion for the selected compound or surrogate compound;
 C_c = concentration of the selected compound or surrogate compound, in micrograms per liter; and
 A_i = GC peak area of the quantitation ion for the internal standard.

The quantitation ions and internal standard references used in these calculations are listed in table 4.

Use the average of the response factors calculated for each standard concentration in subsequent selected compound quantitation. Use of the average response factor is acceptable if the relative standard deviation (RSD) throughout the calibration range is less than or equal to 20 percent. Use a first-order or second-order degree equation if the RSD is greater than 20 percent.

Table 4.--*Quantitation ions, method detection and reporting limits, and internal standard references for volatile organic compounds listed by chromatographic retention times*

[µg/L, micrograms per liter; n/a, not applicable to internal standards or surrogate standards;
IS, Internal Standard]

Compound	Quantitation ion	Method detection limit ¹ (µg/L)	Reporting limit (µg/L)	Chromato-graphic retention time (minutes)	Internal standard reference number
Internal standards					
Fluorobenzene	96	n/a	n/a	10.71	IS 1
1,2-Dichlorobenzene-d ₄	152	n/a	n/a	22.50	IS 2
Surrogate standards					
1,2-Dichloroethane-d ₄	65	n/a	n/a	10.03	1
Toluene-d ₈	98	n/a	n/a	13.76	1
1-Bromo-4-fluorobenzene	95	n/a	n/a	19.23	2
Selected compounds					
Dichlorodifluoromethane	85	0.09	0.2	1.85	1
Chloromethane	50	.08	.2	2.01	1
Vinyl chloride	62	.13	.2	2.24	1
Bromomethane	94	.06	.2	2.68	1
Chloroethane	64	.08	.2	2.86	1
Trichlorofluoromethane	101	.08	.2	3.33	1
1,1-Dichloroethene	96	.08	.2	4.39	1
Methylene chloride	84	.11		5.61	1
<i>trans</i> -1,2-Dichloroethene	96	.08	.2	6.25	1
1,1-Dichloroethane	63	.06	.2	7.17	1
2,2-Dichloropropane	77	.06	.2	8.37	1
<i>cis</i> -1,2-Dichloroethene	96	.05	.2	8.45	1
Bromochloromethane	128	.08	.2	8.89	1
Chloroform	83	.06	.2	9.22	1
1,1,1-Trichloroethane	97	.06	.2	9.38	1
Carbon tetrachloride	117	.09	.2	9.68	1
1,1-Dichloropropene	75	.06	.2	9.70	1
Benzene	78	.06	.2	10.07	1
1,2-Dichloroethane	62	.10	.2	10.19	1
Trichloroethene	95	.16	.2	11.42	1
1,2-Dichloropropane	63	.07		11.81	1
Dibromomethane	93	.07	.2	12.01	1
Bromodichloromethane	83	.06	.2	12.46	1
2-Chloroethyl vinyl ether ²	63	.08	1	13.00	1
<i>cis</i> -1,3-Dichloropropene	75	.06	.2	13.35	1
Toluene	92	.05	.2	13.90	1
<i>trans</i> -1,3-Dichloropropene	75	.06	.2	14.53	1
1,1,2-Trichloroethane	83	.15	.2	14.81	2
Tetrachloroethene	166	.07	.2	14.97	2
1,3-Dichloropropane	76	.13	.2	15.11	2
Dibromochloromethane	129	.06	.2	15.54	2
1,2-Dibromoethane	107	.06	.2	15.66	2
Chlorobenzene	112	.10	.2	16.70	2
1,1,1,2-Tetrachloroethane	131	.06	.2	16.98	2
Ethylbenzene	91	.08	.2	17.04	2

Table 4.-- Quantitation ions, method detection and reporting limits, and internal standard references for volatile organic compounds listed by chromatographic retention times --Continued

Compound	Quantitation ion	Method detection limit ¹ (µg/L)	Reporting limit (µg/L)	Chromatographic retention time (minutes)	Internal standard reference number
Selected compounds--Continued					
<i>meta</i> - and <i>para</i> -Xylenes (1,3 and 1,4-dimethylbenzene)	91	0.13	0.2	17.31	2
<i>ortho</i> -Xylene (1,2-dimethylbenzene)	91	.06	.2	18.12	2
Styrene	104	.10	.2	18.18	2
Bromoform	173	.08	.2	18.46	2
Isopropyl benzene	105	.08	.2	18.79	2
Bromobenzene	156	.06	.2	19.44	2
1,2,3-Trichloropropane	110	.09	.2	19.72	2
1,1,2,2-Tetrachloroethane	83	.16	.2	19.74	2
<i>n</i> -Propylbenzene	91	.09	.2	19.88	2
2-Chlorotoluene	126	.09	.2	19.94	2
4-Chlorotoluene	126	.08	.2	20.19	2
1,3,5-Trimethylbenzene	105	.07	.2	20.29	2
<i>tert</i> -Butylbenzene	119	.07	.2	20.98	2
1,2,4-Trimethylbenzene	105	.07	.2	21.10	2
<i>sec</i> -Butylbenzene	105	.09	.2	21.48	2
1,3-Dichlorobenzene	146	.06	.2	21.57	2
1,4-Dichlorobenzene	146	.09	.2	21.77	2
<i>p</i> -Isopropyltoluene	119	.09	.2	21.85	2
1,2-Dichlorobenzene	146	.07	.2	22.57	2
<i>n</i> -Butylbenzene	91	.07	.2	22.76	2
1,2-Dibromo-3-chloropropane	75	.20	1	24.00	2
Napthalene	128	.06	.2	26.66	2
1,2,4-Trichlorobenzene	180	.09	.2	26.70	2
Hexachlorobutadiene	225	.10	.2	26.70	2
1,2,3-Trichlorobenzene	180	.07	.2	27.23	2

