Methods of Analysis by the U.S. Geological Survey National Water Quality Laboratory—Determination of 86 Volatile Organic Compounds in Water by Gas Chromatography/Mass Spectrometry, Including Detections Less Than Reporting Limits

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U.S. GEOLOGICAL SURVEY

Open-File Report 97-829

Denver, Colorado
1998

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CONVERSION FACTORS AND RELATED INFORMATION

Multiply	By	To Obtain
centimeter (cm)	3.94×10^{-1}	inch
kilopascal (kPa)	1.45×10^{-1}	pounds per square inch
meter (m)	3.94×10^{1}	inch
microliter (μL)	2.64×10^{-7}	gallon
micrometer (μm)	3.94×10^{-5}	inch
milligram (mg)	3.53×10^{-5}	ounce, avoirdupois
milliliter (mL)	2.64×10^{-4}	gallon
millimeter (mm)	3.94×10^{-2}	inch

Temperature can be converted from degree Celsius (°C) to degree Fahrenheit (°F) by using the following equation:

$$°F = 9/5\ (°C) + 32.$$

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

microgram per liter (μg/L)
microgram per milliliter (μg/mL)
milliliter per minute (mL/min)
nanogram per liter (ng/L)

Other abbreviations are as follows:

amu	atomic mass units
ASR	Analytical Services Request form
BFB	*p*-bromofluorobenzene
CAL	calibration standard
CAS	Chemical Abstracts Service
CCV	continuing calibration verification standard
COB	carryover blank
CSB	continuing set blank
eV	electron volt
GC	gas chromatograph
GC/MS	gas chromatography/mass spectrometry
ID	inside diameter
IDL	instrument detection limit
ISTD	internal standard
LOQ	limit of quantitation

LTMDL	long-term method detection limit
M	molarity (moles per liter)
MDL	method detection limit
MRL	method reporting limit
MS	mass spectrometer
m/z	mass-to-charge ratio
na	not applicable
NAWQA	National Water-Quality Assessment Program
nd	not determined
NDV	nondetection value
NIST	National Institute of Standards and Technology
NWQL	National Water Quality Laboratory
RSD	relative standard deviation
RT	retention time
s	second
SURRIS	surrogate/internal standard solution
TIOC	tentatively identified organic compound
USEPA	U.S. Environmental Protection Agency
USGS	U.S. Geological Survey
VBW	volatile-grade blank water
VOC	volatile organic compound
WATSTORE	Water Data Storage and Retrieval System

DEFINITIONS

Analyte — The substance being determined in an analysis.

Long-term method detection limit (LTMDL) — The minimum concentration of a substance that can be identified, measured, and reported with 99-percent confidence that the analyte concentration is greater than zero. The LTMDL is determined from replicate analyses of a known sample in a given matrix containing analyte. The LTMDL includes variability introduced by multiple instruments, multiple analysts, and multiple calibrations over an extended time.

Method detection limit (MDL) — The minimum concentration of a substance that can be identified, measured, and reported with 99-percent confidence that the analyte concentration is greater than zero. The MDL is determined by analyzing a sample in a given matrix containing analyte.

Method reporting limit (MRL) — The default "less-than" concentration reported when a compound is not detected using an analytical method.

Nondetection value (NDV) — The minimum concentration level for a substance not identified, measured, or confirmed with at least 99-percent confidence by an analytical method. A substance not identified, measured, or confirmed by an analytical method will be reported as <NDV. Under normal circumstances, the NDV for the substance is two times the LTMDL concentration for the method. An NDV is used as a specific type of MRL in this method.

METHODS OF ANALYSIS BY THE U.S. GEOLOGICAL SURVEY NATIONAL WATER QUALITY LABORATORY— DETERMINATION OF 86 VOLATILE ORGANIC COMPOUNDS IN WATER BY GAS CHROMATOGRAPHY/MASS SPECTROMETRY, INCLUDING DETECTIONS LESS THAN REPORTING LIMITS

By Brooke F. Connor, Donna L. Rose, Mary C. Noriega, Lucinda K. Murtagh, and Sonja R. Abney

ABSTRACT

This report presents precision and accuracy data for volatile organic compounds (VOCs) in the nanogram-per-liter range, including aromatic hydrocarbons, reformulated fuel components, and halogenated hydrocarbons using purge and trap capillary-column gas chromatography/mass spectrometry. One-hundred-four VOCs were initially tested. Of these, 86 are suitable for determination by this method. Selected data are provided for the 18 VOCs that were not included. This method also allows for the reporting of semiquantitative results for tentatively identified VOCs not included in the list of method compounds. Method detection limits, method performance data, preservation study results, and blank results are presented.

The authors describe a procedure for reporting low-concentration detections at less than the reporting limit. The nondetection value (NDV) is introduced as a statistically defined reporting limit designed to limit false positives and false negatives to less than 1 percent. Nondetections of method compounds are reported as "less than NDV." Positive detections measured at less than NDV are reported as estimated concentrations to alert the data user to decreased confidence in accurate quantitation. Instructions are provided for analysts to report data at less than the reporting limits. This method can support the use of either method reporting limits that censor detections at lower concentrations or the use of NDVs as reporting limits. The data-reporting strategy for providing analytical results at less than the reporting limit is a result of the increased need to identify the presence or absence of environmental contaminants in water samples at increasingly lower concentrations.

Long-term method detection limits (LTMDLs) for 86 selected compounds range from 0.013 to 2.452 micrograms per liter (µg/L) and differ from standard method detection limits (MDLs) in that the LTMDLs include the long-term variance of multiple instruments, multiple operators, and multiple calibrations over a longer time. For these reasons, LTMDLs are expected to be slightly higher than standard MDLs. Recoveries for all of the VOCs tested ranged from 36 (*tert*-butyl formate) to 155 percent (pentachlorobenzene). The majority of the compounds ranged from 85 to 115 percent recovery and had less than 5 percent relative standard deviation for concentrations spiked between 1 to 500 µg/L in volatile blank-, surface-, and ground-water samples. Recoveries

of 60 set spikes at low concentrations ranged from 70 to 114 percent (1,2,3-trimethylbenzene and acetone). Recovery data were collected over 6 months with multiple instruments, operators, and calibrations.

In this method, volatile organic compounds are extracted from a water sample by actively purging with helium. The VOCs are collected onto a sorbent trap, thermally desorbed, separated by a Megabore gas chromatographic capillary column, and finally determined by a full-scan quadrupole mass spectrometer. Compound identification is confirmed by the gas chromatographic retention time and by the resultant mass spectrum, typically identified by three unique ions. An unknown compound 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.

INTRODUCTION

Purge and trap capillary-column gas chromatography/mass spectrometry has been used since the 1980s to determine volatile organic compounds (VOCs). Initially, a packed gas chromatography (GC) column was used for determining VOCs in the U.S. Environmental Protection Agency's (USEPA) Method 624 (U.S. Environmental Protection Agency, 1984). Method 624 is suitable for determining VOCs in municipal and industrial discharges; it analyzes for 31 VOCs with method detection limits (MDLs) ranging from 1.6 to 7.2 µg/L for a 5-mL sample. In USEPA Method 524.2 (Munch, 1995), a fused-silica Megabore column technology is used for determining VOCs in drinking-water samples where a 30-m Megabore capillary column and 25-mL sample volume result in lower method reporting limits (MRLs) than those obtained with Method 624. MRLs using Method 524.2 range from 0.03 to 0.35 µg/L. Baseline separation of many isomers is also achieved with Method 524.2 and allows for the determination of 84 VOCs. Rose and Schroeder (1995) present data for 59 VOCs with reporting limits of 0.2 µg/L and above. One-hundred-four VOCs were tested for inclusion in this method, but 18 were deleted for performance or stability problems. VOCs detected that are not part of the 86 reported compounds for this method are reported semiquantitatively as "tentatively identified organic compounds."

The U.S. Geological Survey (USGS) National Water Quality Laboratory's (NWQL) method described in this report is similar to USEPA Method 524.2 (Munch, 1995) and the method described in Rose and Schroeder (1995). Minor improvements to instrument operating conditions include the following: additional compounds, quantitation ions that are different from those recommended in USEPA Method 524.2 because of interferences from the additional compounds, and a data-reporting strategy for measuring detected compounds extrapolated at less than the lowest calibration standard or measured at less than the reporting limit. This method supersedes Rose and Schroeder (1995).

The present method was developed to increase the number of VOCs considered from 59 (Rose and Schroeder, 1995) to 86 and to lower the reporting limits. The USGS National Water-Quality Assessment Program (NAWQA) requested that the NWQL develop methods that could detect and report concentrations without censoring detections at or less than the reporting limit. The NWQL developed three methods to determine pesticides, herbicides and VOCs in water at ultralow concentrations. In addition, NAWQA requested the inclusion of possibly important environmental contaminants, as follows: *tert*-butyl ethyl ether (ETBE) and *tert*-pentyl methyl ether (TAME), acrolein, acrylamide, acrylonitrile, *bis* (2-chloroethyl) ether, *bis* (2-chloroethyl) sulfide, *bis* (chloromethyl) ether, vinyl bromide, chloromethyl-methyl ether, 1,4-dioxane, formaldehyde, hexachlorocyclopentadiene, hexachloroethane, and pentachlorobenzene.

The basic method was implemented at the NWQL in May 1988 but is updated herein to include additional compounds and lower reporting limits as of April 1996; it also includes the option for reporting concentrations at, or less than, the reporting limit. This NWQL method supplements other methods of the USGS for determination of organic substances in water that are described by Wershaw and others (1987), Zaugg and others (1995), and Werner and others (1996).

ANALYTICAL METHOD
Organic Compounds and Parameter Codes: Volatile organic compounds, whole water, gas chromatography/mass spectrometry, purge and trap, O-4127-96 (see table 1)

1. Scope and application

This method is suitable for determining 86 purgeable VOCs in water samples at nanogram-per-liter concentrations. All 104 VOCs tested are listed alphabetically in table 1, with footnotes for the 18 compounds that are deleted from this method. Available data for all 104 compounds are included in this report. The method is applicable to surface- or ground-water samples. Other water types such as wastewater and storm runoff may introduce interferences and method-performance problems. The method detection limit and the linear range of measurement are both dependent on the chemical characteristics of the compound and the ability of the analytical technique to detect and measure the compound. The major difference between this method and similar ones is that this method includes additional compounds and outlines a statistically defined data-reporting strategy for detections extrapolated at less than the lowest calibration standard or less than the reporting limit. These data are derived from an expanded concept of MDL determination. Long-term method detection limits (LTMDLs), similar to, but including more variability than the standard USEPA MDL definition, range from 0.013 to 2.452 µg/L for 86 VOCs. The linear calibration range for most of the compounds in undiluted samples is 0.1 to 20 µg/L. Some compounds, especially oxygenated compounds, are calibrated at higher concentrations, ranging from 0.2 to 200 µg/L (see table 3 in section 7). Samples containing VOC concentrations outside of the calibration range need to be diluted or results qualified accordingly.

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 into a Megabore capillary gas chromatography column interfaced to a mass spectrometer system.

2.2 Selected compounds are identified by using strict qualification criteria, which include analyzing standard reference materials and comparing retention times and relative ratios of the mass spectra. Tentatively identified compounds are compared to spectra in the National Institute of Standards and Technology (NIST) libraries.

2.3 Compounds are quantitated using internal standard procedures. Quantitation that is extrapolated less than the lowest calibration standard is qualified as "estimated" to signify the lower confidence in the extrapolated concentration. Compounds are not quantitated if they do not strictly adhere to qualification criteria.

Table 1.—*Purgeable volatile organic compounds tested for precision and accuracy in this method, including compounds subsequently deleted from the method for poor performance. Five compounds are reported as "estimated" anytime they are detected because of excessive standard deviations. Compounds numbered 1 through 86 refer to the compounds retained throughout this method and are similarly numbered in subsequent tables*

[CAS, Chemical Abstracts Service; WATSTORE, Water Data Storage and Retrieval System; na, not applicable. Proposed compounds requested by the National Water-Quality Assessment Program for possible inclusion are set in boldface]

	Compound	CAS number	WATSTORE code	Deleted or estimated compounds (see footnotes)
1	Acetone	67-64-1	81552	
2	**Acrolein**	107-02-8	34210	Estimated
	Acrylamide	79-06-1	na	Deleted,1
3	**Acrylonitrile** (2-Propenitrile)	107-13-1	34215	
4	Benzene	71-43-2	34030	
5	Bromobenzene	108-86-1	81555	
6	Bromochloromethane	74-97-5	77297	
7	Bromodichloromethane	75-27-4	32101	
8	Bromoform (Tribromomethane)	75-25-2	32104	
9	Bromomethane	74-83-9	34413	Estimated
10	2-Butanone (Methyl ethyl ketone)	78-93-3	81595	
11	*n*-Butylbenzene	104-51-8	77342	
12	*sec*-Butylbenzene	135-98-8	77350	
13	*tert*-Butylbenzene	98-06-6	77353	
14	***tert*-Butyl ethyl ether** (ETBE)	637-92-3	50004	
	tert-Butyl formate	762-75-4	49992	Deleted,2
15	*tert*-Butyl methyl ether (MTBE)	1634-04-4	78032	
16	Carbon disulfide	75-15-0	77041	
	Chloroacetonitrile	107-14-2	na	Deleted,3
17	Chlorobenzene	108-90-7	34301	
	1-Chlorobutane	109-69-3	77923	Deleted,3
18	Chloroethane	75-00-3	34311	
	***bis* (2-Chloroethyl) ether**	111-44-4	34273	Deleted,3,4
	***bis* (2-Chloroethyl) sulfide** (mustard gas)	505-60-2	na	Deleted,5
19	Chloroform (Trichloromethane)	67-66-3	32106	
20	Chloromethane	74-87-3	34418	Estimated
	***bis* (Chloromethyl) ether**	542-88-1	na	Deleted,1
	Chloromethyl-methyl ether	107-60-2	na	Deleted,1
21	3-Chloropropene (Allyl chloride)	107-05-1	78109	
22	2-Chlorotoluene	95-49-8	77275	
23	4-Chlorotoluene	106-43-4	77277	
24	Dibromochloromethane	124-48-1	32105	
25	1,2-Dibromo-3-chloropropane (DBCP)	96-12-8	82625	
26	1,2-Dibromoethane (EDB)	106-93-4	77651	
27	Dibromomethane	74-95-3	30217	
28	1,2-Dichlorobenzene	95-50-1	34536	

Table 1.—*Purgeable volatile organic compounds tested for precision and accuracy in this method, including compounds subsequently deleted from the method for poor performance. Five compounds are reported as "estimated" anytime they are detected because of excessive standard deviations. Compounds numbered 1 through 86 refer to the compounds retained throughout this method and are similarly numbered in subsequent tables* — Continued

	Compound	CAS number	WATSTORE code	Deleted or estimated compounds (see footnotes)
29	1,3-Dichlorobenzene	541-73-1	34566	
30	1,4-Dichlorobenzene	106-46-7	34571	
31	*trans*-1,4-Dichloro-2-butene	110-57-6	73547	
32	Dichlorodifluoromethane (CFC 12)	75-71-8	34668	Estimated
33	1,1-Dichloroethane	75-34-3	34496	
34	1,2-Dichloroethane	107-06-2	32103	
35	1,1-Dichloroethene	75-35-4	34501	
36	*cis*-1,2-Dichloroethene	156-59-2	77093	
37	*trans*-1,2-Dichloroethene	156-60-5	34546	
38	1,2-Dichloropropane	78-87-5	34541	
39	1,3-Dichloropropane	142-28-9	77173	
40	2,2-Dichloropropane	594-20-7	77170	
	1,1-Dichloropropanone	513-88-2	80336	Deleted,3,4
41	1,1-Dichloropropene	563-58-6	77168	
42	*cis*-1,3-Dichloropropene	10061-01-5	34704	
43	*trans*-1,3-Dichloropropene	10061-02-6	34699	
44	Diethyl ether	60-29-7	81576	
45	Diisopropyl ether (DIPE)	108-20-3	81577	
	1,4-Dioxane	123-91-1	81582	Deleted,3
46	Ethylbenzene	100-41-4	34371	
47	Ethyl methacrylate	97-63-2	73570	
48	*o*-Ethyl toluene	611-14-3	77220	
	Formaldehyde	50-00-0	na	Deleted,1
49	Hexachlorobutadiene	87-68-3	39702	
	Hexachlorocyclopentadiene	77-47-4	na	Deleted,6
50	**Hexachloroethane**	67-72-1	34396	
51	2-Hexanone	591-78-6	77103	
52	Isopropylbenzene	98-82-8	77223	
53	*p*-Isopropyltoluene	99-87-6	77356	
54	Methyl acrylate	96-33-3	49991	
55	Methyl acrylonitrile	126-98-7	81593	
56	Methylene chloride (Dichloromethane)	75-09-2	34423	
57	Methyl iodide (Iodomethane)	74-88-4	77424	Estimated
58	Methyl methacrylate	80-62-6	81597	
59	4-Methyl-2-pentanone (MIBK)	108-10-1	78133	
60	Naphthalene	91-20-3	34696	
	Nitrobenzene	98-95-3	34447	Deleted,3
	2-Nitropropane	79-46-9	77076	Deleted,3
	Pentachlorobenzene	608-93-5	na	Deleted,6
	Pentachloroethane	76-01-7	81501	Deleted,7
61	***tert*-Pentyl methyl ether**, also known as *tert*-amyl methyl ether (TAME)	994-05-8	50005	
	Propionitrile	107-12-0	na	Deleted,3

Table 1.—*Purgeable volatile organic compounds tested for precision and accuracy in this method, including compounds subsequently deleted from the method for poor performance. Five compounds are reported as "estimated" anytime they are detected because of excessive standard deviations. Compounds numbered 1 through 86 refer to the compounds retained throughout this method and are similarly numbered in subsequent tables* — Continued

	Compound	CAS number	WATSTORE code	Deleted or estimated compounds (see footnotes)
62	*n*-Propylbenzene	103-65-1	77224	
63	Styrene	100-42-5	77128	
64	1,1,1,2-Tetrachloroethane	630-20-6	77562	
65	1,1,2,2-Tetrachloroethane	79-34-5	34516	
66	Tetrachloroethene	127-18-4	34475	
67	Tetrachloromethane (Carbon tetrachloride)	56-23-5	32102	
68	Tetrahydrofuran	109-99-9	81607	
69	1,2,3,4-Tetramethylbenzene	488-23-3	49999	
70	1,2,3,5-Tetramethylbenzene	527-53-7	50000	
71	Toluene (Methyl benzene)	108-88-3	34010	
72	1,2,3-Trichlorobenzene	87-61-6	77613	
73	1,2,4-Trichlorobenzene	120-82-1	34551	
74	1,1,1-Trichloroethane	71-55-6	34506	
75	1,1,2-Trichloroethane	79-00-5	34511	
76	Trichloroethene	79-01-6	39180	
77	Trichlorofluoromethane (CFC 11)	75-69-4	34488	
78	1,2,3-Trichloropropane	96-18-4	77443	
79	1,1,2-Trichloro-1,2,2-trifluoroethane	76-13-1	77652	
80	1,2,3-Trimethylbenzene	526-73-8	77221	
81	1,2,4-Trimethylbenzene	95-63-6	77222	
82	1,3,5-Trimethylbenzene	108-67-8	77226	
	Vinyl acetate	108-05-4	77057	Deleted,8
83	**Vinyl bromide** (Bromoethene)	593-60-2	50002	
84	Vinyl chloride (Chloroethene)	75-01-4	39175	
85	*meta*- and *para*-Xylene (Dimethyl benzene)	(*meta*-) 108-38-3 (*para*-)106-42-3	85795	
86	*ortho*-Xylene (Dimethyl benzene)	(*ortho*-) 95-47-6	77135	
	Surrogate standards			
	p-Bromofluorobenzene	460-00-4	99834	
	1,2-Dichloroethane *d*-4	na	99832	
	Toluene *d*-8	na	99833	

Deleted, 1: Not detectable by purge and trap.
Deleted, 2: Not stable at pH 2.0.
Deleted, 3: Poor purging efficiency and low response factor.
Deleted, 4: Co-elutes with another compound and has a similar ion.
Deleted, 5: Not stable for more than 40 minutes in water.
Deleted, 6: Semivolatile compounds — better analyzed by an extraction method.
Deleted, 7: Breaks down into chloroform and tetrachloroethene if not acidified properly.
Deleted, 8: Poor reproducibility over time (refer to table 11 in Appendix).

Compounds identified with concentrations within the calibration range are reported without qualification, unless quality control or holding times are compromised.