¹U.S. Environmental Protection Agency (1984, p. 198 and 199).

²Compound is not in U.S. Environmental Protection Agency Method 524.2 (Eichelberger and Budde, 1989).

11. Quality control

The following discussion represents the minimum quality-control practices established for this method. Perform the following practices daily prior to sample analysis and throughout the sample batch as indicated.

11.1 Bromofluorobenzene (BFB) criteria

11.1.1 Determine if the instrument meets the BFB criteria in table 3 (paragraph 9.1.1).

11.1.2 Determine BFB criteria every 10 samples or every 8 hours. The BFB is added to every sample in the SURRIS solution. Consequently, BFB criteria can be determined in every sample.

11.2 Instrument blanks

11.2.1 Prepare a blank by spiking 25 mL of organic-free water with 5 μ L of the SURRIS solution (paragraph 7.2)

11.2.2 Determine if the system is acceptably free of contaminants. A contaminant is defined as the presence of any compound that interferes with the quantitation or identification of any of the selected compounds in the analysis.

11.2.3 Analyze a blank every 10 samples or every 8 hours.

11.3 Continuing calibration verification (CCV) standard

11.3.1 Prepare a CCV standard by adding 5 μ L of the SURRIS solution (paragraph 7.2) and 25 μ L of the selected compound calibration standard solution (paragraph 7.3) to 25 mL of organic-free water.

11.3.2 Analyze and evaluate the CCV. If the daily response factors differ more than 30 percent from the values derived in paragraph 10.3, prepare fresh standard solutions (paragraph 7.3) or service the PT/GC/MS to improve performance.

11.3.3 Instrument maintenance might involve replacing the trap, column, or ALS transfer line; cleaning the ion source; replacing the electron multiplier and filaments; and replacing or cleaning the jet separator.

11.3.4 Analyze a CCV standard every 10 samples or every 8 hours.

11.4 Quality-control check (QCC) standard

11.4.1 Prepare a QCC standard by adding 5 μ L of the SURRIS solution (paragraph 7.2) and 25 μ L of the QCC solution (paragraph 7.4) to 25 mL of organic-free water.

11.4.2 Analyze the QCC daily and calculate the percent recovery for each compound. If the calculated result is not within 60 to 140 percent of the anticipated value (Slater, 1986, section 9.3.2), consider preparing a fresh QCC or new calibration standard, or service the instrument (paragraph 11.3.3) to improve performance.

11.5 Matrix spike

11.5.1 Prepare a matrix spike by adding 5 µL of SURRIS solution (paragraph 7.2) and 25 µL of the matrix spike solution (paragraph 7.5) to 25 mL of a duplicate water sample to arrive at a concentration of 5 µg/L.

11.5.2 Analyze a matrix spike for every 20 samples. Calculate the percent recovery for each compound. The calculated result needs to be within the following specifications (U.S. Environmental Protection Agency, 1985):

Selected compound	Percent recovery
Benzene	76-127
Chlorobenzene	75-130
1,1-Dichloroethylene	61-145
Toluene	76-125
Trichloroethene	71-120

Percentages might fall outside this range for several reasons. If the CCV and QCC solutions indicate the system is operating within specifications, the sample matrix might be interfering with the measurement. Repeat the analysis if a triplicate sample is available.

11.6 System reproducibility

11.6.1 Analyze a duplicate water sample after every 10 samples. Choose one of the samples in the previous set of 10.

11.6.2 Determine the reproducibility factor (R) by using the following equation:

$$R = \frac{(C_1 - C_2)}{(C_1 + C_2)/2} \times 100 \text{ percent}$$

where C_1 = concentration of the analyte in sample, in micrograms per liter; and
 C_2 = concentration of the analyte in duplicate, in micrograms per liter.

11.7 Internal standard areas

11.7.1 Compare the area of the quantitation ion of the internal standard (IS) solutions in the daily CCV to the IS areas in the samples. The IS areas of the samples need to be within 30 percent of the IS areas of the daily CCV (Eichelberger and Budde, 1989, p. 300).

11.7.2 Internal standard areas outside this range might be caused by matrix effects, leaking purge vessels, leaking fittings, or active sites present in the glassware or in the transfer lines. Repeat the analysis if a duplicate sample is available.

11.8 Surrogate recovery

For each sample, calculate the percent recovery for each surrogate compound. The percent recovery for each surrogate needs to be within the range of 70 to 130 percent (Eichelberger and Budde, 1989, p. 300). If a value falls outside this range, analyze a duplicate sample.

11.9 Limit of quantitation (LOQ) standard

11.9.1 Demonstrate the ability to detect all the selected compounds at the reporting level. Prepare a LOQ by adding 5 μ L of the SURRIS solution (paragraph 7.2) and 1 μ L of the selected compound calibration standard solution (paragraph 7.3) to 25 mL of organic-free water.

11.9.2 Analyze a LOQ weekly, or after any maintenance procedures or instrument tuning. Calculate the percent recovery. If the calculated result is not within 60 to 140 percent of the anticipated value, service the instrument to improve performance (Slater, 1986, section 9.4).

11.10 Sample analysis

11.10.1 Determine which samples will be included in the batch run. Oldest samples have priority. Analyze samples within 14 days of sampling.

11.10.2 Arrange samples in the order of analysis, placing known trip and field blanks after the instrument blank.

11.10.3 If samples are suspected to be contaminated, analyze a dilution first, or place near the end of the run.

11.10.4 After every 10 samples, analyze a CCV at 2 μ g/L, a blank, and a duplicate water sample. Determine BFB criteria in the blank.

11.10.5 To prepare the sample for analysis, rinse a 30-mL syringe with 5 to 10 mL of the sample. Pour the remaining sample into the barrel of the syringe, insert the plunger, remove air bubbles, and adjust the volume to 25 mL. Add 5 μ L of SURRIS solution (paragraph 7.2) to the sample through the needle fitting of the syringe. Transfer the sample to the purge vessel, and analyze according to the PT/GC/MS conditions described in section 4.

12. Identification and quantitation

12.1 Qualitative identification

12.1.1 Initially identify a selected compound by comparing the GC retention time (RT) of the compound to the RT of the standard solution. The RT of the sample needs to be within ± 0.1 minute of the expected RT for the compound in question. Calculate the retention time as follows:

$$RT = RRT_c \times RT_i,$$

where RT = expected retention time of the selected compound or surrogate compound,
RRT_c = relative retention time of the selected compound or surrogate compound, and
Rt_i = uncorrected retention time of the quantitation ion of the internal standard for the compound in question.

12.1.2 Verify mass spectra for each selected compound by comparing the mass spectrum with a reference spectrum obtained from standards analyzed on the GC/MS system (see section 4). It is difficult to define explicitly which features of a sample mass spectrum relative to that of a standard mass spectrum need to be present to consider the identification to be positive. Experience and training are necessary for the analyst to recognize the relevant features of individual mass spectra as well as potential interferences. In general, the sample spectrum needs to have the same base peak, major fragmentation ions, substantial isotope clusters, and molecular ions (where appropriate) as the standard spectrum. It is often beneficial to plot mass spectra of important ions (or suspected interfering ions) to determine whether they maximize at the expected retention time with intensities consistent with the reference mass spectrum. Computerized fit criteria or match factors are valuable interpretation aids but are not to be used exclusively.

12.2 Quantitation

12.2.1 If a compound has passed the aforementioned qualitative identification criteria, calculate the concentration in the sample using the average response factor as follows:

$$C = \frac{C_i \times A_c}{RF_c \times A_i},$$

where C = concentration of the selected compound or surrogate compound in the sample, in micrograms per liter;
C_i = concentration of the corresponding internal standard, in micrograms per liter;
A_c = area of the quantitation ion for the selected compound or surrogate compound identified;
RF_c = response factor (paragraph 10.3) for each selected compound or surrogate compound; and
A_i = area of the quantitation ion for the internal standard solution.

12.2.2 Percent recovery of the surrogate compound is calculated as follows:

$$\% \text{ rec.} = \frac{C_i \times A_c}{RF_c \times A_i \times C_s} \times 100,$$

where % rec. = percent recovery of the surrogate compound;

C_i = concentration of the corresponding internal standard,
in micrograms per liter;

A_c = area of the quantitation ion for the surrogate compound;

RF_c = response factor (paragraph 10.3) for each surrogate compound;

A_i = area of the quantitation ion for the internal standard; and

C_s = concentration of the surrogate compound in the surrogate standard
added to the sample, in micrograms per liter.