3. Interferences

Blanks — Strict quality control is required to maintain cleanliness at the sampling site and in the laboratory. Several types of blanks are used in this method to identify sources of contamination, including the test blank (section 11.2.1), set blank (section 11.2.2), continuing set blanks (section 11.2.3), carryover blanks (section 11.2.4), trip blanks, equipment blanks, field blanks, and source blanks. Multiple types of blanks are required because VOCs can enter samples in many different ways. Possible sources include exhaust fumes from vehicles, industrial stack emissions, and outgasing of solvents from carpets and upholstery inside the sampling vehicles, copier machines, paint, and cleaning solutions. Sampling equipment used at contaminated sites might contain residual contaminants if not cleaned properly. Equipment blanks are intended to provide quality control on this possible source of contamination. Preservation of samples with 1:1 hydrochloric acid:water can also introduce contaminants (sections 6 and 8.1.1). During sample preparation and analysis in the laboratory, samples can be contaminated by common extraction solvents like methylene chloride and acetone that are present in the laboratory atmosphere. In addition, samples might become contaminated with refrigerants, such as dichlorodifluoromethane and trichlorofluoromethane, if the refrigerator used to store the samples is leaking those compounds. Blank detections are discussed in section 14.

Carryover — Since this method allows reporting of any appropriately detected compound, care must be taken to ensure that the results reported are true environmental detections. Carryover contamination can confuse interpretation when a clean sample is analyzed after a contaminated sample. Samples containing high concentrations of VOCs, greater than 10 to 20 µg/L, can contaminate the next analysis at detectable concentrations because of residual VOCs in the trap, purge vessel, or transfer lines, which were not eliminated during the routine bake procedure. Analysts should reanalyze subsequent samples suspected of being contaminated by carryover. If it is known that a given sample contains high concentrations of VOCs, the field-sampling personnel should note this on the Analytical Service Request (ASR) form. In the laboratory, analysts should separate contaminated samples from relatively clean samples. Analyst experience with each instrumental configuration will determine how much carryover of each compound one can expect from differing concentrations. Knowledge of carryover characteristics by instrument and by compound is necessary if this method is to be used with confidence. (See table 12 in the Appendix.)

Hydrogen sulfide — Hydrogen sulfide will interfere with the response of the mass spectrometer. It can also damage columns, traps, multipliers, and quadrapoles. If field personnel detect any odor of hydrogen sulfide (rotten eggs), they should note this clearly on the ASR to forewarn the analyst and prevent instrument downtime. Samples known to contain hydrogen sulfide are diluted at least one to four prior to analysis.

Foamy Samples — Foamy samples, especially wastewater treatment plant effluents and urban runoff samples, will plug the jet separator on the mass spectrometer. Sometimes even slightly foamy samples will interfere with the analysis by raising the baseline, decreasing instrument response, and shifting peak retention times, producing unreliable data. For this reason, all surface-water samples are checked for foaming prior to analysis.

Precautions — Take special care to eliminate all potential organic contaminants from the volatiles laboratory. Only wear clothing that has not been exposed to methylene chloride vapors. Dichlorodifluoromethane is not used to check for leaks in the mass spectrometer. Also, the analytical laboratory for volatiles should be located far from other laboratories where extractions using organic solvents (particularly methylene chloride) are conducted. To reduce the possibility of contaminating samples, laboratory solvents, with the exception of methanol, are stored outside the VOC laboratory. Moreover, VOC stock solutions are not stored near samples.

Acrolein — Use of a moisture-control module on the purge and trap concentrator will negatively affect the amount of acrolein detected using this method. All data for acrolein in this method were collected without a moisture-control module. Use of this type of device will significantly increase the method detection limit (MDL) and nondetection value (NDV) for acrolein.

4. Instrumentation

The instruments and the settings used are summarized in table 2.

- *Purge and trap unit*, Tekmar Model LSC 2000 or 3000 concentrator with a Tekmar Aquatek automatic vial autosampler or equivalent. The autosampler is equipped to hold 25 mL of sample. Suggested configurations follow:

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

2. *Purge pressure*, 138 kPa (20 lb/in^2).

3. *Dry purge*, 2 minutes.

4. *Valve temperature, LSC 2000*, 110°C.

5. *Transfer line, LSC 2000,* nickel, 1.59 x 10^{-1} cm ($^1/_{16}$ in.).

6. *Transfer line temperature,* LSC 2000, 110°C.

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

[GC/MS, gas chromatography/mass spectrometry; mL/min, milliliters per minute; °C, degrees Celsius; kPa, kilopascal; lb/in^2, 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]

Purge and trap configurations	
Purge cycle	11 minutes
Dry purge cycle	2 minutes
Carrier gas	Helium, 40-mL/min flow at 22°C
Desorb preheat temperature	245°C
Desorb temperature	250°C for 1 minute
Bake cycle	12 minutes at 260°C
Transfer line temperature to GC inlet	110°C
Six-port valve temperature	110°C
Purge pressure	138 kPa (20 lb/in^2)
Trap	VOCARB 3000
Gas chromatograph configurations	
Column	DB-624 75-m x 0.53-mm ID
Carrier gas	Helium, 15 mL/min flow at 22°C
GC/MS interface temperature	200°C
Mass spectrometer configurations	
Ionization mode	Electron impact, 70 eV
Scan range	45 to 300 amu, 41 to 300 after CO_2 elutes
Scan rate	1 scan/s
Source temperature	280°C
Bromofluorobenzene criteria	Meets USEPA specifications

7. *Desorb preheat temperature*, 245°C.

8. *Desorb temperature,* 250°C for 1 minute.

9. *Trap*, Supelco VOCARB 3000 or equivalent, 25-cm x 0.27-cm inside diameter (ID). Starting from the purge inlet, the trap contains 10 cm Carbopak B with 60/80 mesh, 6 cm Carboxen 1000 60/80 mesh, and 1 cm Carboxen 1001 60/80 mesh. Use silanized glass wool as a spacer at the trap inlet and outlet. A new trap needs to be conditioned in the bake cycle at 270°C for 60 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 mass spectrometer response, and a decrease in bromoform sensitivity.

10. *Bake time*,12 minutes at 260°C (maximum temperature is 270°C).

- *Gas chromatograph/mass spectrometer (GC/MS),* Hewlett-Packard model 5971 or 5972 mass selective detector, or equivalent, equipped with subambient GC oven-cooling capability, and a jet separator. Suggested gas chromatographic configurations follow:

1. *Column*, fused-silica Megabore, 75-m x 0.53-mm ID, 3.0-µm film thickness, J&W DB-624 or equivalent.

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

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

4. *GC oven temperature program*, initial temperature –20°C, hold 1 minute, then 20°C per minute to 20°C, program at 5°C/min to 160°C and hold at 160°C for 4 to 8 minutes to allow all selected compounds to elute. Allow the column to bake at 200°C for about 5 minutes before beginning the next injection.

5. *Interface between the gas chromatograph and the purge and trap* — Remove the injection port, and connect the LSC 2000 nickel transfer line directly to the Megabore column.

- *Mass spectrometer conditions*:

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

2. *Scan range,* 45 to 300 amu, until CO_2 elutes, then 41 to 300 amu.

3. *Scan rate*, 1 scan/s.

4. *Tune*, adjust the instrument to meet the *p*-bromofluorobenzene (BFB) performance criteria listed in table 4 in section 9.

5. Apparatus and equipment

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

Gas-tight syringes — ranging from 5 to 200 µL for standard solution and field spike preparation.

Volumetric flask —10, 50, 100 or 250 mL, baked at 105°C for at least 15 minutes.

Amber vials — 1 to 2 mL, to store working standard solutions. Cap with a Teflon-faced silicon septa hole cap.

Oven — capable of heating to 105°C.

Freezer — for storing standard solutions at –10°C or lower.

Refrigerator — for storing samples at about 4°C.

VOC vials — 40-mL amber hole-cap vials, Eagle-Picher or equivalent, precleaned, with Teflon-lined septa.

Teflon dropper bottles — 30-mL Teflon dropper bottle, Nalge or equivalent, with attached dropper cap, for hydrochloric acid dispensing.

Erlenmeyer flask — 4-L, Pyrex, Erlenmeyer flask for boiling volatile blank water.

Boiling stones — stored in 105°C oven until use.

Hot plate — for boiling volatile blank water.

Separatory funnel with Teflon stopcock — 2-L funnels for storing and dispensing volatile blank water.

Stainless steel purge line — 1.59×10^{-1} cm ($^{1}/_{16}$ in.), fitted with a stainless steel frit for purging volatile blank water continuously.

Ultrapure nitrogen — liquid and gas; liquid for subambient cooling for the GC column, gas for purging volatile blank water.

6. Reagents

Water, volatile-grade blank (VBW) — deionized or distilled in glass, boiled for 1 hour, cooled and purged with ultrapure grade nitrogen continuously, for a minimum of 1 hour. Prepare daily. Use this water for laboratory standards, spikes, blanks, instrument rinse water, and trip blanks. This water was previously referred to as volatile organic-free water.

Water, commercially purchased, VOC grade — The NWQL is testing a water that will serve as both pesticide-grade and volatile-grade blank water. Since it is difficult to find a consistent source of commercial water for both purposes, the laboratory is experimenting with a commercially available pesticide-grade blank water that is purged with ultrapure

nitrogen to remove trace volatiles before recapping and shipping. This grade water is used for equipment rinsing and field equipment blanks.

Methanol — distilled in glass, purge and trap grade, Burdick and Jackson or equivalent. Verify the quality of the methanol periodically and prior to standards preparation.

Hydrochloric acid — concentrated (37 percent), EM Science, Supra Pur, or equivalent, free of detectable VOCs.

Ascorbic acid — L-(+)-ascorbic acid powder, J.T. Baker or equivalent.

7. Standard solutions

Concentrated methanol solutions of the compounds of interest are used to prepare working standard solutions by spiking the appropriate quantities of the working solutions into VBW. Store all standard solutions in a freezer at –10°C or colder in 2-mL amber vials with minimum headspace. All standard solutions are stored separately from the samples. It is recommended to acidify all standards. Since a small number of VOCs degrade at low pH (acrolein, acrylonitrile, *tert*-butyl formate, and 2-chloroethyl vinyl ether), this method allows the option not to acidify samples and standards, if appropriate.

7.1 *Mass spectrometer performance evaluation standard solution* — *p*-Bromofluorobenzene (BFB), Supelco, USEPA or equivalent. Prepare a 25-µg/mL solution in methanol. Alternatively, mass spectrometer performance may be evaluated from the surrogate/internal standard solution (7.2) which includes BFB in the solution.

7.2 *Surrogate standard/internal standard solution (SURRIS)* — Fluorobenzene, 1,2-dichloroethane-d_4, toluene-d_8, and *p*-bromofluorobenzene, Supelco, USEPA, or equivalent. Prepare an intermediate solution at 10,000 µg/mL of each component in methanol from neat standards based on the density of the parent compound in 10 mL of methanol. Prepare working methanol solutions at appropriate concentrations so that the addition of 1 to 10 µL of this solution will provide 1.0 µg/L in a 25-mL water sample.

7.3 *Stock and intermediate calibration solutions and continuing calibration verification standards (CCVs)* — Concentrated stock solutions of individual compounds are combined to prepare intermediate calibration solutions. The composition and number of separate intermediate calibration solutions are determined by shelf-life limitations, compound class, or commercially available mixes. To prevent frequent remaking, maintain the standard solutions in several mixes to keep compounds with shorter expiration dates separate from more stable compounds. These intermediate calibration solutions are combined to create a working calibration standard solution containing all compounds of interest. Prepare or purchase stock and intermediate calibration solutions (generally at 2,000 µg/mL), in methanol or as methanol/water mixes. All calibration

solutions must be derived from a different source than the spike solutions (section 7.6) because the validity of the calibration is verified against the separate standard.

7.4 *Working calibration standard solutions* — Prepare a working calibration standard solution in ultrapure purge-and-trap grade methanol at concentrations suggested in table 3. Keep the working calibration standard solution concentrated enough so that only a small quantity of the solution is required to obtain even the most concentrated working standard in VBW. Keep the total quantity of methanol added at less than 160 µL per 40 mL of VBW to prevent solvent and/or water vapor from interfering with early eluting compounds. To prepare calibration standards, add appropriate microliter quantities of working calibration standard solutions to acidified VBW.

7.5 *Continuing calibration verification standard (CCV)* — CCVs are prepared from the same working standard solution as the calibration standards. CCV concentrations are recommended at 1.0 µg/L (where some compounds will be at higher concentrations because of higher concentrations in the working solutions). Alternatively, the CCV concentration might be varied during the analysis to collect quality-control information at different concentrations. The concentration of the first CCV in the analytical sequence must remain at 1.0 µg/L because the results of the first CCV are used to collect CCV statistical acceptance criteria. HCl preservation of CCVs is required if calibration standards and samples are preserved with HCl (see section 8.1.1).

7.6 *Spike stock solutions and intermediate spike solutions for set spikes, third-party check standards, field spikes, and nondetection value (NDV) check standards* — Concentrated stock solutions are combined to prepare intermediate spike solutions. These intermediate spike solutions, containing all compounds of interest, are combined to create solutions appropriate for preparing set spikes, third-party check standards, field spikes, and NDVs. Alternatively, a working solution may be purchased commercially, containing all compounds of interest at appropriate concentrations in a single solution.

The spike stock solutions must be prepared from different lots and preferably from a different vendor than the intermediate calibration solutions (section 7.3) because the validity of calibration is verified against this second source.

7.7 *Working spike solution* — Prepare a working spike solution in ultrapure purge-and-trap grade methanol at concentrations suggested in table 3. This solution is used to prepare the set spike (section 11.5), the nondetection value (NDV) check standard (section 11.6), and the third-party check standard (section 7.8). Add appropriate microliter quantities of the working spike solution to acidified VBW to prepare the set spike, the third-party check standard, and the NDV check standard.

Table 3.— *Suggested concentrations for working calibration standard solution, calibration ranges, and working spike solution*

[CAS, Chemical Abstracts Service; µg/mL, micrograms per milliliter; µg/L, micrograms per liter; NDV, nondetection value]

	Compound	CAS number	Concentration of working calibration standard solution (µg/mL)	Calibration range using working calibration standard (µg/L)	Concentration of working spike solution [1] (µg/mL)
1	Acetone	67-64-1	50	1 - 200	40
2	Acrolein	107-02-8	25	0.5 - 100	28
3	Acrylonitrile	107-13-1	20	0.4 - 80	24
4	Benzene	71-43-2	5	0.1 - 20	1.0
5	Bromobenzene	108-86-1	5	0.1 - 20	1.0
6	Bromochloromethane	74-97-5	5	0.1 - 20	1.0
7	Bromodichloromethane	75-27-4	5	0.1 - 20	1.0
8	Bromoform	75-25-2	5	0.1 - 20	2.0
9	Bromomethane	74-83-9	5	0.1 - 20	3.0
10	2-Butanone	78-93-3	50	1 - 200	33
11	*n*-Butylbenzene	104-51-8	5	0.1 - 20	3.8
12	*sec*-Butylbenzene	135-98-8	5	0.1 - 20	1.0
13	*tert*-Butylbenzene	98-06-6	5	0.1 - 20	2.0
14	*tert*-Butyl ethyl ether	637-92-1	5	0.1 - 20	1.0
15	*tert*-Butyl methyl ether	1634-04-4	5	0.1 - 20	2.2
16	Carbon disulfide	75-15-0	5	0.1 - 20	1.6
17	Chlorobenzene	108-90-7	5	0.1 - 20	1.0
18	Chloroethane	75-00-3	5	0.1 - 20	2.4
19	Chloroform	67-66-3	5	0.1 - 20	1.0
20	Chloromethane	74-87-3	5	0.1 - 20	5.0
21	3-Chloropropene	107-05-1	5	0.1 - 20	1.8
22	2-Chlorotoluene	95-49-8	5	0.1 - 20	1.0
23	4-Chlorotoluene	106-43-4	5	0.1 - 20	1.2
24	Dibromochloromethane	124-48-1	5	0.1 - 20	3.6
25	1,2-Dibromo-3-chloropropane	96-12-8	5	0.1 - 20	4.2
26	1,2-Dibromoethane (EDB)	106-93-4	5	0.1 - 20	1.0
27	Dibromomethane	74-95-3	5	0.1 - 20	1.0
28	1,2-Dichlorobenzene	95-50-1	5	0.1 - 20	1.0
29	1,3-Dichlorobenzene	541-73-1	5	0.1 - 20	1.0
30	1,4-Dichlorobenzene	106-46-7	5	0.1 - 20	1.0
31	*trans*-1,4-Dichloro-2-butene	110-57-6	50	1 - 200	14
32	Dichlorodifluoromethane	75-71-8	5	0.1 - 20	2.0
33	1,1-Dichloroethane	75-34-3	5	0.1 - 20	1.4
34	1,2-Dichloroethane	107-06-2	5	0.1 - 20	2.6
35	1,1-Dichloroethene	75-35-4	5	0.1 - 20	1.0
36	*cis*-1,2-Dichloroethene	156-59-2	5	0.1 - 20	1.0
37	*trans*-1,2-Dichloroethene	156-60-5	5	0.1 - 20	1.0
38	1,2-Dichloropropane	78-87-5	5	0.1 - 20	1.4
39	1,3-Dichloropropane	142-28-9	5	0.1 - 20	2.4
40	2,2-Dichloropropane	594-20-7	5	0.1 - 20	1.6
41	1,1-Dichloropropene	563-58-6	5	0.1 - 20	1.0

Table 3.— *Suggested concentrations for working calibration standard solution, calibration ranges, and working spike solution* — Continued

	Compound	CAS number	Concentration of working calibration standard solution (µg/mL)	Calibration range using working calibration standard (µg/L)	Concentration of working spike solution [1] (µg/mL)
42	*cis*-1,3-Dichloropropene	10061-01-5	5	0.1 - 20	1.8
43	*trans*-1,3-Dichloropropene	10061-02-6	5	0.1 - 20	2.6
44	Diethyl ether	60-29-7	5	0.1 - 20	3.4
45	Diisopropyl ether	108-20-3	5	0.1 - 20	2.0
46	Ethylbenzene	100-41-4	5	0.1 - 20	1.0
47	Ethyl methacrylate	97-63-2	5	0.1 - 20	5.6
48	*o*-Ethyl toluene	611-14-3	5	0.1 - 20	2.0
49	Hexachlorobutadiene	87-68-3	5	0.1 - 20	2.8
50	Hexachloroethane	67-72-1	5	0.1 - 20	7.2
51	2-Hexanone	591-78-6	50	1 - 200	15
52	Isopropylbenzene	98-82-8	5	0.1 - 20	1.0
53	*p*-Isopropyltoluene	99-87-6	5	0.1 - 20	2.2
54	Methyl acrylate	96-33-3	10	0.2 - 40	12
55	Methyl acrylonitrile	126-98-7	10	0.2 - 40	11.5
56	Methylene chloride	75-09-2	5	0.1 - 20	7.6
57	Methyl iodide (Iodomethane)	74-88-4	5	0.1 - 20	1.6
58	Methyl methacrylate	80-62-6	10	0.2 - 40	7.0
59	4-Methyl-2-pentanone	108-10-1	50	1 - 200	7.4
60	Naphthalene	91-20-3	5	0.1 - 20	5.0
61	*tert*-Pentyl methyl ether	994-05-8	5	0.1 - 20	2.2
62	*n*-Propylbenzene	103-65-1	5	0.1 - 20	1.0
63	Styrene	100-42-5	5	0.1 - 20	1.0
64	1,1,1,2-Tetrachloroethane	630-20-6	5	0.1 - 20	1.0
65	1,1,2,2-Tetrachloroethane	79-34-5	5	0.1 - 20	2.6
66	Tetrachloroethene	127-18-4	5	0.1 - 20	2.2
67	Tetrachloromethane	56-23-5	5	0.1 - 20	1.8
68	Tetrahydrofuran	109-99-9	50	1 - 200	11.5
69	1,2,3,4-Tetramethylbenzene	488-23-3	5	0.1 - 20	4.6
70	1,2,3,5-Tetramethylbenzene	527-53-7	5	0.1 - 20	4.8
71	Toluene (Methyl benzene)	108-88-3	5	0.1 - 20	1.0
72	1,2,3-Trichlorobenzene	87-61-6	5	0.1 - 20	5.4
73	1,2,4-Trichlorobenzene	120-82-1	5	0.1 - 20	3.8
74	1,1,1-Trichloroethane	71-55-6	5	0.1 - 20	1.0
75	1,1,2-Trichloroethane	79-00-5	5	0.1 - 20	1.2
76	Trichloroethene	79-01-6	5	0.1 - 20	1.0
77	Trichlorofluoromethane	75-69-4	5	0.1 - 20	1.8
78	1,2,3-Trichloropropane	96-18-4	5	0.1 - 20	1.4
79	1,1,2-Trichloro-1,2,2-trifluoroethane	76-13-1	5	0.1 - 20	1.0
80	1,2,3-Trimethylbenzene	526-73-8	5	0.1 - 20	2.4
81	1,2,4-Trimethylbenzene	95-63-6	5	0.1 - 20	1.2
82	1,3,5-Trimethylbenzene	108-67-8	5	0.1 - 20	1.0
83	Vinyl bromide (Bromoethene)	593-60-2	5	0.1 - 20	2.0
84	Vinyl chloride (Chloroethene)	75-01-4	5	0.1 - 20	2.2

Table 3.— *Suggested concentrations for working calibration standard solution, calibration ranges, and working spike solution* — Continued

	Compound	CAS number	Concentration of working calibration standard solution (µg/mL)	Calibration range using working calibration standard (µg/L)	Concentration of working spike solution [1] (µg/mL)
85	*meta*- and *para*-Xylene	108-38-3 106-42-3	10	0.2 - 40	1.2
86	*ortho*-Xylene	95-47-6	5	0.1 - 20	1.2

[1] This solution will be prepared by an alternate vendor, or minimally obtained from a separate lot than that used for calibration standards. This solution will be used to prepare the set spike, the third-party check standard, the NDV check standard, and field spikes.