13. Reporting of results

13.1 Report concentrations of volatile organic compounds as follows: If the quantity is less than the reporting limit, report the concentration as “less than” the reporting limit. If the quantity is greater than the reporting limit, report the concentration to two significant figures. Reporting limits are 0.2 µg/L for all selected compounds except for 2-chloroethyl vinyl ether and 1,2-dibromo-3-chloropropane, which are 1.0 µg/L (see table 4).

13.2 If a selected compound is present at a concentration greater than the highest calibration standard, dilute to accurately quantitate the amount present. Dilute the water sample so that the amount being injected on the column is in the middle of the calibration range. If a sample has several selected compounds at different levels, more than one dilution will be necessary, and the reporting level will be raised accordingly.

13.3 Sample matrices also can cause interferences, resulting in a raised reporting level. A sample might have an unknown compound with similar masses, coeluting with a selected compound. The reporting level may be raised if it is difficult to determine the identity and amount present because of the interfering compounds.

14. Accuracy and precision

Single-operator recovery and precision data were acquired for volatile organic compounds in three matrices at three concentrations listed in table 5.

Table 5.—Precision, recovery, and accuracy data in three matrices for selected volatile organic compounds in water samples--Continued

Compound	Concentration (µg/L)	Reagent water			Surface water 1			Surface water 2		
		No. reps.	Average recovery (percent)	Relative standard deviation (percent)	No. reps.	Average recovery (percent)	Relative standard deviation (percent)	No. reps.	Average recovery (percent)	Relative standard deviation (percent)
Benzene	0.5	8	104	3.0	8	118	9.3	8	101	4.8
	2.0	10	96	3.6	8	103	5.8	8	95	4.6
	10.0	8	100	4.6	8	98	3.8	8	106	4.6
Bromobenzene	0.5	8	110	4.3	8	109	11	8	91	3.4
	2.0	10	103	5.2	8	94	6.9	8	91	4.0
	10.0	8	87	2.5	8	85	4.5	8	92	3.5
Bromochloromethane	0.5	8	114	7.2	8	124	12	8	106	7.7
	2.0	10	96	5.2	8	111	7.4	8	98	3.4
	10.0	8	103	6.3	8	62	5.6	8	111	5.1
Bromodichloromethane	0.5	8	98	6.9	8	93	8.3	8	113	4.4
	2.0	10	100	6.3	8	118	18	8	109	8.6
	10.0	8	114	6.7	8	117	5.3	8	92	5.9
Bromoform	0.5	8	92	7.8	8	77	14	8	97	5.9
	2.0	10	116	5.6	8	89	3.4	8	86	6.7
	10.0	8	102	4.8	8	104	5.0	8	101	4.1
Bromomethane	0.5	8	116	6.1	8	123	10	8	99	4.3
	2.0	10	106	3.2	8	99	6.1	8	94	4.6
	10.0	8	94	4.4	8	94	2.8	8	96	4.1
<i>n</i> -Butylbenzene	0.5	8	104	4.6	8	108	14	8	87	5.8
	2.0	10	111	2.8	8	86	5.0	8	86	5.3
	10.0	8	89	2.1	8	89	5.1	8	84	4.6
<i>sec</i> -Butylbenzene	0.5	8	104	6.3	8	112	11	8	91	5.1
	2.0	10	108	2.7	8	88	4.0	8	89	3.7
	10.0	8	87	1.7	8	86	5.7	8	90	5.0
<i>tert</i> -Butylbenzene	0.5	8	106	4.7	8	110	12	8	89	2.8
	2.0	10	107	2.1	8	84	4.8	8	86	4.3
	10.0	8	82	2.2	8	81	5.3	8	86	4.6
Carbon tetrachloride	0.5	8	110	5.4	8	112	8.4	8	95	5.7
	2.0	10	106	6.3	8	95	5.7	8	89	6.5
	10.0	8	98	5.1	8	100	2.6	8	96	3.5
Chlorobenzene	0.5	8	102	9.8	8	101	12	8	90	3.9
	2.0	10	107	3.8	8	92	6.4	8	93	4.7
	10.0	8	93	2.9	8	92	4.8	8	93	5.1

Table 5.—Precision, recovery, and accuracy data in three matrices for selected volatile organic compounds in water samples—Continued