7.8 *Third-party check standard* — The working spike solution, prepared from different lot numbers than the calibration standards, can serve as a check of the calibration standard validity. This type of standard is referred to as the "third-party check." For this method, the set spike (section 11.5) serves the dual purpose of assessing method precision and accuracy, as well as checking calibration standard validity. Spike appropriate microliter quantities into acidified VBW.

7.9 *Nondetection value (NDV) check standard* — Prepare a low-concentration check standard by adding 2 µL of the set spike solution per 40 mL of acidified VBW. The NDV check standard may be replaced with a more concentrated check standard to verify the low end of the calibration curve.

7.10 *Volatile organic compound (VOC) solution holding times* — VOC solutions sealed in glass ampules may be stable for approximately 1 year. Once opened, the solutions are transferred to 1.8-mL amber screw-cap vials. Depending on the contents, solutions in 1.8-mL amber screw-cap vials may remain stable for months after opening. Any mixed solutions containing compounds that are gases at room temperature will generally be stable no more than 3 weeks in screw-cap vials, depending on the amount of headspace, the number of times opened, and compound volatility. Comparison of two solutions required in every analytical batch will confirm when solutions need to be remade. Prepare fresh working calibration standard solutions once every 3 to 5 weeks from intermediates as determined by CCVs, set spikes, or third-party checks, or more frequently if the calculated concentrations do not meet the criteria in paragraphs 11.3 or 11.5.1. A new concentrated solution of the gases in a sealed glass ampule is opened each time the working calibration standard solution is remade from intermediates. Vinyl acetate (subsequently deleted from this method) and acrolein are not stable in solution, so their concentrated stock solutions in screw-cap vials must be remade every 2 months.

8. Sample collection, blank collection, preservation, and storage

8.1 *Sample collection* — Sampling for VOCs requires special handling because samples easily can become contaminated if the protocol is not followed. Collect samples for VOC analysis in triplicate (ground-water samples) or quadruplicate (surface-water samples) in clean 40-mL borosilicate amber vials (VOC vials) with Teflon-faced silicone septa. Multiple vials are required because each sample may be subjected to multiple analyses (dilutions and reanalyses owing to quality-control failures, carryover problems), each of which consumes one entire vial. Surface-water samples require one additional vial more than ground water because one vial is used to test for foam before purging. Preserve the samples as described in section 8.1.1, if appropriate. 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 losses of VOCs, especially the more volatile compounds, such as dichlorodifluoromethane (Pankow, 1986).

8.1.1 *Sample preservation* — Preserve VOCs with a 1:1 solution of concentrated hydrochloric acid (HCl) until a pH of 2 is achieved. Use only NWQL quality-controlled hydrochloric acid:water solution (1:1 by volume) for sample preservation. Preservation studies have shown that HCl quality degrades with age and when stored in inappropriate containers. HCl that is improperly stored will result in detections of VOCs (chloromethane, chloroethane, hexafluoropropene, and 1,2-dichloroethane) in HCl preserved samples at concentrations large enough to be determined using this method. Store HCl in the dark, keep it cool, and store for no longer than 3 months in Teflon squeeze bottles. Dispense the acid from a Teflon squeeze bottle equipped with a dropper to a full VOC vial. Many water samples require several drops of the 1:1 HCl solution to achieve a pH of 2. To test how much HCl is required, collect an extra water sample in a spare 40-mL VOC vial, and add 1:1 HCl dropwise, until a pH of 2 is achieved. Discard this extra sample in an appropriate container and collect and preserve the replicate VOC samples using the determined number of drops of HCl. If samples are acidified, then similarly acidify field blanks or spikes. Do not acidify the trip blank. Do not add more than six drops of HCl to unbuffered samples such as blanks or field spikes. Less HCl will be required to lower the pH of an unbuffered sample. Moreover, excess acidity will damage the laboratory instruments. 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 adjust the sample to pH 2 according to USEPA Method 524.2 (Munch, 1995, p. 14).

8.1.2 *Shipping* — Store the samples at 4°C. Pack enough ice in each shipping container to ensure that the samples remain chilled throughout transit. Do not use dry ice for shipping volatiles. Wrap the VOC vials in bubble wrap to prevent breakage in transit.

8.1.3 *Labeling* — Do not wrap tape around the cap of the VOC vial because solvents in the glue can outgas and contaminate the sample with compounds such

as toluene, acetone, 2-butanone, and other common solvents. Tape also interferes with the autosampler's ability to pick-up sample vials, causing instrument failure. Use the labels that are supplied with the vials at the time of purchase and a ball-point pen for labeling. Other labels and inks may contaminate samples.

8.2 *Field Blanks*

8.2.1 *Field equipment blanks* — Prepare a field equipment blank when applicable. A field equipment blank goes through the same procedures as the samples. Use VOC-grade water (see section 6) for field equipment blanks, which is available at NWQL. 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. If the environmental samples are preserved with HCl, then acidify the field blank to pH 2 with the 1:1 HCl:H_2O solution. The field equipment blanks are useful for determining if the field equipment used to collect samples is a source of contamination.

8.2.2 *Trip blanks* — Trip blanks need to accompany the samples throughout the sampling and transit period. Purchase trip blanks from the NWQL. Do not acidify the trip blanks. Trip blanks are useful for determining sources of contamination caused by sampling and transportation.

8.2.3 *Source solution blank* — Prepare a source solution blank, if desired, from the same VOC-grade water used for rinsing equipment prior to obtaining the field equipment blank. The VOC-grade water is poured directly into two or three VOC vials and acidified. It does not go through any field equipment. This blank is not routinely required if field contamination is under control. Results of this blank indicate the quality of the VOC-grade water prior to equipment rinsing to differentiate between contaminants present in the water itself as opposed to contaminants present in the equipment.

8.3 *Field spike* — The same solution used by the laboratory for the set spike is used by personnel on site to spike field samples. The field and set spike solutions are identical so that matrix effects can be noted when comparing laboratory results with field spike results. Keep a stock of the last lot number on hand in case straggler field spikes are submitted after lot numbers have changed. Laboratory personnel must verify the lot number recorded on the ASR form to ensure that the correct solution is used in the laboratory set spike. Acidify the field spike with NWQL supplied HCl stored in a Teflon squeeze bottle (see section 8.1.1). Field spikes should use the same quantity of 1:1 HCl as was required to achieve pH 2 in the unspiked sample. Spike 20 µL of the field spike solution into the acidified field sample using a 25-µL syringe. Prepare the field spikes in triplicate.

8.4 *Sample receipt and storage* — The laboratory stores samples for VOC analysis in the dark at 4°C and analyzes them within 14 days of collection. Ship samples

immediately to allow sufficient time at the laboratory for analysis. If samples are received that are more than 10 days old, every effort will be made to analyze them within 14 days of collection. Tables 14 and 15 in the Appendix provide results of holding-time tests for VOCs up to 56 days. The holding time may be extended beyond 14 days if data-quality objectives do not require analysis within 14 days.

9. Instrument performance

Mass spectrometer performance evaluation — Prior to analyzing the samples, determine if the instrument performance meets the *p*-bromofluorobenzene (BFB) criteria listed in table 4 by analyzing a set blank containing the SURRIS solution (section 7.2), or by analyzing a direct injection of a MS performance evaluation standard solution. Mass spectral peak-abundance averaging and background correction may be used to obtain a BFB spectrum for evaluation. If the mass spectrum for BFB fails to meet the criteria specified in table 4, retune or clean the mass spectrometer, and reanalyze BFB until the criteria are passed.

Gas chromatograph performance evaluation — The GC performance is evaluated by examining the variation of the selected compound response factors, relative to response factors obtained using a new chromatographic column and freshly prepared standard solutions. The NDV check standard is used to judge whether the instrument is sensitive enough to qualitatively identify compounds but is not used to accept or reject gas chromatographic performance. Several performance indicator compounds are known to link specific performance problems with indicator compound failure (section 11.4.1). Gas chromatographic performance is assessed using data obtained with the calibration standards or CCVs.

10. Calibration

10.1 *Initial calibration curve* — A minimum of three calibration standards defining the expected concentration range is required for each quantitated compound. Calibration standards are prepared in VBW to arrive at individual compound concentrations ranging from 0.1 to 20 µg/L (the concentrations of some compounds will range from 1.0 to 200 µg/L). Refer to table 3 for the suggested calibration range for each VOC. Acidification of the calibration standards in VBW is recommended. Note that less HCl will be required in VBW than in an environmental sample because VBW has little buffering capacity. Generally, one drop of 1:1 HCl is sufficient to achieve pH 2 in an unbuffered sample.

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

Table 4.—*Gas chromatograph/mass spectrometer evaluation using p-bromofluorobenzene*

[m/z, mass to charge ratio] Munch, 1995

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

to 20 percent. Use a higher order degree equation or a power curve if the RSD is greater than 20 percent. Check the standards for accuracy by requantitating the calibration standards used to create the calibration curve against the new calibration curve. Observed concentrations should be within ± 20 percent of the expected concentrations.

10.2 *Acceptance criteria for initial calibration curve* — The range of the calibration curve should be limited by its ability to produce reliable data. If a calibration standard compound is not within ± 20 percent of the expected value or if the RSD is greater than 20 percent, then shorten the range, perform maintenance, or prepare fresh working standard solutions.

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

$$RF = \frac{C_i \, A_c}{C_c \, A_i} \qquad (1)$$

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 used in these calculations are listed in table 5.

Table 5. — *Quantitation ions and secondary and tertiary ions for volatile organic compounds listed in order of chromatographic retention time*

[See section 4 and table 2 for operating conditions. Numbers to the left of the compound name refer to compound numbers listed in all other tables]

	Compound	Quantitation ion	Secondary qualifying ion	Tertiary qualifying ion	Retention time (minutes)
	Internal standards				
	Fluorobenzene	96	70	50	17.008
	Surrogate standards				
	1,2-Dichloroethane-d_4	65	67	102	16.384
	Toluene-d_8	98	100	70	20.578
	p-Bromofluorobenzene	95	174	176	27.337
	Selected compounds				
32	Dichlorodifluoromethane	85	87	50	4.904
20	Chloromethane	50	52	49	5.862
84	Vinyl chloride	62	64	60	6.374
9	Bromomethane	94	96	81	7.666
18	Chloroethane	64	66	49	8.065
83	Vinyl bromide	106	108	79	8.585
77	Trichlorofluoromethane	101	103	66	8.775
44	Diethyl ether	59	45	74	9.729
2	Acrolein	56	55	53	10.214
79	1,1,2-Trichloro-1,2,2-trifluoroethane	151	101	85	10.248
35	1,1-Dichloroethene	96	61	98	10.266
1	Acetone	43	58	42	10.630
57	Methyl iodide	142	127	141	10.664
16	Carbon disulfide	76	78	44	10.716
21	3-Chloropropene	76	49	78	11.288
56	Methylene chloride	84	49	51	11.652
15	*tert*-Butyl methyl ether	73	57	43	12.138
37	*trans*-1,2-Dichloroethene	96	61	98	12.190
3	Acrylonitrile	53	52	51	12.397
45	Diisopropyl ether	59	87	45	13.229
33	1,1-Dichloroethane	63	65	83	13.246
	Vinyl acetate	86	43	42	13.332
14	*tert*-Butyl ethyl ether	59	57	87	14.043
40	2,2-Dichloropropane	77	97	79	14.477
36	*cis*-1,2-Dichloroethene	96	61	98	14.564
10	2-Butanone	43	72	57	14.616
54	Methyl acrylate	55	85	58	14.753
	Propionitrile	54	51	52	14.962
6	Bromochloromethane	128	49	130	15.084
68	Tetrahydrofuran	72	71	42	15.084
55	Methyl acrylonitrile	67	52	66	15.153
19	Chloroform	83	85	47	15.240
	tert-Butyl formate	59	57	87	15.515

Table 5. — *Quantitation ions and secondary and tertiary ions for volatile organic compounds listed in order of chromatographic retention time* — Continued

	Compound	Quantitation ion	Secondary qualifying ion	Tertiary qualifying ion	Retention time (minutes)
74	1,1,1-Trichloroethane	97	99	61	15.552
67	Tetrachloromethane	117	119	84	15.829
41	1,1-Dichloropropene	75	110	77	15.916
	1-Chlorobutane	56	49	92	15.999
4	Benzene	78	77	50	16.349
61	*tert*-Pentyl methyl ether	73	55	87	16.522
34	1,2-Dichloroethane	62	64	100	16.557
76	Trichloroethene	95	130	97	17.787
38	1,2-Dichloropropane	63	65	76	18.411
58	Methyl methacrylate	69	99	100	18.567
	1,4-Dioxane	88	58	43	18.577
27	Dibromomethane	93	95	174	18.689
7	Bromodichloromethane	83	85	47	19.018
	2-Nitropropane	43	41	46	19.643
	Chloroacetonitrile	75	48	77	19.898
42	*cis*-1,3-Dichloropropene	110	75	49	20.028
59	4-Methyl-2-pentanone	58	85	43	20.387
	1,1-Dichloropropanone	63	83	43	20.575
71	Toluene	92	91	65	20.734
43	*trans*-1,3-Dichloropropene	110	75	49	21.444
47	Ethyl methacrylate	69	99	86	21.479
75	1,1,2-Trichloroethane	97	83	85	21.878
66	Tetrachloroethene	166	164	129	21.999
39	1,3-Dichloropropane	76	78	63	22.311
51	2-Hexanone	43	58	100	22.415
24	Dibromochloromethane	129	127	48	22.796
26	1,2-Dibromoethane	107	109	188	23.108
17	Chlorobenzene	112	114	77	24.287
46	Ethylbenzene	91	106	65	24.477
64	1,1,1,2-Tetrachloroethane	131	133	119	24.512
85	*meta*- and *para*-Xylene	91	106	65	24.789
86	*ortho*-Xylene	91	106	65	25.846
63	Styrene	104	103	78	25.916
8	Bromoform	173	171	175	26.470
52	Isopropylbenzene	105	120	77	26.800
5	Bromobenzene	156	77	158	27.718
65	1,1,2,2-Tetrachloroethane	83	85	60	27.822
62	*n*-Propylbenzene	120	91	65	27.909
78	1,2,3-Trichloropropane	110	112	99	27.961
31	*trans*-1,4-Dichloro-2-butene	75	53	88	27.995
22	2-Chlorotoluene	126	91	128	28.221
23	4-Chlorotoluene	126	91	128	28.550
82	1,3,5-Trimethylbenzene	105	120	91	28.429
48	*o*-Ethyl toluene	105	120	91	28.966
13	*tert*-Butylbenzene	91	51	77	29.278
	Pentachloroethane	167	165	130	29.457

Table 5. — *Quantitation ions and secondary and tertiary ions for volatile organic compounds listed in order of chromatographic retention time* — Continued

	Compound	Quantitation ion	Secondary qualifying ion	Tertiary qualifying ion	Retention time (minutes)
81	1,2,4-Trimethylbenzene	105	120	91	29.469
12	*sec*-Butylbenzene	105	134	91	29.902
	bis (2-Chloroethyl) ether	63	65	93	30.153
29	1,3-Dichlorobenzene	146	111	148	30.318
53	*p*-Isopropyltoluene	119	134	91	30.318
30	1,4-Dichlorobenzene	146	111	148	30.578
80	1,2,3-Trimethylbenzene	105	120	91	30.647
11	*n*-Butylbenzene	91	92	134	31.462
28	1,2-Dichlorobenzene	146	111	148	31.635
50	Hexachloroethane	201	166	203	32.172
70	1,2,3,5-Tetramethyl benzene	119	134	91	33.559
25	1,2-Dibromo-3-chloropropane	157	75	155	33.645
	Nitrobenzene	123	77	51	34.298
69	1,2,3,4-Tetramethyl benzene	119	134	91	34.512
73	1,2,4-Trichlorobenzene	180	182	145	35.430
	bis (2-Chloroethyl) sulfide	109	63	158	35.640
49	Hexachlorobutadiene	225	223	227	35.673
60	Naphthalene	128	63	75	35.950
72	1,2,3-Trichlorobenzene	180	182	145	36.453
	Hexachlorocyclopentadiene	203	167	237	37.728
	Pentachlorobenzene	250	180	215	42.030

11. Quality control

The following discussion represents the minimum quality-control practices established for this method. Perform the following practices as indicated.

11.1 *Analytical sequence* — Analyze samples in a consistent sequence. Table 6 lists the suggested analytical sequence for a 45-minute analysis. Always start the instrument with a test blank to prove the system is free of contaminants before beginning any sample analyses. The test blank is only a check and does not need to be analytically processed because this is not the blank used for quality control. After the instrument is shown to be free of contaminants, either begin a series of calibrants (section 1 of table 6) or analyze an NDV, a CCV, and a set spike to prove the existing calibration is accurate before starting the sample analysis (section 2 of table 6). Check the instrument tune using BFB against the criteria listed in table 4. Bracket each group of samples with a CCV, a carryover blank (COB), and a continuing set blank (CSB), repeating CCVs, COBs, and CSBs every 8 hours (as measured from the beginning of injection time to injection time, not to elution of BFB). Recheck the BFB criteria every 8 hours in the set blanks or other clean sample. Include carryover blanks after suspected highly contaminated samples. The

Table 6. Suggested analytical sequence, ensuring required quality-control samples are analyzed every 8 hours, based on a 45-minute analysis[1]

[The first section describes the injection sequence of the initial calibration curve. If an initial calibration curve is not required, start the sequence at section 2. hr:min, hours:minutes; µg/L, micrograms per liter; CAL, calibration standard; COB*, optional carryover blank depending on individual instrument performance; COB, carryover blank; NDV, nondetection value check standard; CCV, continuing calibration verification standard; CSB, continuing set blank]

Section 1.		***Section 2.***			
Time (hr:min)	Sample type	Time (hr:min)	Sample type	Time (hr:min)	Sample type
00:00	Test blank	00:00	Test blank	18:00	1.0 µg/L CCV
00:00	Set blank	00:00	0.05 µg/L NDV	18:45	COB*
00:45	0.1 µg/L CAL	00:45	1.0 µg/L CCV	19:30	CSB
01:30	0.2 µg/L CAL	01:30	0.5 µg/L set spike	20:15	sample
02:15	0.5 µg/L CAL	02:15	COB*	21:00	sample
03:00	1.0 µg/L CAL	03:00	Set blank	21:45	sample
03:45	2.0 µg/L CAL	03:45	sample	22:30	sample
04:30	5.0 µg/L CAL	04:30	sample	23:15	sample
05:15	COB*	05:15	sample	24:00	sample
06:00	10 µg/L CAL	06:00	sample	24:45	sample
06:45	COB*	06:45	sample	00:30	sample
07:30	20 µg/L CAL	07:30	sample	01:15	1.0 µg/L CCV
08:15	COB	08:15	sample	02:00	COB*
09:00	COB*	09:00	sample	02:45	CSB
To continue, go to section 2		09:45	1.0 µg/L CCV	03:30	sample
		10:30	COB*	04:15	sample
		11:15	CSB	05:00	sample
		12:00	sample	05:45	sample
		12:45	sample	06:30	sample
		13:30	sample	07:15	sample
		14:15	sample	08:00	sample
		15:00	sample	08:45	sample
		15:45	sample	09:30	1.0 µg/L CCV
		16:30	sample	10:15	COB*
		17:15	sample	11:00	CSB

[1]Actual round-trip analysis time from one injection to the next may vary depending on the column flow rates and the column itself, as much as 5 minutes shorter to 10 minutes longer. Sequence may vary with different equipment to minimize carryover as required.

actual number of COBs necessary to prevent carryover into adjacent samples is instrument dependent. Adjust the analytical sequence to minimize carryover by adding or deleting COBs as needed from the sequence. End the analytical sequence with a CCV, a COB (if necessary), and a CSB. If there are fewer samples than a full block (7 – 8 samples between CCVs), the analysis must still end with a CCV, a COB (if necessary), and a CSB, even if there was only one sample in the last block.

11.2 *Instrument blanks* — This method defines four types of laboratory blanks: (1) test blank, (2) set blank, (3) continuing set blank (CSB), and (4) carryover blank (COB). Refer to figure 1 for an example of a chromatogram from a typical blank. The five largest peaks shown are the internal standard and four surrogates. Additional peaks are produced when the analytical column breaks down. The baseline rises at 10 minutes because of water vapors eluting off the gas chromatographic column.

11.2.1 *Test blank* — Prior to beginning an analytical sequence, a blank is analyzed to ensure the instrument is operating properly. The data from this blank are used to verify that the instrument can be loaded and sample analysis started without sacrificing samples because of unacceptable background or instrument problems. Its purpose is to assess gross error in analysis.

11.2.2 *Set blank and acceptance criteria* — Set blanks are analyzed throughout the sequence (see table 6). The purpose of the set blank is to measure and record background concentrations of VOCs. Use VBW to prepare set blanks. Acidify set blanks if the calibration standards and CCVs are acidified. If unacceptable blanks are present, reanalyze the affected samples after determining the source of contamination.

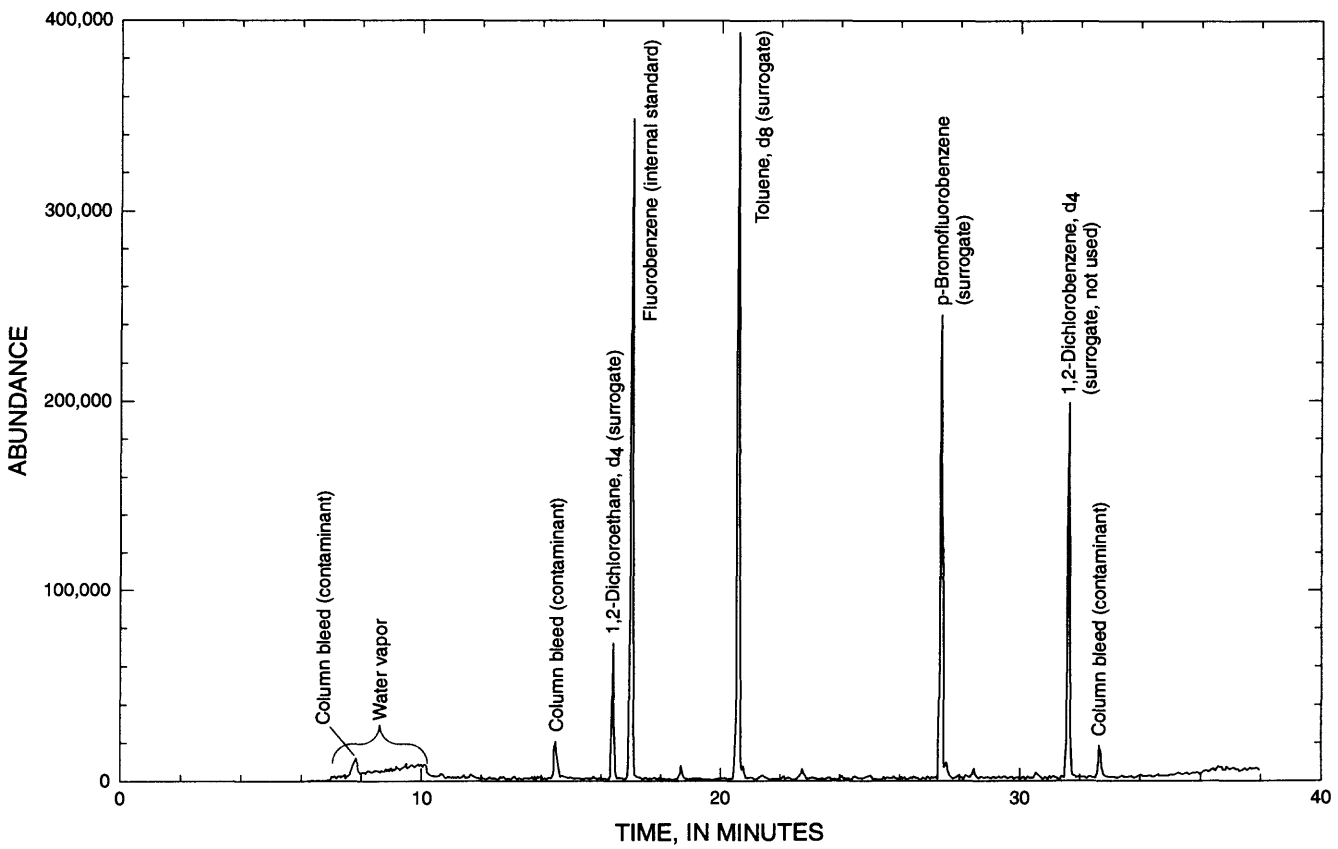

Figure 1.--Chromatogram of a typical set blank.

11.2.3 *Continuing set blanks and acceptance criteria* — Continuing set blanks (CSB) are analyzed periodically throughout the sequence (see table 6) to confirm the continued absence of contamination in the instrument and subsequent samples. CSBs are used to help distinguish between true low-concentration environmental contamination and blank contamination. Samples are bracketed by CSBs, and both bracketing CSB concentrations may be reported to the customer. If either of the bracketing CSBs has detections, then the associated sample detections are compared to the CSB. Corrective actions for detections in bracketing CSBs are described in section 14. CSBs are designed to measure system or laboratory contamination but not sample or standard contamination caused by carryover.

11.2.4 *Carryover blanks and acceptance criteria* — Carryover blanks (COBs) are analyzed after injections in which concentrations are known to produce carryover greater than the NDV or MRL. For an Aquatek 50 purge and trap autosampler with an LSC 2000 concentrator, a COB is necessary after the highest standard in each calibration curve and after any sample with compounds present at greater than 20 µg/L. The analytical sequence (table 6) describes where the COBs should be analyzed, but does not mandate how many are required to control carryover from one sample or standard to another. Carryover is instrument and operating-condition dependent. Additional COBs may be included in the analytical sequence to protect from spiked or highly contaminated samples. Refer to table 12 in the Appendix for average carryover concentrations after 1-µg/L CCVs and 20-µg/L calibration standards. The authors recommend that each laboratory attempting to use this method define the concentrations, by compound, at which carryover occurs. The laboratory should also define how many COBs are required to bring carryover concentrations down to an acceptable level. Some higher molecular weight compounds may take two or three COBs before carryover concentrations are acceptably low. There are no acceptance criteria for COBs themselves. COBs are designed to prevent carryover into quality-control or environmental samples. Include a sufficient number of COBs to ensure that carryover is limited to the COBs and not to subsequent samples.

11.3 *Continuing calibration verification (CCV) standard* — Analyze a CCV or a complete initial calibration curve prior to analyzing samples. To confirm that calibration is consistent, analyze additional CCVs no later than every twelfth injection, based on a maximum analytical time of 1 hour. See table 6 for placement of CCV standards. Samples must be bracketed by CCVs. Refer to figure 2 for a chromatogram of a CCV. Chromatograms are scaled to the tallest peak, including internal standards or surrogates.

11.3.1 *Determining acceptance criteria for CCVs* — Initial criteria (before a minimum of 30 CCVs is collected per instrument) for the CCV are ± 30 percent of the expected amount for all compounds. After 30 CCVs are collected on an instrument,

calculate ± 3 standard deviations of the mean to create statistical control limits, if applicable. Update these limits at least every 6 months or upon method modification. See table 11 in the Appendix for a summary of CCV data collected during method validation. Assuming the control limits define a 99-percent confidence interval around the mean recovery, and given that there are 86 compounds in this method, it is likely there will be at least one compound failing in the CCVs owing to statistical anomaly in each analysis that includes more than one CCV. Therefore, strict adherence to reanalyzing all samples associated with a few failed compounds in a CCV would necessitate reanalyzing samples more often than would be desirable. Nonideal VOCs (section 11.4) are exempt from CCV criteria. In addition, 5 percent of the remaining VOCs are allowed to fail the criteria of ± 3 standard deviations (four compounds out of the 86 in this method).

11.3.2 *Corrective action for failed CCVs* — If a CCV fails, prepare fresh standards, change the trap, or clean the instrument. Samples bracketed by a failed CCV on either side must be accounted for. However, if reanalysis is not practical because sample holding times will be missed, or an additional sample is not available, consider qualifying the associated sample compounds.

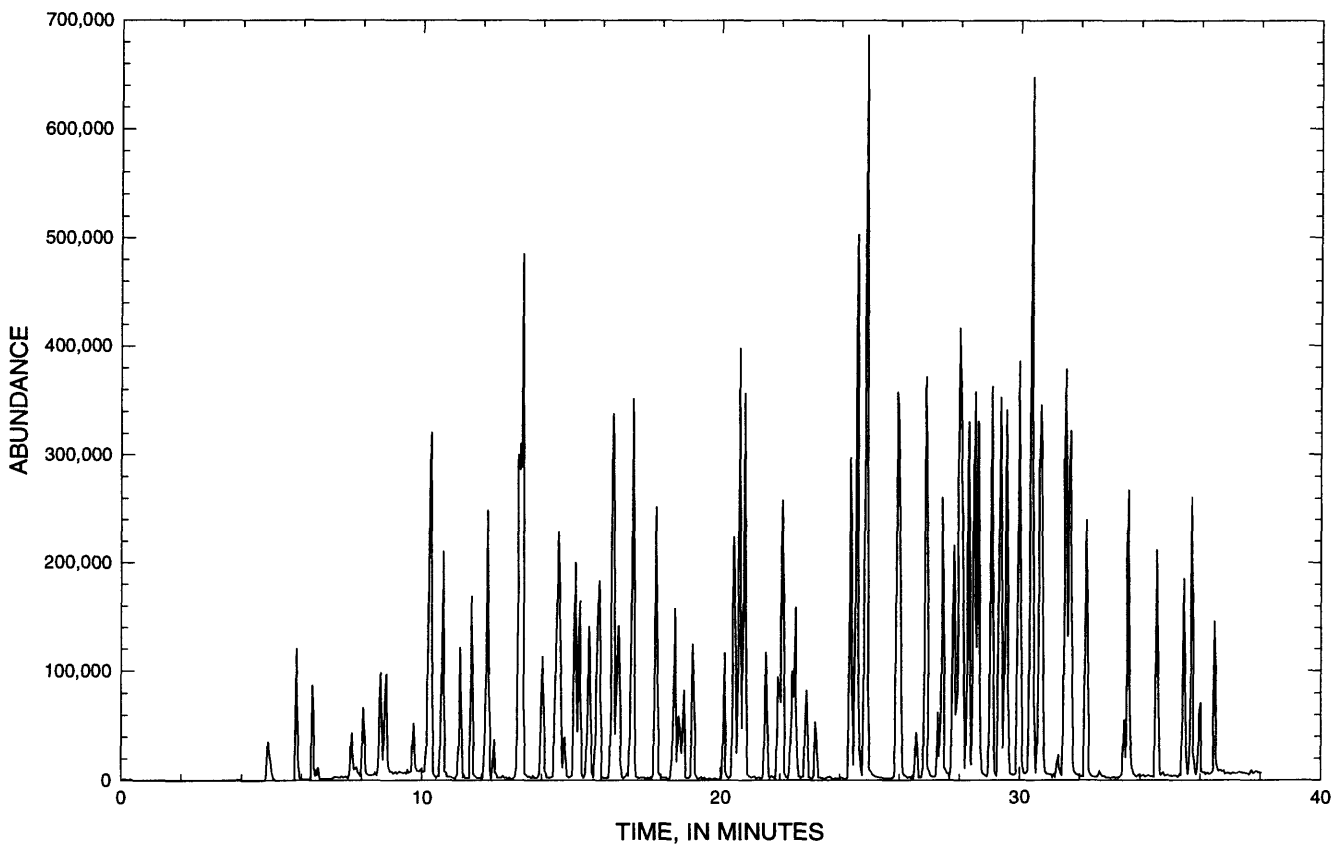

Figure 2.--Chromatogram of a continuing calibration verification standard at 1 microgram per liter.

11.4 *Nonideal volatile organic compounds in the continuing calibration verification standards* — Some compounds are not ideally suited to this method and so will fail quality-control criteria more frequently. Compounds with unusually high and low acceptance limits identify VOCs that exhibit large fluctuations in daily performance, including the compounds acrolein, bromomethane, chloromethane, methyl iodide, and dichlorodifluoromethane. Results for these compounds will include a data qualifier to signify the concentration is estimated. These compounds might be removed from non-ideal classification as the method progresses or as additional equipment changes method performance. Other nonideal VOCs might include the gases and more water soluble and less volatile compounds that are difficult to purge. These compounds might be qualified because of wide acceptance ranges for quality control compared to the other compounds.

11.4.1 *Performance indicator compounds* — Performance indicator compounds are sensitive to slight changes in analytical conditions and may fail. These compounds react more readily than others to specific deteriorating analytical conditions. For example, recoveries of bromomethane and methyl iodide decrease in the presence of hydrogen sulfide. If it is known that a sample contains hydrogen sulfide, the sample will be diluted at least one to four times to minimize analytical problems. Low recoveries for bromoform indicate active sites somewhere in the sample pathway, or a failing trap. Low recoveries for any of the gases indicate new standards need to be prepared. Service the instrument to achieve acceptable concentrations when the performance indicator compounds fail.

11.5 *Set spike* — The set spike is prepared from a source independent of the calibration standards, so it also serves as a third-party check of the calibration standards. The set spike is equivalent to the USEPA definition of the laboratory fortified blank. The set spike is used to assess overall method performance. See section 7.7 for preparation instructions and table 3 for appropriate concentration levels.

11.5.1 *Acceptance criteria for set spike* — Analyze the set spike once per analytical sequence. See table 6 for suggested analysis order. Calculate and report the percentage recovery for each compound. If the calculated result is not within ± 3 sigma of the mean of at least 10 or more previous set spikes, or ± 30 percent of the expected concentration when 10 set spikes are not available, consider preparing a fresh spike solution or new calibration standard, or service the instrument. Reanalyze samples associated with a failed set spike if appropriate. If reanalysis is not practical because sample holding times will be missed, or additional sample is not available, consider qualifying the associated sample compounds or preparing fresh spike solution and including a replacement spike somewhere in the analytical sequence. Follow the replacement spike with a COB to avoid carryover, if necessary.

11.6 *Nondetection value check standard* — This standard is used to determine if instrument sensitivity is sufficient to meet all identification criteria. Results for the NDV check standard are reported with the same qualification criteria as analytical samples, so that compounds that fail to meet minimum identification criteria are reported

as not detected even though the analyst knows the compound is present in the solution. This NDV check standard should fail to meet minimum identification criteria 1 percent of the time or less. Positive results are reported in micrograms per liter. There are no acceptance criteria for recovery of the NDV check standard, although analysts may interpret a failing NDV check standard to indicate instrument failure and may wish to reanalyze samples after maintenance. Keep in mind, however, that accumulated NDV check standards are used to update the calculated method detection limits.

11.7 *Internal standard areas* — Compare the area of the quantitation ion of the internal standard (ISTD) fluorobenzene in the first daily CCV (or average calibration standard ISTD areas) to the ISTD areas in the samples. The ISTD areas of the samples should be within ± 50 percent of the ISTD areas of the daily CCV (Munch, 1995, p. 17). Reanalyze samples with unacceptable internal standards after instrument maintenance, by replacing ISTD solutions or by correcting the source of the error.

11.8 *Surrogate recovery* — For each sample, spike, and blank, calculate the percentage recovery for each surrogate compound. The percentage recovery for each surrogate should be within ± 3 standard deviations of the mean of at least 10 set blanks and set spikes, or use 70 to 130 percent for the limits if statistical data are not available. Update the surrogate control limits every 6 months or upon major method modification. Reanalyze samples if all three sample surrogates are outside of the control limits. If the surrogates fail a second time, the sample matrix may be the cause; therefore, report the sample data along with the failed surrogate recovery concentration. If only some of the surrogates fail, first consider reanalyzing. If reanalysis is not possible, report the data and qualify associated method compounds, if appropriate.

12. Procedure for sample analysis

Determine which samples to include in the analysis. Oldest samples have priority. Analyze samples within 14 days of sampling to comply with USEPA sampling requirements. However, preservation studies and techniques using this method show that these VOCs are stable for much longer periods even at low concentrations (tables 14 and 15 in the Appendix).

12.1 *Field and trip blanks* — Place any known trip or field blank after an instrument blank if possible to avoid carryover effects.

12.2 *Surface-water samples* — Check all surface-water samples for foam. Remove about 5 mL from one of the extra vials, recap, and shake the sample to see if any foam is produced. If foam is produced, then dilute the sample according to how much foam is produced, and how long the foam persists. Usually a 1:2 or a 1:4 dilution is needed. Reporting limits are raised for all compounds, according to the dilution factor.

12.3 *Highly contaminated samples* — If samples are suspected of being highly contaminated with VOCs, analyze a diluted sample first, or follow the samples with COBs, or place the samples near the end of the analytical sequence, or all of the preceding, especially if compounds are present at 100 µg/L or greater. Samples containing greater than 100 µg/L of any one VOC can contaminate several subsequent samples and possibly the rest of the analysis sequence, depending on the concentration and the volatility of the compound(s) present. Reanalyze samples suspected of containing carryover VOCs. Samples containing suspected carryover detections, but quantitating at less than the NDV or MRL, will be reported as "less than NDV" or "less than MRL," or the result will be qualified as possible carryover, until a continuing set blank shows the contaminant as not detected. Samples containing known concentrations greater than 500 µg/L will not be analyzed full strength. Analyze all of the least contaminated samples first, followed by those more likely to create carryover or interference problems.

12.4 *Analytical sequence* — Follow the analytical sequence outlined in table 6. If the last block of samples bracketed by CCVs is fewer than 7 or 8, follow the last sample with a CCV, a COB (if necessary), and a CSB.

13. Identification and quantitation

13.1 *Qualitative identification* — 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.

Verify the mass spectrum for each selected compound by comparing the mass spectrum with a reference spectrum obtained from standards analyzed on the GC/MS system. For the compound to be considered detected, all qualification ions (table 5), including the quantitation ion, must be present in the expected ratios as based on in-house library ratios. Not all compounds have two qualification ions in addition to the quantitation ion. Carbon disulfide, naphthalene, and 1,2-dibromoethane each have only one qualification ion in addition to the quantitation ion. Given the current (1998) software, NWQL analysts have determined that a minimum of 500 area counts must be present to qualify a compound's presence for all qualification ions. This minimum area would likely change with different quantitation and integration parameters. The total ion chromatogram and the extracted ion peaks must be Gaussian in shape summed over a minimum width of 10 scans. The peak areas of none of the qualification ions may be less than two times the instrument noise. It is often beneficial to compare the extracted ion profiles 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. Refer to figure 3 for an example of a VOC passing the

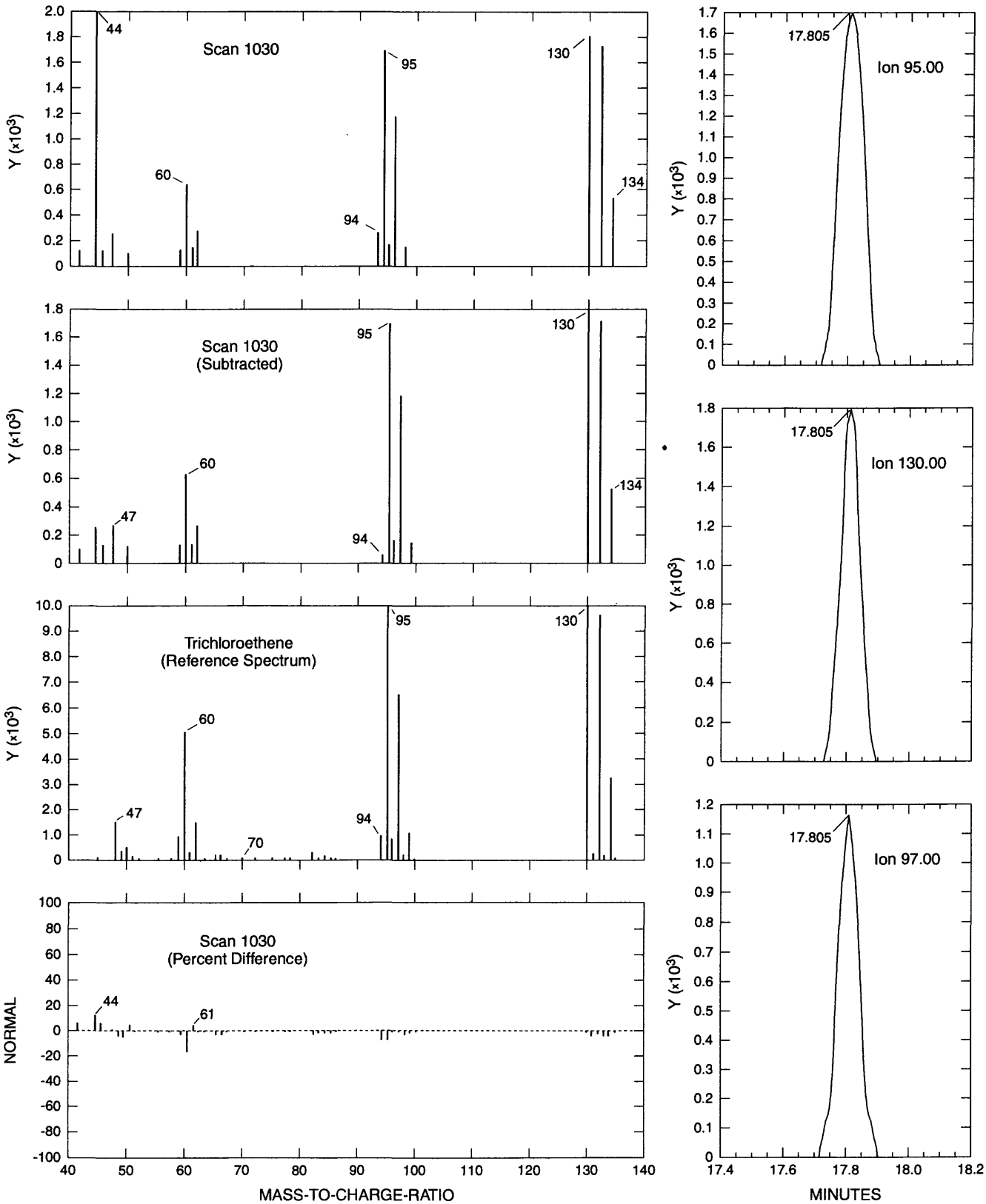

Figure 3.—Example of trichloroethene sample that passed all identification criteria, detected at an estimated concentration of 0.03 microgram per liter.

identification criteria, and to figure 4 for an example of a VOC not passing identification criteria.