Compound	Concentration (µg/L)	Reagent water			Surface water 1			Surface water 2		
		No. reps.	Average recovery (percent)	Relative standard deviation (percent)	No. reps.	Average recovery (percent)	Relative standard deviation (percent)	No. reps.	Average recovery (percent)	Relative standard deviation (percent)
Chloroethane	0.5	8	119	4.5	8	106	7.7	8	95	3.5
	2.0	10	102	4.1	8	108	6.4	8	101	5.5
	10.0	8	99	4.9	8	100	3.6	8	97	2.8
2-Chloroethyl vinyl ether	0.5	8	82	7.2	8	27	56	8	141	35
	2.0	10	107	11	8	148	4.3	8	137	3.4
	10.0	8	108	6.6	8	110	8.3	8	98	15
Chloroform	0.5	8	116	5.0	8	119	11	8	145	4.7
	2.0	10	104	3.8	8	103	7.1	8	105	4.7
	10.0	8	102	4.6	8	100	4.2	8	107	4.0
Chloromethane	0.5	8	98	5.7	8	112	13	8	100	8.6
	2.0	10	136	9.6	8	120	5.4	8	105	6.3
	10.0	8	102	6.1	8	96	8.7	8	115	12
2-Chlorotoluene	0.5	8	110	4.7	8	117	13	8	88	4.0
	2.0	10	106	2.3	8	85	4.9	8	87	3.9
	10.0	8	87	2.5	8	85	5.0	8	91	4.0
4-Chlorotoluene	0.5	8	100	13	8	93	10	8	97	11
	2.0	10	105	4.4	8	99	8.9	8	100	6.4
	10.0	8	95	2.5	8	93	5.7	8	89	5.0
Dibromochloromethane	0.5	8	86	4.9	8	96	17	8	93	7.7
	2.0	10	107	5.4	8	96	9.8	8	96	5.3
	10.0	8	99	4.3	8	100	4.6	8	93	2.8
1,2-Dibromo-3-chloropropane	0.5	10	70	12	8	95	60	8	39	86
	2.0	10	134	12	8	90	6.8	8	85	14
	10.0	8	99	5.9	8	97	6.4	8	93	7.2
1,2-Dibromoethane	0.5	8	86	13	8	89	14	8	98	11
	2.0	10	105	3.9	8	95	8.5	8	93	6.1
	10.0	8	105	4.4	8	105	5.4	8	102	4.2
Dibromomethane	0.5	8	120	21	8	127	14	8	97	9.7
	2.0	10	104	18	8	89	9.8	8	85	6.1
	10.0	8	101	4.9	8	102	5.6	8	95	5.1
1,2-Dichlorobenzene	0.5	8	114	5.0	8	113	12	8	97	8.4
	2.0	10	107	3.2	8	86	6.2	8	84	3.5
	10.0	8	99	3.0	8	98	5.6	8	88	3.0

Table 5.—Precision, recovery, and accuracy data in three matrices for selected volatile organic compounds in water samples—Continued

Compound	Concentration (µg/L)	Reagent water			Surface water 1			Surface water 2		
		No. reps.	Average recovery (percent)	Relative standard deviation (percent)	No. reps.	Average recovery (percent)	Relative standard deviation (percent)	No. reps.	Average recovery (percent)	Relative standard deviation (percent)
1,3-Dichlorobenzene	0.5	8	100	3.9	8	112	12	8	93	3.9
	2.0	10	105	3.5	8	94	5.9	8	94	5.0
	10.0	8	92	2.3	8	90	4.0	8	94	4.1
1,4-Dichlorobenzene	0.5	8	96	7.0	8	116	16	8	93	8.6
	2.0	10	105	4.5	8	97	4.4	8	97	5.5
	10.0	8	92	2.2	8	91	4.1	8	95	3.7
Dichlorodifluoromethane	0.5	8	98	10	8	112	11	8	97	7.6
	2.0	10	110	6.6	8	88	6.9	8	91	5.8
	10.0	8	94	7.8	8	98	5.6	8	96	6.3
1,1-Dichloroethane	0.5	8	118	4.6	8	116	11	8	102	5.0
	2.0	10	101	2.6	8	112	8.4	8	98	3.3
	10.0	8	111	4.8	8	107	5.6	8	112	6.4
1,2-Dichloroethane	0.5	8	126	7.7	8	118	13	8	104	4.9
	2.0	10	110	5.0	8	103	5.9	8	90	6.4
	10.0	8	102	4.7	8	102	5.4	8	104	4.5
1,1-Dichloroethene	0.5	8	120	6.1	8	113	12	8	105	6.3
	2.0	10	98	4.6	8	109	5.9	8	101	4.6
	10.0	8	107	5.3	8	106	5.2	8	108	4.8
<i>cis</i> -1,2-Dichloroethene	0.5	8	112	3.4	8	122	11	8	105	6.7
	2.0	10	97	4.4	8	109	7.7	8	98	3.6
	10.0	8	104	4.7	8	102	4.8	8	108	5.1
<i>trans</i> -1,2-Dichloroethene	0.5	8	116	4.8	8	113	11	8	101	4.9
	2.0	10	96	3.3	8	109	6.5	8	98	4.4
	10.0	8	107	5.2	8	105	4.5	8	109	6.0
1,1-Dichloropropene	0.5	8	108	3.8	8	115	11	8	98	4.5
	2.0	10	103	3.2	8	100	6.1	8	91	5.1
	10.0	8	97	5.6	8	97	2.8	8	101	3.7
<i>cis</i> -1,3-Dichloropropene	0.6	8	77	5.4	8	75	16	8	105	9.7
	2.6	10	88	11	8	130	9.7	8	100	5.7
	12.8	8	110	5.4	8	114	4.0	8	113	4.3
<i>trans</i> -1,3-Dichloropropene	0.4	8	64	9.7	8	147	5.9	8	76	22
	1.4	10	93	6.9	8	113	8.0	8	94	4.7
	7.2	8	105	7.0	8	109	8.5	8	108	4.6