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

$$C = \frac{C_i \, A_c}{RF \, A_i} \tag{2}$$

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 = response factor (section 10.4) for each selected compound or surrogate compound; and
A_i = area of the quantitation ion for the internal standard solution.

Percent recovery of the surrogate compound is calculated as follows:

$$\%\ recovery = \frac{C_i \, A_c}{RF \, A_i \, C_s} \times 100 \tag{3}$$

where $\%\ recovery$ = 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 = response factor (section 10.4) 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.

14. Reporting of results

This method is intended to prevent the censoring of positive VOC detections at low concentrations. Any positively identified compound may be reported, but the concentration uncertainty increases as the concentration is extrapolated further from the

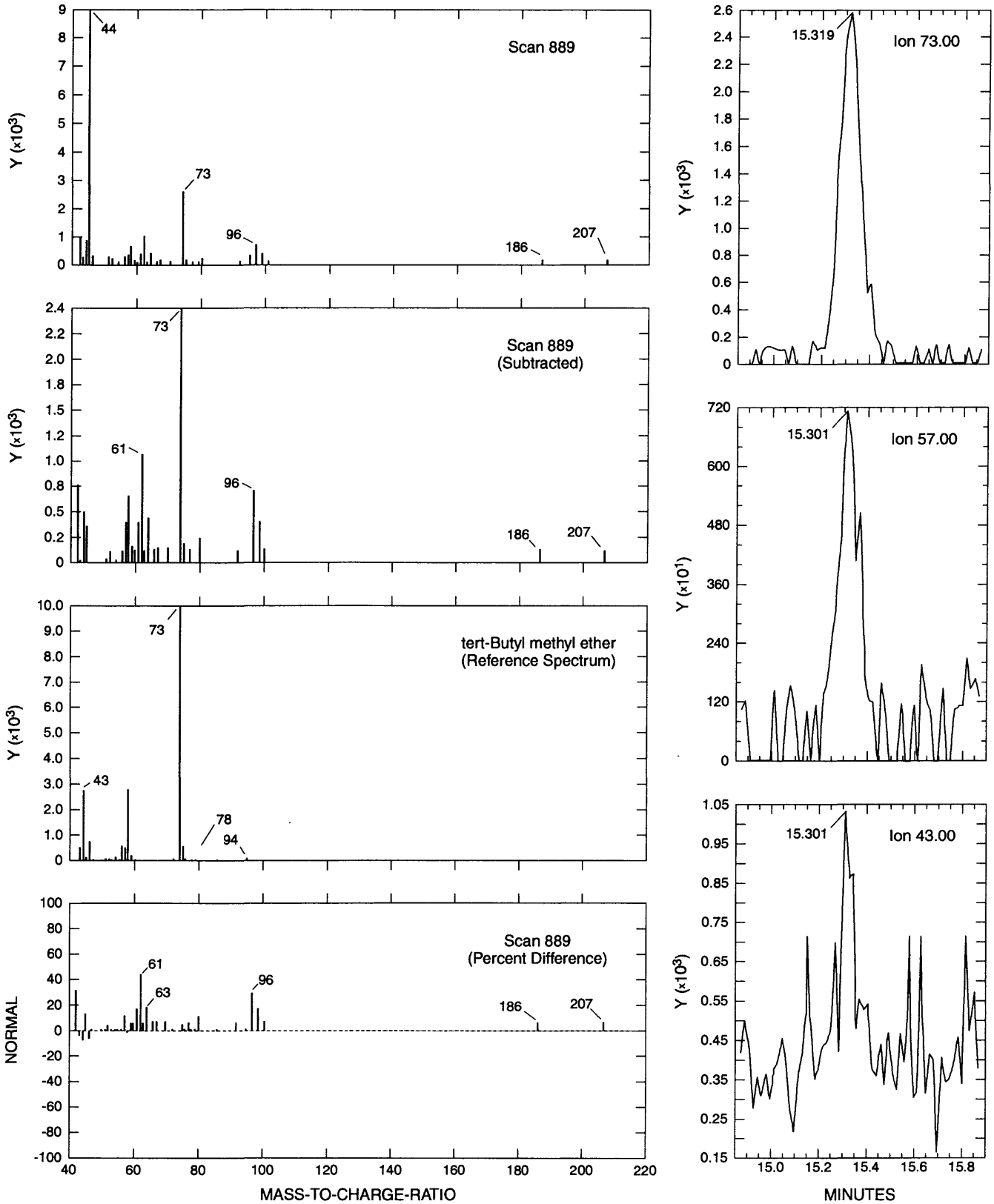

Figure 4.--Example of volatile organic compound that does not pass qualitative identification criteria.

lowest calibration standard. There are four ways to convey quantitative information using this method given the current (1998) software. The NWQL (1) reports the concentration as found if the measurement is within the calibration range, (2) dilutes the contaminated sample to within the calibration concentration range, (3) estimates the concentration if the measurement is less than the lowest calibration standard or less than the nondetection value, or (4) chooses to censor detections at less than the reporting limit. Censoring detections at less than the reporting limit is the normal operating procedure for analytical laboratories, and the result returned on these data is "less than the method reporting limit." The method reporting limit (MRL) is the typical broad-spectrum analytical tool for stating nondetection of a compound.

The analytical result may be reported by the NWQL as "less than NDV" when a compound is not detected. The NDV does not attempt to provide a conservative buffer for difficult matrices. The NDV is statistically defined for each compound so that it limits the chance of false positives and false negatives to less than 1 percent each. NDV check standards are used by NWQL to ensure detection at the NDV concentrations. The following discussion outlines the basic rules for data reporting.

14.1 *Not detected* — If a compound fails the qualification criteria, report the concentration as "less than NDV" or "less than MRL." Compounds detected that are equivalent in concentration to the surrounding blanks are considered "not detected" (see section 14.3). The analyst will annotate the data packet when sample results have been censored because of blank contribution.

14.2 *Detected in the sample, but not in the blanks* — If the qualification criteria are met and the quantity detected and measured is greater than the lowest calibration standard, report the concentration. Report data at less than the lowest calibration standard as "estimated" data.

14.3 *Detected in the sample and in at least one bracketing blank* — If the sample result is within five times any bracketing blank result, the analyst may either report the result as "<NDV" or "<MRL", reanalyze the sample, or determine with supporting data that the environmental measurement is not the result of background contamination.

14.4 *Dilutions, interferences, and raised reporting limits* — If a selected compound is present at a concentration greater than the highest calibration standard, dilute the sample so that the predicted concentration will be within the range of the current calibration curve. The reporting limits of the affected compounds may be raised according to the dilution factor. If a compound is known to be present at a high concentration, the sample may be diluted prior to the first analysis so that all results will be reported with raised reporting limits. This practice minimizes instrument contamination. Complex sample matrices also can cause interferences, resulting in a

raised reporting limit. A sample might contain an unknown compound with similar masses coeluting with a selected compound. A reporting limit can be raised when it is difficult to determine a compound because of the coelution. Also, as noted above, samples that foam when shaken will plug the jet separator and must be diluted before analysis, resulting in raised reporting limits for all compounds. Finally, as already discussed, the presence of hydrogen sulfide damages analytical instruments. As a result, samples with the characteristic odor of hydrogen sulfide should be diluted.

14.5 *Interpreting sample results on the basis of nondetection value check standard results* — NDV check standards are analyzed with every batch of samples, if appropriate. The NDV check standards are designed to assess daily instrument performance at the reporting limit. The ability to detect a spiked compound present in the NDV check standard is an important indicator of daily instrument performance; it is imperative to have this information for correctly interpreting environmental sample data. The reporting limits for sample results are not adjusted by the analysts when analysis of the daily NDV check standard yields nondetected compounds. The reason this reporting limit is not adjusted by analysts is two-fold. First, the NDV is a calculated concentration with a normal distribution. At this concentration, there is a slight (less than 1 percent) chance that any compound might fail to be detected. The second reason that analysts will not adjust NDVs is because there are no statistical data to support the concentration that the reporting limit should be raised to in any given matrix, or under any particular circumstances.

15. Calculation of the nondetection value

The calculation of the nondetection value (NDV) for uncensored data reporting is cumulative, each step defining the process required for the next. A suggested starting point first is to assess an instrument detection limit (IDL) for each compound on the least sensitive instruments. Each compound is then prepared in a solution at a concentration two to five times the IDL. This standard is analyzed at least seven times over several days to calculate the initial or short-term MDL. The concentrations of the compounds in the standard are increased if the resulting calculated MDLs using these standards are less than the IDLs. The results of long-term replicates of the adjusted (if necessary) standard, using multiple instruments, operators, and calibrations, are used to calculate the long-term MDL (LTMDL). The LTMDL data (approximately 3 sigma) are used to derive the NDV (approximately 6 sigma).

15.1 *Instrument detection limits* — An instrument detection limit (IDL) is defined as the lowest concentration of a given compound that an instrument is able to detect according to method-specific qualification criteria described in section 13. The standards used to determine the IDL do not go through any sample preparation steps. Standards are analyzed in stepwise dilutions, typically twofold, until the instrument fails to pass any qualification criterion (section 13.1) for any selected compound. The last concentration that passes all qualification criteria is the IDL. IDLs are specific for each

instrument and each compound. Use the IDLs to estimate the spiking concentration for the short-term MDL spike samples.

15.2 *Short-term method detection limits* — Once IDLs are determined for each compound, prepare a standard at two to five times the IDL of each individual compound in methanol. Short-term method detection limits (MDLs) are determined from seven replicate NDV check standards analyzed over 3 days using the USEPA protocol as described in the Federal Register (U.S. Environmental Protection Agency, 1992, p. 565 through 567). The MDL is referred to as a short-term MDL in this report to distinguish it from the LTMDL. These results are listed later in this section in table 7. Short-term MDLs are calculated as approximately three standard deviations of the mean recovery.

$$MDL = S\ t_{(n-1,\ 1-\alpha\ =\ 0.99)} \qquad (4)$$

where S = standard deviation of replicate analyses, in micrograms per liter;

n = number of replicate analyses; and

$t_{(n-1,\ 1-\alpha\ =\ 0.99)}$ = Student's t-value for the 99-percent confidence level with n-1 degrees of freedom. $t = 3.143$ for 7 replicates, 6 degrees of freedom (U.S. Environmental Protection Agency, 1992).

The Student's t defines a 1 percent chance of false positives (falsely stating presence when in truth the compound is not present). The MDL is then defined as the minimum concentration of a substance that can be identified, measured, and reported with 99 percent confidence that the compound concentration is greater than zero (U.S. Environmental Protection Agency, 1992). This short-term MDL is used to confirm an appropriate concentration for the standards used for the collection of long-term MDL (LTMDL) data. If this short-term MDL is less than the calculated IDL, the concentration in the standard was too low in the initial short-term MDL experiment. The concentration in the standard must be increased between two and five times, until the short-term MDL is equal to, or greater than, the calculated IDL.

15.3 *Long-term method detection limits* —The LTMDL is derived from at least 30 standards prepared at concentrations derived from the short-term MDL study described above. The LTMDL accounts for more analytical variation owing to multiple operators, instruments, and calibrations with a tendency to be higher in concentration than the USEPA short-term MDLs. The key to accurately determine the LTMDL is to include 30 or more standards in the calculation, so that enough data are collected to define the entire range of method performance. All data from these standards must be retained, including nondetections because of missing qualification data, to ensure proper determination of the standard deviation.

$$LTMDL = S\ t_{(n-1,\ 1-\alpha=0.99)} \qquad (5)$$

where S = standard deviation of replicate analyses, in micrograms per liter;

n = number of replicate analyses, greater than 30; and

$t_{(n-1,\ 1-\alpha\ =\ 0.99)}$ = Student's t-value for the 99-percent confidence level with n-1 degrees of freedom (U.S. Environmental Protection Agency, 1992).

15.4 *Determination of the nondetection value* — Once 30 or more standards for the LTMDL calculation are analyzed (using multiple instruments, operators, and calibrations), the analyst can determine an appropriate reporting limit for the method (table 7). Until this time, it is appropriate to use an MRL instead of an NDV for reporting nondetections. The temporary MRL should be at least two times the short-term MDL. The NDV, then, is two times the LTMDL, or approximately 6 sigma. Use this concentration as the "less-than" result on data for nondetection.

Additionally, once the proper concentrations for this standard are determined, this standard solution is named the NDV check standard. The results of the NDV check standard collected during use of this method provide data for updating the LTMDLs and reporting limits as needed.

If a compound fails qualitative identification criteria in any standard used for the compilation of MDL data, include zero as the data point in the calculation. If enough data points are collected (30 or more), then this anomaly will have little effect on the final MDL. If the nondetection is "ignored" by simply deleting the data point, the standard deviation will not reflect the inability of the instrument to occasionally detect at this concentration, and therefore the resultant MDL will be too low. The next time MDLs are updated, spike at a higher concentration to avoid frequent nondetections in the NDV check standard. Probability plot technique can be alternately used to handle situations where frequent nondetections occur, until a proper concentration for the NDV check standard is obtained.

Table 7. Method detection limits, method reporting limits, long-term method detection limits, and calculated nondetection values

[MDL, method detection limit; MRL, method reporting limit; LTMDL, long-term method detection limit calculated from 0.05 microgram-per-liter spikes (except where noted in parentheses); NDV, nondetection value; µg/L, micrograms per liter; nd, not determined]

U.S. Environmental Protection Agency (1992, p. 565–567)

	Compound	MDL[1] (µg/L) n=7	MRL[2] used from 4/96 to 5/97 (µg/L)	LTMDL[3] (µg/L) n=41	NDV[4] (µg/L) valid from 5/97 to 2/98
1	Acetone	(2.0) 1.205	5	(0.5) 2.452	4.904
2	Acrolein	(2.0) 0.504	2	(0.5) 0.716	1.432
	Acrylamide	nd	nd	nd	nd
3	Acrylonitrile [5] n=22	(1.6) 0.505	2	(2.0) 0.613	1.226
4	Benzene	.031	.05	.016	.032
5	Bromobenzene	.026	.05	.018	.036
6	Bromochloromethane	.061	.1	.022	.044
7	Bromodichloromethane	.049	.1	.024	.048
8	Bromoform	.052	.2	.052	.104
9	Bromomethane	.051	.1	.074	.148
10	2-Butanone	(2.0) 0.919	5.	(0.5) 0.825	1.65
11	*n*-Butylbenzene	.032	.05	.093	.186
12	*sec*-Butylbenzene	.027	.05	.024	.048
13	*tert*-Butylbenzene	.030	.05	.048	.096
14	*tert*-Butyl ethyl ether	.060	.1	.027	.054
	tert-Butyl formate	(0.4) 0.22	nd	nd	nd
15	*tert*-Butyl methyl ether	.072	.1	.056	.112
16	Carbon disulfide	.026	.05	.040	.080
	Chloroacetonitrile	(20) 7.50	nd	nd	nd
17	Chlorobenzene	.032	.05	.014	.028
	1-Chlorobutane	(0.8) 0.112	nd	nd	nd
18	Chloroethane	.052	.1	.060	.120
	bis (2-Chloroethyl) ether	(20) 7.55	nd	nd	nd
	bis (2-Chloroethyl) sulfide	not stable	nd	nd	nd
19	Chloroform	.029	.05	.026	.052
20	Chloromethane	.102	.2	.127	.254
	bis-Chloromethyl ether	nd	nd	nd	nd
	Chloromethyl-methyl ether	nd	nd	nd	nd
21	3-Chloropropene [5] n=22	.060	.1	(0.1) 0.098	.196
22	2-Chlorotoluene	.033	.05	.021	.042
23	4-Chlorotoluene	.029	.05	.028	.056
24	Dibromochloromethane	.050	.1	.091	.182
25	1,2-Dibromo-3-chloropropane[6]	.107	.5	nd	.214
26	1,2-Dibromoethane	.053	.1	.018	.036
27	Dibromomethane	.055	.1	.025	.050
28	1,2-Dichlorobenzene	.038	.05	.024	.048
29	1,3-Dichlorobenzene	.023	.05	.027	.054
30	1,4-Dichlorobenzene	.042	.05	.025	.050

Table 7. Method detection limits, method reporting limits, long-term method detection limits, and calculated nondetection values — Continued

	Compound	MDL[1] (µg/L) n=7	MRL[2] used from 4/96 to 5/97 (µg/L)	LTMDL[3] (µg/L) n=41	NDV[4] (µg/L) valid from 5/97 to 2/98
31	*trans*-1,4-Dichloro-2-butene	(2.0) 0.615	5	(0.5) 0.346	0.692
32	Dichlorodifluoromethane	.182	.2	.048	.096
33	1,1-Dichloroethane	.026	.05	.033	.066
34	1,2-Dichloroethane	.045	.05	.067	.134
35	1,1-Dichloroethene	.047	.1	.022	.044
36	*cis*-1,2-Dichloroethene	.036	.05	.019	.038
37	*trans*-1,2-Dichloroethene	.037	.05	.016	.032
38	1,2-Dichloropropane	.026	.05	.034	.068
39	1,3-Dichloropropane	.049	.05	.058	.116
40	2,2-Dichloropropane	.041	.05	.039	.078
	1,1-Dichloropropanone	(20) 11.4	nd	nd	nd
41	1,1-Dichloropropene	.028	.05	.013	.026
42	*cis*-1,3-Dichloropropene	.048	.1	.046	.092
43	*trans*-1,3-Dichloropropene	.072	.1	.067	.134
44	Diethyl ether[5] n=19	.078	.1	(0.05) 0.085	.170
45	Diisopropyl ether	.053	.1	.049	.098
	1,4-Dioxane	(20) 11.5	nd	nd	nd
46	Ethylbenzene	.024	.05	.015	.030
47	Ethyl methacrylate	(1) 0.378	.1	(0.25) 0.139	.278
48	2-Ethyl toluene	.028	.05	.050	.10
	Formaldehyde	nd	nd	nd	nd
49	Hexachlorobutadiene	.029	.2	.071	.142
	Hexachlorocyclopentadiene	(125) 52	nd	nd	nd
50	Hexachloroethane	.026	.05	.181	.362
51	2-Hexanone	(2.0) 0.800	5	(0.5) 0.373	.746
52	Isopropyl benzene	.026	.05	.016	.032
53	*p*-Isopropyltoluene	.032	.05	.055	.110
54	Methyl acrylate	(1.0) 0.322	2	(0.25) 0.306	.612
55	Methyl acrylonitrile	(1.0) 0.360	2	(0.25) 0.285	.570
56	Methylene chloride	.050	.1	.191	.382
57	Methyl iodide (iodomethane)	.035	.05	.038	.076
58	Methyl methacrylate	.417	1	(0.25) 0.175	.350
59	4-Methyl-2-pentanone	(2.0) 0.822	5	(0.5) 0.187	.374
60	Naphthalene	.069	.2	.125	.250
	Nitrobenzene	(100) 30.2	nd	nd	nd
	2-Nitropropane	(10) 4.54	nd	nd	nd
	Pentachlorobenzene	(250) 115	nd	nd	nd
	Pentachloroethane	.043	nd	nd	nd
61	*tert*-Pentyl methyl ether	.060	.1	.056	.112
	Propionitrile	(20) 4.88	nd	nd	nd
62	*n*-Propylbenzene	.030	.05	.021	.042
63	Styrene	.039	.05	.021	.042
64	1,1,1,2-Tetrachloroethane	.032	.05	.022	.044
65	1,1,2,2-Tetrachloroethane	.077	.1	.066	.132
66	Tetrachloroethene	.027	.05	.019	.038
67	Tetrachloromethane	.023	.05	.044	.088

Table 7. Method detection limits, method reporting limits, long-term method detection limits, and calculated nondetection values — Continued

	Compound	MDL[1] (µg/L) n=7	MRL[2] used from 4/96 to 5/97 (µg/L)	LTMDL[3] (µg/L) n=41	NDV[4] (µg/L) valid from 5/97 to 2/98
68	Tetrahydrofuran	(2.0) 1.028	5	(0.5) 0.574	1.148
69	1,2,3,4-Tetramethyl benzene	.044	.05	.115	.230
70	1,2,3,5-Tetramethyl benzene	.036	.05	.120	.240
71	Toluene	.027	.05	.019	.038
72	1,2,3-Trichlorobenzene	.054	.2	.133	.266
73	1,2,4-Trichlorobenzene	.060	.2	.094	.188
74	1,1,1-Trichloroethane	.032	.05	.016	.032
75	1,1,2-Trichloroethane	.055	.1	.032	.064
76	Trichloroethene	.028	.1	.019	.038
77	Trichlorofluoromethane	.044	.1	.046	.092
78	1,2,3-Trichloropropane	.075	.2	.035	.070
79	1,1,2-Trichloro-1,2,2-trifluoroethane	.035	.05	.016	.032
80	1,2,3-Trimethylbenzene	.036	.05	.062	.124
81	1,2,4-Trimethylbenzene	.039	.05	.028	.056
82	1,3,5-Trimethylbenzene	.026	.05	.022	.044
	Vinyl acetate[5] n=22	(4.0) 0.918	5	(0.5) 0.631	1.262
83	Vinyl bromide	.059	.1	.050	.100
84	Vinyl chloride	.057	.1	.056	.112
85	*meta-* and *para-*Xylene	(0.4) 0.041	.05	(0.1) 0.032	.064
86	*ortho-*Xylene	.027	.05	.032	.064

[1] U.S. Environmental Protection Agency (1992, p. 565–567). MDL calculated from seven individual spikes at 0.2 µg/L (except where noted in parenthesis), over a 3-day period. MDLs were determined independently on two instruments. The highest MDL was chosen.

[2] The MRL is approximately twice the MDL for most VOCs and was arbitrarily chosen. Some are higher than twice the MDL, depending on laboratory background, carryover contamination, and previous performance. Most were rounded to the nearest 0.05-, 0.1- or 0.2-µg/L increment.

[3] LTMDLs were determined from 41 samples over a 6-month period using daily standards spiked at 0.05 µg/L (except where noted in parenthesis) using multiple instruments, calibrations and operators. VOCs with "nd" in the LTMDL column were deleted from the method for various reasons (refer to table 1). VOCs with occasional nondetections in individual standards used zero as an estimated concentration.

[4] The NDV is calculated as twice the LTMDL. The NDV will be updated approximately yearly, and may result in different results over time and with new instrumentation. These values will be in use minimally from 5/97 through 2/98, unless otherwise indicated.

[5] The concentration in the spike solution changed during the collection of 41 spiked samples for these compounds. The alternate "n" for the more appropriate spike concentration is listed next to the compound name. The new concentration is noted in parenthesis with the LTMDL calculated for each concentration.

[6] 1,2-Dibromo-3-chloropropane (DBCP) was detected only once out of 41 injections at 0.05 µg/L. DBCP is in a commercial mix where other compound concentrations are appropriate, and therefore its concentration could not be increased.

INITIAL METHOD DEVELOPMENT

This method was developed to increase the number of volatile organic compounds (VOCs) determined from 59 (Rose and Schroeder, 1995) to 86. Initial method development efforts included adding the proposed compounds requested by NAWQA. These proposed compounds are set in boldface in table 1 but most were subsequently deleted from this method because they failed certain portions of the validation studies. Simultaneously, additional VOCs were being evaluated for inclusion in this method to remain current with USEPA methodology. Therefore, tables 1 through 15 list decreasing numbers because compounds failed and were dropped during method development. Compounds that are numbered in this report were retained throughout the method validation process (see compound numbers 1 through 86 in various tables).

Standards were prepared for each new compound and analyzed according to Rose and Schroeder (1995). Four compounds — acrylamide, *bis* (chloromethyl) ether, chloromethyl-methyl ether, and formaldehyde — were not detected at concentrations up to 500 µg/L in either acidified or unacidified standards. The compound *bis* (2-chloroethyl) sulfide, also known as mustard gas, was stable for only about 40 minutes in aqueous solution and was dropped from the method. The analysis was extended an additional 20 minutes to elute hexachlorocyclopentadiene and pentachlorobenzene. These two compounds were dropped from the method because they are semivolatiles and can be determined much more easily by an extraction method (Wershaw and others, 1987). Additionally, because these semivolatile compounds gave lower responses, it was necessary to spike them at higher concentrations than the VOCs in the standard mixes. The carryover resulting from these higher spike concentrations proved unacceptable in the creation of an acceptable calibration curve and in sample carryover contamination. MDLs (table 7) and limited precision data (see table 8 in Appendix) were collected for these two semivolatile compounds.

The next phase of method development included adding *tert*-butyl formate and diisopropyl ether (DIPE) to the prospective compound list. DIPE is a fuel oxygenate and *tert*-butyl formate is the major atmospheric oxidation by-product of *tert*-butyl methyl ether (MTBE), which was the second most frequently detected VOC in the NAWQA program in 1994 in urban wells (Squillace and others, 1995). MDLs (table 7) and precision and accuracy were determined in three matrices at two concentrations (see table 8 in Appendix). *tert*-Butyl formate was deleted from the method because it was not stable at pH 2. The erratic recoveries obtained for *tert*-butyl formate are listed in table 8 and become apparent with increasing time on the autosampler. DIPE was retained as a method compound.

After this round of method development, more compounds were eliminated from the method. 1,4-Dioxane and *bis* (2-chloroethyl) ether were eliminated because both compounds have low response factors and have to be spiked at high concentrations, resulting in carryover contamination. The compound *bis* (2-chloroethyl) ether coeluted

with an alkylated benzene and had similar ions, making it difficult to positively identify. Six compounds in USEPA's Method 524.2, Revision 4.1 (Munch, 1995) (chloroacetonitrile, 1-chlorobutane, 1,1-dichloropropanone, nitrobenzene, 2-nitropropane, and propionitrile) were excluded from this method because of performance problems. Pentachloroethane was eliminated because if the standards are not preserved, it breaks down into chloroform and tetrachloroethene, creating calibration errors for all three compounds. Initial method procedures did not require acid preservation of standards because HCl seemed to cause corrosion of the autosampler lines and valves. Attempts to minimize leaks from corrosion included analyzing unacidified standards and blanks even though environmental samples may be acidified. It was later decided to acidify all samples, standards, blanks and quality-control samples to alleviate other compound stability problems and to keep samples and standards analyzed under similar conditions. If the standards are preserved, pentachloroethane is not a problem. Performance data for pentachloroethane are included in the tables, but pentachloroethane is not included as a method compound because of previous problems.

Vinyl acetate was dropped from the method after summary data on CCVs showed that quality-control samples did not perform consistently (see table 11 in Appendix). The authors determined that vinyl acetate has intermittent performance problems and decided to delete it as a method compound.

METHOD PERFORMANCE

Quality control is important for reporting VOC concentrations at less than the NDV. For appropriate data interpretation, the data users must have additional information from the analysis that tells users how confident they should be about a reported concentration, especially one that is estimated by extrapolating at less than the calibration range. This information includes a positive identification of the compound, a level of certainty that the detected compound is not part of the "blank" population, that the instrument can positively detect compounds at the NDV, and that extrapolated quantitations are appropriately qualified.

One benefit of this method is that it can be used to provide reports of all detections regardless of concentration. However, positive identifications of VOCs are required before quantitative results are returned, including results for spikes and CCVs. Strict adherence to rules regarding signal-to-noise ratios, ion ratios, and retention times should help the analyst identify if an instrument is distinguishing between a true detection and a false positive. Over time, this detection capability is quantitated, resulting in the long-term method detection limit (LTMDL). The NDV as a reporting limit is based on the LTMDL, and is designed to account for more than 99 percent of the cases where daily detection capability fluctuations could potentially result in false negatives or false positives.

Additionally, these analyses are susceptible to background levels of many common VOCs, including laboratory air, exhaust fumes, photocopier chemicals, paints, and household cleaning products. When using this method to report detections at or less than the NDV, the analyst provides additional quality control to minimize false positives caused by contamination. Instrumental carryover from heavy molecular weight compounds and from high-concentration environmental samples is reduced by increasing the number of blanks and organizing the analytical sequence to separate clean samples from more contaminated samples. Laboratory background is minimized by carefully preparing VBW away from common laboratory solvents and keeping the VOC laboratory air isolated from other contaminated air sources.

Precision and accuracy estimates for this VOC method were evaluated by analyzing seven spiked replicates in VBW, surface water, and ground water at concentrations of 1 and 10 µg/L for most compounds (see table 8 in Appendix). The surface-water sample was collected from Bear Creek in Morrison, Colorado. The ground-water sample was collected from a private well in Conifer, Colorado. The water was collected in 1-L amber bottles and stored in the VOC refrigerator. Then, 40-mL vials were filled, adjusted to pH 2, spiked with the selected compound standard solution, and analyzed. Replicate spikes were analyzed on the same day. A sample of the unspiked matrix water was analyzed to determine if detectable VOCs were present. Analysis of the surface-water sample indicated that *tert*-butyl methyl ether (MTBE) was present at 0.43 µg/L, resulting in high recoveries (153 percent); however, when the concentration present in the creek was subtracted from the quantity spiked, the recovery of MTBE was 110 percent.

Additional precision data, not required for method validation but essential to understand how the lower concentration spikes performed, are provided from the accumulated set spike data (table 9 in Appendix) and the NDV check standards (table 10 in Appendix). These data are useful to show routine method performance since the individual data points were collected from several separate analytical sequences of up to 35 samples each over approximately 9 months.

Accumulated set spike data at 0.5 µg/L (and greater for compounds with lower instrument response) show excellent recoveries and low standard deviations (table 9 in Appendix). Recoveries ranged from 70 percent for 1,2,3-trimethylbenzene to 114 percent for acetone. Standard deviations were less than 20 percent for all but seven compounds — acetone, bromomethane, carbon disulfide, chloromethane, 1,2-dibromo-3-chloropropane, dichlorodifluoromethane, and vinyl chloride. All relative standard deviations were less than 26 percent.

The summary of 41 NDV check standards accumulated over approximately 6 months is listed in table 10 (see Appendix). These check standards provided the data for calculating an interim MRL used in this method. Most compounds were spiked at 0.05 µg/L or higher, depending on relative response. Some compounds were spiked at

inappropriate (too low) concentrations because NWQL did not have access to standard mixes with desired concentrations for all compounds. When the spike concentration was near or less than the MDL, the frequency of nondetections increased. For the purposes of estimating the most accurate LTMDL, these nondetections were treated as zero recovery, rather than decreasing "n" for the total results. Even at these low concentrations, the performance of this method is excellent for most compounds.

Summary data for 182 CCVs (acidified) collected over 6 months are listed in table 11 (see Appendix). The VOCs with RSDs greater than 20 percent in these tables were later identified as problem compounds and are estimated in data reports. These VOCs are acrolein, bromomethane, chloromethane, dichlorodifluoromethane, and methyl iodide. Other compounds may show greater RSDs under different analytical conditions and may be qualified in future data reports. "Estimated" is used as a data qualifier on these five compounds to alleviate the need for reanalyzing failed compounds when these compounds are more likely to fail with this method.

One VOC, vinyl acetate, had an RSD of 32 percent from 182 10-µg/L CCV standards. Vinyl acetate can exhibit erratic performance, ranging from 20 to 180 percent recovery in the CCVs. Vinyl acetate was deleted from the method as of May 1997. Since vinyl acetate was recovered with acceptable precision and accuracy for extended periods in the past, and because the authors are unsure of the cause of the intermittent poor performance, vinyl acetate may be analyzed using a custom method approach.

Carryover blank (COB) results were tabulated using the instrumentation described in section 4. The results of 62 COBs collected after 1-µg/L CCVs and 9 COBs collected after 20-µg/L calibration standards during method validation are listed in table 12 (see Appendix). These results are specific to the type of instruments used to collect the data. The most recurrent compounds found in COBs after the 1-µg/L CCV were methylene chloride, 1,4-dichlorobenzene, hexachlorobutadiene, naphthalene, 1,2,4-trichlorobenzene and 1,2,3-trichlorobenzene. All of these compounds except methylene chloride are semivolatile compounds, and probably carry over more frequently because of their decreased volatility. The least problematic compounds under these analytical conditions were volatile, low molecular weight compounds, or compounds with low response.

A limited preservation study was conducted to determine if the proposed compounds were compatible with hydrochloric acid preservation. Seven replicate spikes in VBW were prepared at pH 2 and 4 and analyzed on days 1, 7, and 14. The spike concentration for this limited study was 2 µg/L or greater. The pH 4 was chosen because USEPA recommends a pH of 4 to 5 for acrolein and acrylonitrile. Results of the preservation study are listed in table 13 (see Appendix). All results were acceptable, and most decreased less than 15 percent between day 1 and day 14. The 1-, 7-, and 14-day recoveries for acrolein at pH 2 were rounded to 91, 83, and 72 percent. At pH 4, acrolein at 1, 7, and 14 days was recovered and rounded to 97, 91, and 82 percent. Acrylonitrile still had recoveries in the 90-percent range at pH 2 and 4 during the 14-day trial. The

recoveries were considered sufficiently high to permit inclusion of both of these compounds in the method provided analysis was within 14 days of sample collection.

A more extensive preservation study is in progress (1998) for all method compounds at pH 2 with low concentration spikes in ground- and surface-water samples for a 112-day period. Percent recoveries were normalized to day 1 results. Five replicate spikes were analyzed on each day. Many compounds showed little loss even at these extended time periods when stored at pH 2 in the dark with no headspace. Tables 14 and 15 (see Appendix) list results up to day 56 for all compounds in ground water (table 14) and surface water (table 15).

Ground-water results showed less percentage loss overall than did surface water. Four compounds were recovered between 50 to 70 percent at 56 days: vinyl acetate, acrolein, 2,2-dichloropropane, and styrene. All remaining compounds were equal to or greater than 70 percent recovery on day 56.

Surface-water losses were more prevalent than for ground water at low concentrations for extended periods. Four compounds in surface water were less than 50 percent recovery at 56 days — 2-hexanone, *p*-isopropyltoluene, ethyl methacrylate, and methyl acrylate. In addition, two compounds showed zero percent recovery — vinyl acetate and acrolein. All the remaining compounds were greater than 70 percent recovery on day 56, except for 2,2,-dichloropropane (63 percent) and bromomethane (69 percent).

Nonselected method compounds or deleted method 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 tentatively identify the compound. The compound cannot be positively identified until a reference standard confirms the mass spectrum and chromatographic retention time. The term "tentatively identified organic compounds" (TIOCs) is preferred for referring to nonselected compounds identified by gas chromatography/mass spectrometry (GC/MS) 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 listed results, as in the following example:

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

TIOCs are censored minimally at 0.1 µg/L on the basis of an assumed one-to-one response with the internal standard. Actual concentrations reported might be an order of magnitude larger or smaller since the quantitation is only approximated.

CONCLUSIONS

This method is suitable for analysis of VOCs in samples of surface water and ground water. This technique can be a highly sensitive analytical tool for characterizing the volatile organic compounds of a whole-water sample. The method is precise and reproducible, providing both quantitative and qualitative information. Data do not need to be censored because of an arbitrary reporting limit, and additional quality control and blanks are included to ensure data quality.

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APPENDIX

DATA TABLES

Table 8. Precision and accuracy for selected volatile organic compounds in volatile blank, ground, and surface water for seven replicates, each spiked at 1 and 10 micrograms per liter (µg/L) for most samples, ranging up to 500 µg/L

[µg/L, micrograms per liter; %, percent; RSD, relative standard deviation; nd, not determined]

	Compound	Amount spiked	Volatile blank water		Surface water		Ground water	
		(µg/L)	% Recovery	% RSD	% Recovery	% RSD	% Recovery	% RSD
1	Acetone	10	114.7	4.5	99.4	2.3	108.9	3.3
		100	91.2	3.4	90.7	2.3	89.6	2.1
2	Acrolein	10	109.9	2.9	103.1	3.0	111.4	2.1
		40	95.5	1.4	96.8	2.6	97.1	2.2
3	Acrylonitrile	8	112.4	3.1	102.2	3.1	110.4	1.1
		40	104.5	1.0	103.8	2.4	101.9	2.6
4	Benzene	1	110.0	1.0	106.7	1.8	109.7	1.4
		10	100.0	0.4	100.3	1.0	98.9	1.5
5	Bromobenzene	1	108.9	1.4	101.5	1.4	109.9	1.8
		10	103.0	1.2	101.0	4.2	100.7	1.7
6	Bromochloromethane	1	111.0	2.8	102.6	1.7	111.1	1.4
		10	104.0	1.1	104.3	1.7	103.0	1.7
7	Bromodichloromethane	1	107.3	2.6	103.0	1.0	108.3	1.8
		10	106.0	0.5	107.0	1.4	105.3	2.3
8	Bromoform	1	114.9	2.3	110.7	1.8	116.1	0.8
		10	108.0	1.4	109.0	1.6	107.7	2.1
9	Bromomethane	1	106.3	1.9	101.6	2.5	109.3	1.9
		10	94.3	1.9	93.1	1.1	91.1	2.0
10	2-Butanone	10	119.1	4.8	108.4	3.1	114.0	3.3
		100	105.0	1.7	105.3	2.7	103.0	2.7
11	*n*-Butylbenzene	1	103.7	3.1	104.9	1.5	106.3	1.3
		10	104.0	1.2	103.7	1.4	102.0	1.3
12	sec-Butylbenzene	1	103.1	1.3	101.8	1.3	104.4	1.6
		10	104.0	0.8	104.0	1.4	102.4	1.1
13	*tert*-Butylbenzene	1	101.4	2.5	99.4	1.2	101.7	3.9
		10	102.0	1.4	101.6	1.6	100.0	1.3
14	*tert*- Butyl ethyl ether	1	114.6	3.1	105.7	2.4	112.4	2.2
		10	106.0	1.2	105.4	1.9	102.2	2.7
	tert-Butyl formate	2	43.9	7.8	99.0	5.5	99.6	4.5
		20	35.5	29.8	77.8	27.4	90.8	10.7
15	*tert*-Butyl methyl ether	1	121.4	2.3	[1]110.0	2.0	122.3	1.5
		10	100.0	0.9	104.0	2.0	98.2	2.8
16	Carbon disulfide	1	95.8	1.9	98.2	1.3	93.7	1.7
		10	116.0	2.4	116.9	1.0	112.7	1.8
	Chloroacetonitrile[2]	100	129.0	4.6	114.6	1.6	124.7	1.3
		100	104.0	3.9	104.7	1.5	103.9	2.5

Table 8. Precision and accuracy for selected volatile organic compounds in volatile blank, ground, and surface water for seven replicates, each spiked at 1 and 10 micrograms per liter (µg/L) for most samples, ranging up to 500 µg/L — Continued

	Compound	Amount spiked	Volatile blank water		Surface water		Ground water	
		(µg/L)	% Recovery	% RSD	% Recovery	% RSD	% Recovery	% RSD
17	Chlorobenzene	1	101.4	1.7	98.2	1.0	102.3	1.7
		10	103.0	1.1	102.1	1.0	100.5	1.6
	1-Chlorobutane	4	100.8	1.2	101.0	0.9	102.0	1.5
		10	103.0	1.0	102.6	1.1	100.6	1.3
18	Chloroethane	1	112.3	0.8	107.9	2.2	112.7	3.9
		10	104.0	1.1	103.6	0.9	101.7	1.2
	bis (2-Chloroethyl) ether [2]	100	137.4	6.7	119.9	3.8	131.9	3.9
		100	99.6	9.1	99.2	3.4	96.0	4.1
19	Chloroform	1	111.6	1.3	114.4	2.0	111.9	1.1
		10	102.0	0.9	101.8	1.2	99.7	1.7
20	Chloromethane	1	112.4	0.7	104.3	1.5	117.3	1.6
		10	103.0	3.1	101.6	1.9	97.9	1.5
21	3-Chloropropene	1	102.9	2.9	108.3	2.0	103.4	3.5
		10	114.0	1.0	114.6	1.2	113.9	1.1
22	2-Chlorotoluene	1	102.2	2.3	99.7	1.3	103.1	2.4
		10	102.0	0.9	102.3	1.6	99.9	1.0
23	4-Chlorotoluene	1	100.3	2.3	98.0	1.7	102.5	2.4
		10	100.0	1.1	99.9	1.6	98.6	1.1
24	Dibromochloromethane	1	112.6	1.9	105.3	1.1	113.0	1.3
		10	116.0	1.3	116.0	1.7	115.0	2.5
25	1,2-Dibromo-3-chloropropane	1	107.7	5.0	96.6	3.3	106.3	5.2
		10	111.0	2.1	109.4	2.6	107.3	3.1
26	1,2-Dibromoethane	1	110.7	3.1	101.6	2.6	110.3	1.0
		10	106.0	1.3	106.0	1.7	103.1	2.0
27	Dibromomethane	1	109.0	3.3	102.2	3.4	108.4	1.2
		10	100.0	1.1	100.1	1.6	98.5	1.6
28	1,2-Dichlorobenzene	1	107.0	2.0	101.8	1.5	107.6	1.1
		10	99.2	1.0	99.3	1.4	97.5	1.6
29	1,3-Dichlorobenzene	1	102.6	2.1	98.6	1.6	103.1	1.9
		10	99.6	1.0	99.8	2.6	97.7	1.8
30	1,4-Dichlorobenzene	1.0	102.0	1.8	97.3	1.6	103.7	0.9
		10	99.6	1.0	99.8	2.6	97.7	1.8
31	*trans*-1,4-Dichloro-2-butene	10	118.6	1.9	119.4	2.9	122.4	2.6
		100	112.0	2.1	117.0	3.6	112.3	1.5
32	Dichlorodifluoromethane	1	109.9	1.8	92.7	4.5	120.1	2.7
		10	108.0	4.5	99.2	4.5	95.1	3.8
33	1,1-Dichloroethane	1	110.3	1.4	108.6	1.3	111.7	1.8
		10	102.0	0.5	101.5	1.0	99.9	1.1