Table 5.—*Precision, recovery, and accuracy data in three matrices for selected volatile organic compounds in water samples—Continued*

Compound	Concentration (µg/L)	Reagent water			Surface water 1			Surface water 2		
		No. reps.	Average recovery (percent)	Relative standard deviation (percent)	No. reps.	Average recovery (percent)	Relative standard deviation (percent)	No. reps.	Average recovery (percent)	Relative standard deviation (percent)
1,2-Dichloropropane	0.5	8	108	5.7	8	120	12	8	101	5.8
	2.0	10	98	8.4	8	98	7.0	8	89	4.3
	10.0	8	100	4.7	8	99	4.4	8	101	4.8
1,3-Dichloropropane	0.5	8	100	12	8	99	14	8	91	9.1
	2.0	10	115	5.0	8	100	7.1	8	95	6.4
	10.0	8	97	2.5	8	97	4.1	8	103	2.6
2,2-Dichloropropane	0.5	8	72	4.8	8	110	13	8	87	7.4
	2.0	10	84	9.3	8	85	6.0	8	70	7.7
	10.0	8	82	3.8	8	90	6.0	8	85	8.0
Ethylbenzene	0.5	8	102	4.0	8	104	13	8	90	4.6
	2.0	10	110	2.7	8	92	5.8	8	92	4.3
	10.0	8	92	2.9	8	91	5.7	8	93	4.6
Hexachlorobutadiene	0.5	8	114	5.3	8	118	13	8	87	3.3
	2.0	10	116	3.1	8	79	6.3	8	80	5.5
	10.0	8	75	2.7	8	75	5.7	8	79	4.0
Isopropylbenzene	0.5	8	102	4.1	8	111	14	8	89	4.7
	2.0	10	108	2.7	8	87	7.0	8	91	3.6
	10.0	8	88	2.0	8	88	5.4	8	90	4.8
<i>p</i> -Isopropyltoluene	0.5	8	104	4.4	8	116	14	8	84	6.5
	2.0	10	107	2.7	8	85	4.8	8	80	5.5
	10.0	8	88	2.0	8	87	5.3	8	84	4.1
Methylene chloride	0.5	8	108	5.1	8	117	12	8	2146	14
	2.0	10	99	4.0	8	108	8.4	8	107	3.2
	10.0	8	111	5.9	8	108	6.8		117	6.2
Naphthalene	0.5	8	100	4.2	8	103	11	8	93	5.5
	2.0	10	107	7.2	8	102	7.9	8	91	10
	10.0	8	101	2.7	8	100	5.9	8	96	3.1
<i>n</i> -Propylbenzene	0.5	8	102	6.7	8	109	11	8	89	4.0
	2.0	10	106	3.6	8	90	4.8	8	90	5.8
	10.0	8	88	2.1	8	88	6.2	8	89	4.5
Styrene	0.5	8	92	7.8	8	98	12	8	93	5.0
	2.0	10	108	3.9	8	105	5.6	8	103	4.5
	10.0	8	99	1.8	8	98	3.5	8	97	4.8

Table 5.—Precision, recovery, and accuracy data in three matrices for selected volatile organic compounds in water samples--Continued