Table 8. Precision and accuracy for selected volatile organic compounds in volatile blank, ground, and surface water for seven replicates, each spiked at 1 and 10 micrograms per liter (µg/L) for most samples, ranging up to 500 µg/L — Continued

	Compound	Amount spiked	Volatile blank water		Surface water		Ground water	
		(µg/L)	% Recovery	% RSD	% Recovery	% RSD	% Recovery	% RSD
34	1,2-Dichloroethane	1	118.3	1.9	114.3	1.8	118.4	2.1
		10	101.0	1.5	99.4	1.1	98.6	1.6
35	1,1-Dichloroethene	1	95.6	1.3	92.2	0.8	98.0	1.6
		10	97.4	0.6	96.6	1.2	94.6	1.4
36	*cis*-1,2-Dichloroethene	1	102.1	1.5	98.5	1.2	102.9	2.4
		10	103.0	1.3	102.7	1.5	100.6	1.4
37	*trans*-1,2-Dichloroethene	1	100.6	1.2	97.1	1.6	100.3	2.1
		10	102.0	0.9	102.1	1.3	100.9	1.2
38	1,2-Dichloropropane	1	105.9	2.0	104.1	1.0	107.0	1.5
		10	101.0	0.7	100.7	1.4	99.0	1.5
39	1,3-Dichloropropane	1	106.3	2.3	100.3	1.9	105.1	1.3
		10	99.6	1.0	99.8	2.6	97.7	1.8
40	2,2-Dichloropropane	1	88.0	1.7	101.7	2.5	93.4	2.5
		10	86.6	4.4	92.6	3.4	91.4	2.2
	1,1-Dichloropropanone	100	120.7	5.1	106.7	2.7	117.6	2.4
		200	101.5	4.1	101.4	3.1	96.5	2.7
41	1,1-Dichloropropene	1	98.2	2.4	99.6	2.0	100.5	1.8
		10	101.0	1.2	100.9	1.4	99.5	0.6
42	*cis*-1,3-Dichloropropene	1	106.7	2.0	102.5	3.5	109.6	1.9
		10	106.0	1.4	107.9	1.1	105.0	1.5
43	*trans*-1,3-Dichloropropene	1	110.4	2.5	105.7	2.9	113.3	3.1
		10	109.0	1.5	111.7	1.3	109.6	2.3
44	Diethyl ether	1	119.4	2.7	108.1	2.0	119.3	2.5
		10	100.0	1.0	100.2	2.0	98.3	2.4
45	Diisopropyl ether	1	106.8	4.3	103.0	2.5	106.4	2.0
		10	105.0	2.1	108.7	2.0	107.1	2.4
	1,4-Dioxane[2]	100	116.2	13.8	103.2	10.0	109.6	14.0
		100	117.0	18.4	119.3	2.7	116.1	4.7
46	Ethyl benzene	1	103.4	1.6	101.1	1.3	104.1	1.5
		10	101.0	0.7	100.9	1.2	99.0	1.5
47	Ethyl methacrylate	5	116.6	3.3	107.0	1.8	115.9	1.9
		10	108.0	1.3	109.4	2.0	106.7	3.2
48	*o*-Ethyl toluene	1	93.9	1.6	90.7	1.0	95.0	1.0
		10	104.0	0.7	104.0	1.2	102.1	1.3
49	Hexachlorobutadiene	1	107.3	3.1	103.6	1.5	106.1	2.1
		10	100.0	1.5	101.1	1.6	100.0	1.4
	Hexachlorocylcopentadiene[3]	125	115.3	11.5	nd	nd	127.0	7.1
		250	nd	nd	nd	nd	147.3	4.1

Table 8. Precision and accuracy for selected volatile organic compounds in volatile blank, ground, and surface water for seven replicates, each spiked at 1 and 10 micrograms per liter (µg/L) for most samples, ranging up to 500 µg/L — Continued

	Compound	Amount spiked (µg/L)	Volatile blank water % Recovery	Volatile blank water % RSD	Surface water % Recovery	Surface water % RSD	Ground water % Recovery	Ground water % RSD
50	Hexachloroethane	1	112.3	1.8	111.9	0.8	114.1	1.7
		10	116.0	1.1	116.1	1.4	114.4	1.7
51	2-Hexanone	10	116.3	4.3	105.4	2.7	115.6	2.1
		100	106.0	1.8	106.1	2.3	103.7	3.4
52	Isopropylbenzene	1	105.9	0.8	103.6	1.6	106.6	1.5
		10	104.0	0.8	104.3	1.2	102.9	1.5
53	*p*-Isopropyltoluene	1	106.3	2.3	105.4	1.2	108.6	0.9
		10	105.0	0.9	104.3	2.8	103.3	1.2
54	Methyl acrylate	5	104.1	3.5	95.0	2.6	102.9	1.0
		20	108.5	1.2	107.6	2.7	105.4	2.9
55	Methyl acrylonitrile	5	113.7	4.4	103.8	2.2	112.6	3.1
		20	107.5	1.6	106.5	2.8	105.3	2.8
56	Methylene chloride	1	107.6	2.0	103.4	1.8	111.6	1.4
		10	98.9	0.9	99.7	1.2	98.3	1.7
57	Methyl iodide	1	104.4	1.7	100.3	1.9	105.3	1.4
		10	106.0	0.9	102.1	1.5	101.4	0.8
58	Methyl methacrylate	5	130.0	3.5	116.8	2.0	128.7	1.5
		20	108.5	1.2	107.6	2.7	105.4	2.9
59	4-Methyl-2-pentanone	10	119.0	3.6	108.4	1.8	116.7	2.5
		100	106.0	1.6	106.4	2.4	103.2	3.0
60	Naphthalene	1	120.9	4.5	109.3	1.8	119.9	1.3
		10	105.0	2.4	103.9	2.5	100.3	2.9
	Nitrobenzene	500	138.1	4.2	128.4	3.0	141.7	3.0
		200	117.0	10.1	118.6	2.7	115.9	2.4
	2-Nitropropane	50	128.2	3.2	118.6	2.1	126.9	2.3
		100	116.0	1.8	115.3	2.3	113.7	2.3
	Pentachlorobenzene [3]	250	155.0	9.4	nd	nd	75.7	4.7
		500	nd	nd	nd	nd	152.1	1.5
	Pentachloroethane	1	104.6	1.6	101.2	1.3	106.9	1.7
		10	109.0	1.2	106.6	3.1	108.0	2.1
61	*tert*-Pentyl methyl ether	1	112.7	3.1	104.5	2.4	111.7	1.7
		10	105.0	1.5	104.3	2.5	101.3	2.5
	Propionitrile	20	121.6	4.6	110.6	1.3	117.4	2.1
		100	109.0	2.0	108.9	2.2	107.3	2.2
62	*n*-Propylbenzene	1	100.2	1.8	97.7	1.7	100.7	0.5
		10	103.0	1.0	103.9	0.9	102.1	1.0
63	Styrene	1	109.4	1.8	102.2	1.3	109.6	1.2
		10	107.0	0.8	106.0	1.3	106.1	1.6

Table 8. Precision and accuracy for selected volatile organic compounds in volatile blank, ground, and surface water for seven replicates, each spiked at 1 and 10 micrograms per liter (µg/L) for most samples, ranging up to 500 µg/L — Continued

	Compound	Amount spiked	Volatile blank water		Surface water		Ground water	
		(µg/L)	% Recovery	% RSD	% Recovery	% RSD	% Recovery	% RSD
64	1,1,1,2-Tetrachloroethane	1	106.4	1.4	100.2	1.8	106.7	1.9
		10	106.0	1.0	106.0	1.7	104.4	1.7
65	1,1,2,2-Tetrachloroethane	1	115.4	4.6	105.4	3.5	116.7	2.4
		10	108.0	1.6	106.3	3.0	105.4	3.3
66	Tetrachloroethene	1	102.4	1.6	98.6	1.7	103.4	2.1
		10	96.8	1.2	97.2	0.9	95.0	0.9
67	Tetrachloromethane	1	107.1	1.0	106.3	1.5	108.7	1.7
		10	105.0	0.7	105.1	1.0	103.3	1.1
68	Tetrahydrofuran	10	126.9	5.2	117.0	1.6	124.4	0.8
		100	110.0	1.8	108.4	2.5	105.0	2.6
69	1,2,3,4-Tetramethylbenzene	1	102.1	2.9	95.2	1.3	102.3	0.5
		10	107.0	1.3	106.3	2.2	103.8	2.3
70	1,2,3,5-Tetramethylbenzene	1	96.7	2.6	90.6	0.9	97.0	1.0
		10	106.0	1.5	105.6	1.7	103.4	2.0
72	Toluene	1	106.4	0.9	104.4	1.4	107.6	0.9
		10	102.0	0.8	100.9	1.3	99.3	1.5
72	1,2,3-Trichlorobenzene	1	119.6	4.2	111.7	1.8	119.6	1.9
		10	106.0	2.5	106.7	2.3	102.7	2.2
73	1,2,4-Trichlorobenzene	1	108.9	3.5	102.2	2.6	110.0	1.3
		10	102.0	1.5	102.5	1.5	98.9	1.6
74	1,1,1-Trichloroethane	1	109.3	1.7	107.7	1.9	110.4	1.6
		10	103.0	0.7	102.7	1.2	100.7	1.3
75	1,1,2-Trichloroethane	1	113.9	2.9	105.1	2.5	111.0	1.5
		10	104.0	1.4	103.3	2.7	101.1	2.6
76	Trichloroethene	1	101.2	1.0	99.3	1.4	101.6	1.4
		10	98.1	0.7	99.8	1.0	98.2	1.4
77	Trichlorofluoromethane	1	111.3	1.6	110.1	1.0	115.9	1.4
		10	95.3	3.1	94.5	1.4	92.9	1.0
78	1,2,3-Trichloropropane	1	115.1	3.4	106.9	4.4	114.0	2.0
		10	104.0	2.0	104.1	2.2	102.8	3.4
79	1,1,2-Trichloro-1,2,2-trifluoroethane	1	92.5	1.8	89.2	2.0	95.0	1.8
		10	97.1	1.0	97.2	1.5	95.5	1.3
80	1,2,3-Trimethylbenzene	1	98.4	2.3	93.6	1.2	98.8	1.9
		10	104.0	1.1	103.7	1.8	101.6	1.8
81	1,2,4-Trimethylbenzene	1	109.7	1.9	106.6	1.3	111.4	1.3
		10	102.0	1.0	103.9	2.5	100.9	1.6
82	1,3,5-Trimethylbenzene	1	107.3	1.8	103.9	1.0	108.1	0.8
		10	105.0	0.6	103.2	2.1	103.0	1.4

Table 8. Precision and accuracy for selected volatile organic compounds in volatile blank, ground, and surface water for seven replicates, each spiked at 1 and 10 micrograms per liter (µg/L) for most samples, ranging up to 500 µg/L — Continued

	Compound	Amount spiked	Volatile blank water		Surface water		Ground water	
		(µg/L)	% Recovery	% RSD	% Recovery	% RSD	% Recovery	% RSD
	Vinyl acetate	20	113.9	3.1	106.6	1.5	114.6	1.1
		100	104.0	0.9	105.0	1.6	104.1	2.0
83	Vinyl bromide	1	93.1	1.4	91.8	1.4	96.3	2.1
		10	97.0	2.4	96.0	1.1	94.7	1.1
84	Vinyl chloride	1	100.6	1.2	95.3	2.4	104.1	1.6
		10	105.0	2.5	102.1	1.6	99.7	1.4
85	*m*- and *p*-Xylene	2	101.4	1.7	99.6	1.4	102.7	1.3
		20	98.5	0.8	98.2	1.8	97.2	1.6
86	*o*-Xylene	1	104.0	1.2	100.6	1.1	105.1	1.6
		10	102.0	0.9	102.0	1.3	100.4	1.7
	Surrogates							
	p-Bromofluorobenzene	1	101.7	0.5	93.0	1.1	105.0	1.1
		1	93.0	1.1	92.6	1.2	89.8	3.7
	1,2-Dichloroethane-d_4	1	106.3	3.3	95.0	1.6	105.0	1.6
		1	95.0	1.6	97.2	3.2	96.4	3.6
	Toluene-d_8	1	101.7	0.5	97.3	1.0	101.6	1.0
		1	97.3	1.0	99.0	1.2	97.6	1.9

[1]The surface water contained 0.43 µg/L of MTBE. The percent recovery for the 1-µg/L spike was corrected for the amount of MTBE present in the surface water. The high spike was not corrected since 0.43 µg/L does not contribute significantly to a 10-µg/L spike.

[2]Two different solutions were used for collecting these data. The calibration standard solution was used for the first row of data (typically 1.0 µg/L), and the third-party check was used for the second row of data (typically 10.0 µg/L). A few compounds ended up being at the same concentration in both mixes.

[3]Limited precision and accuracy testing was done on these two compounds in the initial phase. The ground-water matrices used were chosen from random duplicate ground-water samples received for analysis at the NWQL.

Table 9. Precision and accuracy of 60 set spikes in distilled water, spiked at 0.5 to 20 micrograms per liter, using multiple instruments, operators, and calibrations acquired over 6 months

[µg/L, micrograms per liter; %, percent; % RSD, percent relative standard deviation]

	Compound	Spike concentration (µg/L)	Mean recovery (%)	RSD (%)
1	Acetone	5.0	114	24.6
2	Acrolein	20	95	15.5
3	Acrylonitrile	10	99	12.4
4	Benzene	0.5	97	7.4
5	Bromobenzene	0.5	95	9.3
6	Bromochloromethane	0.5	99	5.2
7	Bromodichloromethane	0.5	95	8.9
8	Bromoform	0.5	91	11.6
9	Bromomethane	0.5	95	23.3
10	2-Butanone	5.0	102	11.2
11	*n*-Butylbenzene	0.5	88	13.1
12	sec-Butylbenzene	0.5	92	10.3
13	*tert*-Butylbenzene	0.5	92	9.2
14	*tert*-Butyl ethyl ether	0.5	83	15.8
15	*tert*-Butyl methyl ether	0.5	88	11.3
16	Carbon disulfide	0.5	105	22.2
17	Chlorobenzene	0.5	96	5.8
18	Chloroethane	0.5	96	16.1
19	Chloroform	0.5	101	12.4
20	Chloromethane	0.5	106	24.1
21	3-Chloropropene	1.0	86	8.5
22	2-Chlorotoluene	0.5	94	6.4
23	4-Chlorotoluene	0.5	96	7.2
24	Dibromochloromethane	0.5	92	8.8
25	1,2-Dibromo-3-chloropropane	0.5	88	25.5
26	1,2-Dibromoethane	0.5	96	7.7
27	Dibromomethane	0.5	99	7.9
28	1,2-Dichlorobenzene	0.5	97	8.1
29	1,3-Dichlorobenzene	0.5	96	7.8
30	1,4-Dichlorobenzene	0.5	94	8.7
31	*trans*-1,4-Dichloro-2-butene	5.0	85	16.1
32	Dichlorodifluoromethane	0.5	104	25.0
33	1,1-Dichloroethane	0.5	99	8.8
34	1,2-Dichloroethane	0.5	100	9.5
35	1,1-Dichloroethene	0.5	98	15.4
36	*cis*-1,2-Dichloroethene	0.5	95	7.3
37	*trans*-1,2-Dichloroethene	0.5	96	7.1
38	1,2-Dichloropropane	0.5	97	8.9

Table 9. Precision and accuracy of 60 set spikes in distilled water, spiked at 0.5 to 20 micrograms per liter, using multiple instruments, operators, and calibrations acquired over 6 months — Continued

	Compound	Spike concentration (µg/L)	Mean recovery (%)	RSD (%)
39	1,3-Dichloropropane	0.5	95	9.1
40	2,2-Dichloropropane	0.5	97	7.3
41	1,1-Dichloropropene	0.5	95	6.7
42	*cis*-1,3-Dichloropropene	0.5	89	9.4
43	*trans*-1,3-Dichloropropene	0.5	88	12.7
44	Diethyl ether	1.0	96	11.4
45	Diisopropyl ether	0.5	81	14.7
46	Ethyl benzene	0.5	93	6.8
47	Ethyl methacrylate	2.5	91	7.4
48	*o*-Ethyl toluene	0.5	77	8.1
49	Hexachlorobutadiene	0.5	95	11.6
50	Hexachloroethane	0.5	99	13.4
51	2-Hexanone	5.0	95	12.8
52	Isopropylbenzene	0.5	98	7.2
53	*p*-Isopropyl toluene	0.5	89	16.4
54	Methyl acrylate	2.5	92	9.8
55	Methyl acrylonitrile	2.5	98	9.1
56	Methylene chloride	0.5	107	13.0
57	Methyl iodide	0.5	96	19.4
58	Methyl methacrylate	2.5	103	9.9
59	4-Methyl-2-pentanone	5.0	95	11.4
60	Naphthalene	0.5	97	17.2
61	*tert*-Pentyl methyl ether	0.5	83	11.0
62	*n*-Propylbenzene	0.5	94	6.4
63	Styrene	0.5	92	7.4
64	1,1,1,2-Tetrachloroethane	0.5	97	8.0
65	1,1,2,2-Tetrachloroethane	0.5	95	16.0
66	Tetrachloroethene	0.5	97	5.6
67	Tetrachloromethane	0.5	96	8.2
68	Tetrahydrofuran	5.0	90	11.8
69	1,2,3 4-Tetramethylbenzene	0.5	89	16.3
70	1,2,3,5-Tetramethylbenzene	0.5	76	10.8
71	Toluene	0.5	98	5.9
72	1,2,3-Trichlorobenzene	0.5	93	12.0
73	1,2,4-Trichlorobenzene	0.5	89	11.8
74	1,1,1-Trichloroethane	0.5	98	6.1
75	1,1,2-Trichloroethane	0.5	99	8.6
76	Trichloroethene	0.5	95	5.9
77	Trichlorofluoromethane	0.5	95	14.3
78	1,2,3-Trichloropropane	0.5	94	11.1
79	1,1,2-Trichloro-1,2,2-trifluoroethane	0.5	91	14.8

Table 9. Precision and accuracy of 60 set spikes in distilled water, spiked at 0.5 to 20 micrograms per liter, using multiple instruments, operators, and calibrations acquired over 6 months — Continued

	Compound	Spike concentration (µg/L)	Mean recovery (%)	RSD (%)
80	1,2,3-Trimethylbenzene	0.5	70	10.6
81	1,2,4-Trimethylbenzene	0.5	91	9.4
82	1,3,5-Trimethylbenzene	0.5	93	7.5
	Vinyl acetate	5.0	88	14.9
83	Vinyl bromide	0.5	92	9.5
84	Vinyl chloride	0.5	110	23.3
85	*m*- and *p*-Xylene	1.0	94	6.8
86	*o*-Xylene	0.5	95	7.2

Table 10. Summary of 41 nondetection value check standards

[MRL, method reporting limit; µg/L, micrograms per liter; NDV, nondetection value; <, less than; nd, not determined]

	Compound	Interim MRL (µg/L)	Interim spike concentration (µg/L)	Mean[3] (µg/L)	Standard deviation[3] (µg/L)	Count[5]
1	Acetone [1]	<5.0	0.5	0.661	1.022	17
2	Acrolein [1]	<0.05	0.5	0.164	0.298	9
3	Acrylonitrile	<2.0	0.4	0.491	0.21	17/19
			2.0	1.92	0.554	22/22
4	Benzene	<0.05	0.05	0.058	0.007	41
5	Bromobenzene	<0.05	0.05	0.048	0.007	41
6	Bromochloromethane	<0.1	0.05	0.055	0.009	41
7	Bromodichloromethane	<0.1	0.05	0.048	0.010	40
8	Bromoform [1]	<0.2	0.05	0.033	0.022	30
9	Bromomethane	<0.05	0.05	0.037	0.031	24
10	2-Butanone [1]	<5.0	0.5	0.309	0.344	18
11	*sec*-Butylbenzene	<0.05	0.05	0.047	0.010	41
12	*n*-Butylbenzene	<0.05	0.05	0.057	0.039	41
13	*tert*-Butylbenzene	<0.05	0.05	0.041	0.020	35
14	*tert*-Butyl ethyl ether [1]	<0.1	0.05	0.041	0.011	39
15	*tert*-Butyl methyl ether [1]	<0.1	0.05	0.017	0.024	15
16	Carbon disulfide	<0.05	0.05	0.054	0.017	39
17	Chlorobenzene	<0.05	0.05	0.050	0.007	41
18	Chloroethane	<0.1	0.05	0.047	0.025	33
19	Chloroform	<0.05	0.05	0.055	0.011	40
20	Chloromethane	<0.2	0.05	0.058	0.053	33
21	3-Chloropropene [1]	<0.1	0.05	0.067	0.029	5/19
			0.1	0.08	0.014	15/22
22	2-Chlorotoluene	<0.05	0.05	0.048	0.008	41
23	4-Chlorotoluene	<0.05	0.05	0.048	0.011	41
24	Dibromochloromethane	<0.1	0.05	0.051	0.038	39
25	1,2-Dibromo-3-chloropropane [1,4]	<0.5	0.05	0.001	nd	1
26	1,2-Dibromoethane	<0.1	0.05	0.051	0.007	41
27	Dibromomethane	<0.1	0.05	0.054	0.010	41
28	1,2-Dichlorobenzene	<0.05	0.05	0.053	0.010	41
29	1,3-Dichlorobenzene	<0.05	0.05	0.050	0.011	41
30	1,4-Dichlorobenzene	<0.05	0.05	0.049	0.010	41
31	trans-1,4-Dichloro-2-butene [1]	<5.0	0.5	0.408	0.144	39
32	Dichlorodifluoromethane	<0.2	0.05	0.049	0.020	36
33	1,1-Dichloroethane	<0.05	0.05	0.051	0.014	39
34	1,2-Dichloroethane [2]	<0.05	0.05	0.031	0.028	23
35	1,1-Dichloroethene	<0.1	0.05	0.058	0.009	41
36	*trans*-1,2-Dichloroethene	<0.05	0.05	0.054	0.007	41
37	*cis*-1,2-Dichloroethene	<0.05	0.05	0.052	0.008	41
38	1,2-Dichloropropane	<0.05	0.05	0.051	0.014	39
39	1,3-Dichloropropane [2]	<0.05	0.05	0.041	0.024	32
40	2,2-Dichloropropane	<0.05	0.05	0.050	0.017	38