Compound	Concentration (µg/L)	Reagent water			Surface water 1			Surface water 2		
		No. reps.	Average recovery (percent)	Relative standard deviation (percent)	No. reps.	Average recovery (percent)	Relative standard deviation (percent)	No. reps.	Average recovery (percent)	Relative standard deviation (percent)
1,1,1,2-Tetrachloroethane	0.5	8	110	4.6	8	110	13	8	88	4.7
	2.0	10	115	3.1	8	88	7.0	8	86	4.4
	10.0	8	87	1.6	8	86	4.0	8	88	4.1
1,1,2,2-Tetrachloroethane	0.5	8	100	30	8	119	15	8	94	7.4
	2.0	10	113	6.1	8	90	7.3	8	85	3.9
	10.0	8	63	26	8	88	4.6	8	99	3.1
Toluene	0.5	8	114	4.5	8	106	11	8	108	4.4
	2.0	10	93	4.7	8	123	7.6	8	106	4.0
	10.0	8	104	4.9	8	106	4.0	8	116	3.8
1,2,3-Trichlorobenzene	0.5	8	110	2.9	8	117	13	8	105	5.1
	2.0	10	106	5.9	8	94	6.6	8	94	4.1
	10.0	8	84	3.1	8	83	3.6	8	92	3.1
1,2,4-Trichlorobenzene	0.5	8	100	6.6	8	113	9.9	8	97	5.7
	2.0	10	105	4.3	8	96	5.0	8	96	4.8
	10.0	8	90	2.9	8	89	3.3	8	89	3.0
1,1,1-Trichloroethane	0.5	8	108	3.1	8	112	12	8	94	3.4
	2.0	10	102	3.9	8	92	6.7	8	85	5.2
	10.0	8	99	4.6	8	97	3.5	8	95	5.0
1,1,2-Trichloroethane	0.5	8	116	13	8	100	20	8	117	12
	2.0	10	116	7.5	8	93	7.5	8	88	5.1
	10.0	8	91	3.9	8	92	6.4	8	94	6.7
Tetrachloroethene	0.5	8	108	2.9	8	116	12	8	98	4.5
	2.0	10	104	2.8	8	87	4.3	8	89	4.4
	10.0	8	78	2.0	8	78	4.8	8	88	3.6
Trichloroethene	0.5	8	129	12	8	117	13	8	97	4.4
	2.0	10	105	5.2	8	89	6.7	8	86	4.4
	10.0	8	115	15	8	95	3.6	8	90	3.0
Trichlorofluoromethane	0.5	8	92	6.2	8	118	51	8	128	32
	2.0	10	111	25	8	109	14	8	99	20
	10.0	8	115	25	8	154	20	8	100	13

Table 5.—Precision, recovery, and accuracy data in three matrices for selected volatile organic compounds in water samples—Continued

Compound	Concentration (µg/L)	Reagent water			Surface water 1			Surface water 2		
		No. reps.	Average recovery (percent)	Relative standard deviation (percent)	No. reps.	Average recovery (percent)	Relative standard deviation (percent)	No. reps.	Average recovery (percent)	Relative standard deviation (percent)
1,2,3-Trichloropropane	0.5	8	94	6.7	8	139	31	8	127	33
	2.0	10	140	14	8	92	14	8	90	20
	10.0	8	80	4.9	8	77	7.9	8	86	7.0
1,2,4-Trimethylbenzene	0.5	8	108	4.0	8	111	14	8	85	4.9
	2.0	10	111	3.4	8	86	5.3	8	84	5.8
	10.0	8	91	2.7	8	89	5.2	8	87	4.6
1,3,5-Trimethylbenzene	0.5	8	112	6.8	8	114	13	8	90	5.9
	2.0	10	113	2.3	8	85	5.1	8	84	5.3
	10.0	8	88	2.2	8	88	5.7	8	87	5.1
Vinyl chloride	0.5	8	98	6.2	8	117	16	8	110	5.9
	2.0	10	121	4.8	8	125	8.5	8	109	4.2
	10.0	8	99	6.7	8	102	5.5	8	119	7.1
Xylene, <i>meta</i> - and <i>para</i> - ^{3,4}	1.0	8	101	4.8	8	107	7.6	8	89	4.1
	4.0	10	108	3.3	8	93	5.0	8	92	4.7
	20.0	8	89	2.5	8	89	5.7	8	93	3.8
Xylene, <i>ortho</i> - ⁴	0.5	8	114	10	8	118	11	8	93	6.6
	2.0	10	109	2.8	8	92	6.0	8	92	4.6
	10.0	8	89	2.0	8	89	5.3	8	93	5.5

¹Chloroform present at 0.3 µg/L in surface water 2.²Methylene chloride present at 0.4 µg/L in surface water 2.³*Meta*- and *para*-xylene cannot be separated. Recoveries represent the sum of *meta*- and *para*-xylene.⁴Xylenes are reported as total xylenes (*meta*-, *para*-, and *ortho*-).

DISCUSSION OF RESULTS

Precision and accuracy were evaluated by analyzing eight to ten spiked replicates of organic-free reagent-water and two surface-water samples at concentrations of 0.5, 2.0, and 10.0 µg/L. Organic-free reagent water was prepared by boiling distilled water for 1 hour and purging with ultrahigh purity nitrogen gas for at least 1 hour. The samples of surface water were collected from Clear Creek, in Golden, Colorado, and Standley Lake, in Westminster, Colorado. The Clear Creek water was collected in glass carboys and stored in a refrigerator in the organic-sample-preparation laboratory. The Clear Creek water contained traces of methylene chloride and chloroform probably caused by laboratory contamination. The Standley Lake water was collected a few feet from the shore in 40-mL VOC vials with no headspace; the vials were stored in a refrigerator in the VOC laboratory. The Standley Lake water did not contain VOCs.

Method detection limits (MDLs) were determined using USEPA protocol in the Federal Register (U.S. Environmental Protection Agency, 1984, p. 198-199). Seven spiked organic-free reagent-water replicates were analyzed at 2.0 µg/L to determine an estimated MDL by multiplying the standard deviation by 2.998 (Student's *t*-value for 6 degrees of freedom).

Another set of seven spiked organic-free reagent-water replicates was analyzed at 0.5 µg/L. The standard deviation and variance (s^2) were calculated for each data set. The data sets were compared using the F-ratio, which was computed from the ratio of the larger variance (s^2_A) to the smaller variance (s^2_B). If $s^2_A/s^2_B < 3.05$, the pooled standard deviation was calculated according to the following equation:

$$s_{\text{pooled}} = [(6s^2_A + 6s^2_B)/12]^{1/2}$$

If $s_{\text{pooled}} > 3.05$, another set of seven spiked organic-free reagent-water replicates was analyzed at 0.2 µg/L. The F-ratio was applied again to the 0.5- and 0.2-µg/L data sets. If the F-ratio was still greater than 3.05, the MDL was reported as a concentration between the quantity and previous MDL, which permitted qualitative identification. If the F-ratio was less than 3.05, s_{pooled} was calculated. The final MDL was calculated by the following equation:

$$\text{MDL final} = 2.681 (s_{\text{pooled}})$$

where 2.681 is the Student's *t*-value, appropriate for a 99-percent confidence level and a standard deviation estimate with 12 degrees of freedom.

Method detection limits are compound and column dependent. Values ranged from 0.05 to 0.2 µg/L for all of the VOCs listed. DBCP (1,2-dibromo-3-chloropropane) has the highest MDL at 0.2 µg/L. A more sensitive but less specific method for analyzing halogenated organics in water samples involves a hexane extraction followed by electron-capture detection (USEPA Method 504). The MDL for DBCP using this method is 0.04 µg/L. The MDLs for each selected compound are listed in table 4.

The PT/GC/MS method for determining VOCs is valid for the analysis of drinking water and surface water. USEPA Method 524.2 (Eichelberger, 1988), which was established for drinking water, provides precision and recovery data. Since the NWQL receives samples of surface water and drinking water for VOC analysis, two surface-water samples were chosen for validating the NWQL method.

The precision and recovery data for the majority of the VOCs are within USEPA's recommendation in Method 524.2 (Eichelberger, 1988). The RSD is less than 10 percent, and the percent recovery is within 80 to 120 percent for most VOCs. Notable exceptions include DBCP, 2-chloroethyl vinyl ether (2CEVE), 1,1,2-trichloroethane, and trichlorofluoromethane (TCFM) at the lowest spiked concentration of 0.5 µg/L. The RSDs range from 20 percent for 1,1,2-trichloroethane to 86 percent for DBCP. Trichlorofluoromethane, a gas at room temperature, is particularly sensitive to operating conditions. If the temperature of the laboratory is greater than 25°C, some of the TCFM may be lost while loading the sample into the purge vessel. Oxygenated compounds generally are not purged efficiently from the aqueous matrix, especially at small concentrations. The percent recovery for 2CEVE was 27 percent with a RSD of 56 percent in the Standley Lake water samples. However, the reagent-water matrix showed a recovery of 82 percent with a 7.2 percent RSD. The precision and accuracy data represent single-operator/instrument conditions. Water samples of the seven replicates for each concentration were analyzed at the same time.

Nonselected compounds detected in samples can be tentatively identified by searching the National Institute for Standards and Technology (NIST) library which includes about 70,000 compounds. The computer searches for a compound with a similar mass spectrum and selects 5 to 10 of the most similar mass spectra. The analyst then reviews each mass spectrum and may assign a tentative identification to the compound. Positive identification cannot be assigned until a reference standard has been determined to confirm the mass spectrum and chromatographic retention time. The term "tentatively identified organic compounds" is preferred for referring to nonselected compounds identified by gas chromatography/mass spectrometry library search routines. All published reports that contain nonselected compound results need to include a disclaimer which is directly under the table heading for any tabulated results. The following disclaimer is an example:

Tentatively identified compounds are based on comparison with NIST library spectra and examination by GC/MS analysts. Reported concentrations are approximate.

The USEPA has updated Method 524.2 in Revision 4.0 to include several selected compounds not listed in table 4 (Eichelberger and others, 1992). The purge and trap instrumentation also has been updated to include an autosampler that will accept samples in 40-mL VOC vials, transfer the sample automatically to the ALS, and add the SURRIS solution.

CONCLUSIONS

This method is suitable for analysis of VOCs in samples of surface water and ground water. The results obtained from the precision, recovery, and accuracy fall within USEPA specifications. This technique is a highly sensitive and specific analytical tool for characterizing the volatile organic fraction of a whole-water sample. The method is rapid, precise, and reproducible, providing both quantitative and qualitative information.

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