Table 10. Summary of 41 nondetection value check standards — Continued

	Compound	Interim MRL (µg/L)	Interim spike concentration (µg/L)	Mean[3] (µg/L)	Standard deviation[3] (µg/L)	Count[5]
41	1,1-Dichloropropene	<0.05	0.05	0.050	0.005	41
42	*cis*-1,3-Dichloropropene	<0.1	0.05	0.045	0.019	37
43	*trans*-1,3-Dichloropropene	<0.1	0.05	0.036	0.028	36
44	Diethyl ether	<0.1	0.05	0.077	0.025	13/19
			0.1	0.102	0.022	22/22
45	Diisopropyl ether [1]	<0.1	0.05	0.032	0.021	31
46	Ethyl methacrylate	<1.0	0.25	0.214	0.058	39
47	Ethylbenzene	<0.05	0.05	0.047	0.007	41
48	*o*-Ethyl toluene	<0.05	0.05	0.047	0.021	41
49	Hexachlorobutadiene	<0.2	0.05	0.062	0.030	41
50	Hexachloroethane [1]	<0.05	0.05	0.084	0.075	34
51	2-Hexanone [1]	<5.0	0.5	0.488	0.155	38
52	Isopropylbenzene	<0.05	0.05	0.049	0.007	41
53	*p*-Isopropyltoluene	<0.05	0.05	0.053	0.023	41
54	Methacrylonitrile	<2.0	0.25	0.218	0.119	33
55	Methyl iodide	<0.05	0.05	0.051	0.016	40
56	Methyl methacrylate	<1.0	0.25	0.253	0.073	39
57	4-Methyl-2-pentanone [1]	<5.0	0.5	0.481	0.078	41
58	Methylacrylate [1]	<2.0	0.25	0.148	0.128	24
59	Methylene chloride	<0.1	0.05	0.104	0.080	41
60	Naphthalene	<0.2	0.05	0. 057	0.052	36
61	*tert*-Pentyl methyl ether [1]	<0.1	0.05	0.029	0.023	26
62	*n*-Propylbenzene	<0.05	0.05	0.047	0.009	41
63	Styrene	<0.05	0.05	0.044	0.008	41
64	1,1,1,2-Tetrachloroethane	<0.05	0.05	0.051	0.009	41
65	1,1,2,2-Tetrachloroethane [1]	<0.1	0.05	0.030	0.028	23
66	Tetrachloroethene	<0.05	0.05	0.052	0.008	41
67	Tetrachloromethane	<0.05	0.05	0.050	0.018	40
68	Tetrahydrofuran [1]	<5.0	0.5	0.369	0.239	31
69	1,2,3,4-Tetramethylbenzene	<0.05	0.05	0.062	0.048	40
70	1,2,3,5-Tetramethylbenzene	<0.05	0.05	0.062	0.050	40
71	Toluene	<0.05	0.05	0.056	0.008	41
72	1,2,3-Trichlorobenzene [1]	<0.2	0.05	0.055	0.055	35
73	1,2,4-Trichlorobenzene	<0.2	0.05	0.054	0.039	39
74	1,1,1-Trichloroethane	<0.05	0.05	0.052	0.007	41
75	1,1,2-Trichloroethane	<0.1	0.05	0.052	0.013	40
76	Trichloroethene	<0.05	0.05	0.052	0.008	41
77	1,2,3-Trichloropropane [1]	<0.2	0.05	0.005	0.014	3
78	1,1,2-Trichloro-1,2,2-trifluoroethane	<0.05	0.05	0.047	0.006	41
79	Trichlorofluoromethane	<0.1	0.05	0.048	0.019	37
80	1,2,3-Trimethylbenzene	<0.05	0.05	0.044	0.026	38
81	1,2,4-Trimethylbenzene	<0.05	0.05	0.046	0.012	40
82	1,3,5-Trimethylbenzene	<0.05	0.05	0.047	0.010	41
	Vinyl acetate [1]	<5.0	1	0.899	0.37	19/19
			0.5	0.48	0.223	21/22
83	Vinyl bromide	<0.1	0.05	0.040	0.021	32
84	Vinyl chloride	<0.1	0.05	0.048	0.023	34

Table 10. Summary of 41 nondetection value check standards — Continued

	Compound	Interim MRL (µg/L)	Interim spike concentration (µg/L)	Mean[3] (µg/L)	Standard deviation[3] (µg/L)	Count[5]
85	*m*- and *p*-Xylene	<0.05	0.1	0.095	0.013	41
86	*o*-Xylene	<0.05	0.05	0.047	0.013	39

[1]Concentration available in commercial mix was too low, resulting in nondetection.

[2]Long-term method detection limits indicate this concentration was not appropriate.

[3]The mean and standard deviation were determined using a value of zero for the volatile organic compounds that were not detected at the interim spike concentration.

[4]1,2-Dibromo-3-chloropropane (DBCP) was detected only once out of 41 injections at 0.05 µg/L. Standard deviation could not be determined for DBCP.

[5]"Count" represents the number of times the compound was positively identified out of 41 NDV check standards (or if represented as a fraction, identified "numerator" out of "denominator" times). Nondetections occur because spike levels were too close to, or lower than, the method detection limit.

Table 11. One-hundred eighty-two acidified continuing calibration verification standards

[CCVs, continuing calibration verification standards; STDEV, standard deviation; RSD, relative standard deviation; %, percent. Concentration is 1 microgram per liter except where noted in parentheses]

	Preserved CCVs n = 182			
	Compound	Mean percent recovery	% STDEV	% RSD
1	Acetone (10)	100.4	11.6	11.5
2	Acrolein (5)	107.4	22.7	21.2
3	Acrylonitrile (4)	96.8	11.1	11.5
4	Benzene	97.9	10.4	10.6
5	Bromobenzene	99.6	10.7	10.7
6	Bromochloromethane	99.2	11.4	11.5
7	Bromodichloromethane	98.7	11.1	11.3
8	Bromoform	100.1	13.5	13.5
9	Bromomethane	95.2	25.5	26.8
10	2-Butanone (10)	98.3	12.6	12.8
11	*n*-Butylbenzene	99.8	13.2	13.3
12	*sec*-Butylbenzene	100.7	10.7	10.7
13	*tert*-Butylbenzene	100.3	12.0	12.0
14	*tert*-Butyl ethyl ether	98.2	11.2	11.5
15	*tert*-Butyl methyl ether	97.7	10.9	11.2
16	Carbon disulfide	101.9	14.8	14.5
17	Chlorobenzene	98.9	10.3	10.4
18	Chloroethane	91.7	12.2	13.3
19	Chloroform	99.0	11.1	11.2
20	Chloromethane	104.6	24.7	23.6
21	3-Chloropropene	100.2	9.8	9.8
22	2-Chlorotoluene	100.8	10.7	10.6
23	4-Chlorotoluene	100.6	10.7	10.7
24	Dibromochloromethane	99.5	11.3	11.3
25	1,2-Dibromo-3-chloropropane	100.8	11.0	10.9
26	1,2-Dibromoethane	98.7	5.4	5.4
27	Dibromomethane	99.3	10.7	10.8
28	1,2-Dichlorobenzene	100.2	11.2	11.2
29	1,3-Dichlorobenzene	100.7	10.9	10.9
30	1,4-Dichlorobenzene	100.0	11.1	11.1
31	*trans*-1,4-Dichloro-2-butene (10)	103.7	18.6	18.0
32	Dichlorodifluoromethane	95.6	28.0	29.3
33	1,1-Dichloroethane	99.0	11.3	11.5
34	1,2-Dichloroethane	99.6	8.0	8.0
35	1,1-Dichloroethene	99.8	12.5	12.6
36	*cis*-1,2-Dichloroethene	98.5	11.2	11.4
37	*trans*-1,2-Dichloroethene	97.6	11.5	11.8
38	1,2-Dichloropropane	99.3	10.8	10.9

Table 11. One-hundred eighty-two acidified continuing calibration verification standards — Continued

	Preserved CCVs n = 182			
	Compound	Mean percent recovery	% STDEV	% RSD
39	1,3-Dichloropropane	99.6	10.6	10.6
40	2,2-Dichloropropane	95.1	11.5	12.1
41	1,1-Dichloropropene	98.3	11.5	11.7
42	*cis*-1,3-Dichloropropene	99.0	8.9	9.0
43	*trans*-1,3-Dichloropropene	98.6	10.9	11.0
44	Diethyl ether	99.6	11.6	11.7
45	Diisopropyl ether	99.5	11.5	11.5
46	Ethyl benzene	99.9	10.5	10.5
47	Ethyl methacrylate	99.8	9.1	9.1
48	2-Ethyl toluene	100.9	10.5	10.4
49	Hexachlorobutadiene	99.2	11.2	11.3
50	Hexachloroethane	101.2	11.6	11.4
51	2-Hexanone	101.4	11.3	11.1
52	Isopropylbenzene	100.5	10.5	10.4
53	*p*-Isopropyl toluene	101.4	11.2	11.1
54	Methyl acrylate (2)	99.7	11.0	11.0
55	Methyl acrylonitrile (2)	99.9	11.6	11.6
56	Methylene chloride	96.7	11.1	11.5
57	Methyl iodide	92.9	20.4	22.0
58	Methyl methacrylate (2)	98.3	11.8	12.0
59	4-Methyl-2-pentanone (10)	101.8	11.0	10.8
60	Naphthalene	103.3	16.5	16.0
61	*tert*-Pentyl methyl ether	98.5	10.3	10.4
62	*n*-Propylbenzene	101.0	10.7	10.6
63	Styrene	101.0	10.7	10.6
64	1,1,1,2-Tetrachloroethane	99.3	10.6	10.6
65	1,1,2,2-Tetrachloroethane	101.5	11.3	11.1
66	Tetrachloroethene	97.7	11.0	11.3
67	Tetrachloromethane	98.5	11.3	11.5
68	Tetrahydrofuran (10)	100.5	11.1	11.0
69	1,2,3 4-Tetramethyl benzene	103.4	15.4	14.9
70	1,2,3,5-Tetramethyl benzene	102.8	15.1	14.7
71	Toluene	98.4	10.3	10.5
72	1,2,3-Trichlorobenzene	99.5	13.6	13.6
73	1,2,4-Trichlorobenzene	99.7	13.3	13.3
74	1,1,1-Trichloroethane	97.7	11.0	11.3
75	1,1,2-Trichloroethane	99.2	10.6	10.7
76	Trichloroethene	97.9	10.8	11.0
77	Trichlorofluoromethane	98.4	13.3	13.5
78	1,2,3-Trichloropropane	100.4	10.5	10.5
79	1,1,2-Trichloro-1,2,2-trifluoroethane	99.3	12.8	12.9
80	1,2,3-Trimethylbenzene	101.3	13.2	13.1
81	1,2,4-Trimethylbenzene	100.5	10.8	10.8
82	1,3,5-Trimethylbenzene	101.0	10.6	10.5

Table 11. One-hundred eighty-two acidified continuing calibration verification standards — Continued

	Preserved CCVs n = 182			
	Compound	Mean percent recovery	% STDEV	% RSD
	Vinyl acetate (10)	109.3	35.0	32.0
83	Vinyl bromide	95.8	11.4	11.9
84	Vinyl chloride	97.5	17.7	18.2
85	*m*- and *p*-Xylene (2)	100.3	10.5	10.5
86	*o*-Xylene	99.8	10.4	10.5

Table 12. Number of detections, mean concentration, and concentration ranges from carryover blanks in micrograms per liter following low- and high-concentration standards known to produce carryover at detectable concentrations using Tekmar Aquatek 50 autosamplers with LSC 2000 concentrators

[No., number of detections. All measurements in microgram per liter (µg/L)]

	Compound	Following a 1-µg/L standard (n=62)				Following a 20-µg/L standard (n=9)			
				Range				Range	
		No.	Mean	Low	High	No.	Mean	Low	High
1	Acetone (10, 200)[1]	16	0.75	0.42	1.8	6	12.150	5.000	33.90
2	Acrolein (5, 100)[1]	0				3	2.727	0.540	7.100
3	Acrylonitrile (4, 80)[1]	3	0.043	0.039	0.047	7	1.510	0.040	7.000
4	Benzene	15	0.019	0.005	0.016	5	0.014	0.010	0.020
5	Bromobenzene	10	0.005	0.003	0.009	8	0.031	0.007	0.060
6	Bromochloromethane	0				6	0.018	0.010	0.050
7	Bromodichloromethane	0				5	0.011	0.007	0.020
8	Bromoform	0				5	0.032	0.010	0.070
9	Bromomethane	0				0			
10	2-Butanone (10, 200)[1]	14	0.279	0.210	0.390	6	8.283	3.300	25.20
11	*n*-Butylbenzene	15	0.007	0.004	0.009	9	0.046	0.010	0.090
12	*sec*-Butylbenzene	11	0.005	0.004	0.007	8	0.034	0.009	0.050
13	*tert*-Butylbenzene	0				6	0.033	0.020	0.040
14	*tert*-Butyl ethyl ether	0				5	0.024	0.010	0.070
15	*tert*-Butyl methyl ether	0				4	0.055	0.020	0.160
16	Carbon disulfide	6	0.005	0.003	0.007	5	0.009	0.004	0.010
17	Chlorobenzene	7	0.004	0.003	0.006	7	0.019	0.004	0.040
18	Chloroethane	0				0			
19	Chloroform	2	0.082	0.004	0.16	6	0.012	0.010	0.020
20	Chloromethane	3	0.123	0.05	0.26	1	0.090	0.090	0.090
21	3-Chloropropene	0				0			
22	2-Chlorotoluene	7	0.006	0.003	0.009	7	0.027	0.006	0.040
23	4-Chlorotoluene	8	0.006	0.004	0.009	8	0.025	0.007	0.040
24	Dibromochloromethane	0				3	0.026	0.008	0.040
25	1,2-Dibromo-3-chloropropane	0				6	0.362	0.120	1.500
26	1,2-Dibromoethane	0				4	0.070	0.020	0.190
27	Dibromomethane	0				6	0.038	0.020	0.110
28	1,2-Dichlorobenzene	10	0.007	0.003	0.012	9	0.048	0.009	0.070
29	1,3-Dichlorobenzene	14	0.007	0.004	0.011	9	0.036	0.007	0.060
30	1,4-Dichlorobenzene	23	0.009	0.005	0.014	9	0.040	0.010	0.060
31	*trans*-1,4-Dichloro-2-butene	0				7	1.066	0.060	5.300
32	Dichlorodifluoromethane	0				0			
33	1,1-Dichloroethane	0				3	0.009	0.008	0.010
34	1,2-Dichloroethane	0							
35	1,1,-Dichloroethene	0				4	0.015	0.010	0.020

Table 12. Number of detections, mean concentration, and concentration ranges from carryover blanks in micrograms per liter following low- and high-concentration standards known to produce carryover at detectable concentrations using Tekmar Aquatek 50 autosamplers with LSC 2000 concentrators — Continued

Compound	Following a 1-µg/L standard (n=62)				Following a 20-µg/L standard (n=9)			
			Range				Range	
	No.	Mean	Low	High	No.	Mean	Low	High
36 *cis*-1,2-Dichloroethene	1	0.012	0.012	0.012	6	0.015	0.010	0.020
37 *trans*-1,2-Dichloroethene	0				6	0.015	0.010	0.030
38 1,2-Dichloropropane	0				4	0.013	0.010	0.020
39 1,3-Dichloropropane	0				5	0.046	0.020	0.120
40 2,2-Dichloropropane	0				0			
41 1,1-Dichloropropene	0				3	0.009	0.009	0.009
42 *cis*-1,3-Dichloropropene	0				5	0.018	0.010	0.030
43 *trans*-1,3-Dichloropropene	0				5	0.024	0.010	0.050
44 Diethyl ether	2	0.021	0.017	0.024	2	0.065	0.030	0.100
45 Diisopropyl ether	0				4	0.015	0.010	0.030
46 Ethylbenzene	7	0.005	0.003	0.009	6	0.013	0.010	0.030
47 Ethyl methacrylate	0				5	0.082	0.030	0.270
48 *o*-Ethyl toluene	5	0.005	0.003	0.007	8	0.021	0.004	0.030
49 Hexachlorobutadiene	28	0.021	0.009	0.030	9	0.218	0.010	0.490
50 Hexachloroethane	0				8	0.022	0.005	0.040
51 2-Hexanone (10, 200)[1]	18	0.134	0.086	0.180	8	3.931	0.050	19.90
52 Isopropylbenzene	8	0.127	0.003	0.99	8	0.016	0.006	0.030
53 *p*-Isopropyltoluene	10	0.004	0.003	0.005	9	0.028	0.006	0.050
54 Methyl acrylate (2, 40)[1]	0				5	0.460	0.100	1.900
55 Methylacrylonitrile (2, 40)[1]	0				5	0.420	0.100	1.700
56 Methyl iodide	1	0.03	0.03	0.03	8	0.041	0.010	0.070
57 Methyl methacrylate (2,40)[1]	0				5	0.270	0.080	1.000
58 Methylene chloride	38	0.054	0.008	0.70	7	0.030	0.010	0.090
59 4-Methyl-2-pentanone (10,200)[1]	10	0.071	0.024	0.094	6	3.300	1.000	14.00
60 Naphthalene	23	0.062	0.012	0.24	8	0.523	0.050	1.000
61 *tert*-Pentyl methyl ether	0				4	0.045	0.020	0.120
62 *n*-Propylbenzene	9	0.004	0.002	0.007	7	0.024	0.006	0.030
63 Styrene	10	0.007	0.004	0.010	8	0.028	0.005	0.040
64 1,1,1,2-Tetrachloroethane	1	0.004	0.004	0.004	6	0.017	0.009	0.040
65 1,1,2,2,-Tetrachloroethane	2	0.006	0.005	0.006	5	0.128	0.040	0.420
66 Tetrachloroethene	8	0.004	0.002	0.012	8	0.019	0.003	0.030
67 Tetrachloromethane	0				0			
68 Tetrahydrofuran (10, 200)[1]	12	0.170	0.084	0.210	6	8.067	2.800	26.60
69 1,2,3,4-Tetramethylbenzene	12	0.012	0.006	0.015	8	0.094	0.010	0.170
70 1,2,3,5-Tetramethylbenzene	13	0.009	0.004	0.021	8	0.070	0.010	0.130
71 Toluene	16	0.012	0.003	0.026	8	0.017	0.007	0.030
72 1,2,3-Trichlorobenzene	31	0.026	0.012	0.160	9	0.187	0.030	0.500
73 1,2,4-Trichlorobenzene	25	0.019	0.008	0.03	9	0.141	0.020	0.370
74 1,1,1-Trichloroethane	0				3	0.010	0.004	0.020

Table 12. Number of detections, mean concentration, and concentration ranges from carryover blanks in micrograms per liter following low- and high-concentration standards known to produce carryover at detectable concentrations using Tekmar Aquatek 50 autosamplers with LSC 2000 concentrators — Continued

	Compound	Following a 1-µg/L standard (n=62)				Following a 20-µg/L standard (n=9)			
				Range				Range	
		No.	Mean	Low	High	No.	Mean	Low	High
75	Trichloroethene	4	0.003	0.002	0.005	7	0.013	0.003	0.020
76	1,1,2-Trichloroethane	1	0.003	0.003	0.003	6	0.047	0.020	0.140
77	Trichlorofluoromethane	0				1	0.007	0.007	0.007
78	1,2,3-Trichloropropane	0				5	0.186	0.050	0.620
79	1,1,2-Trichloro-1,2,2-trifluoroethane	0				3	0.009	0.007	0.010
80	1,2,3-Trimethylbenzene	5	0.004	0.003	0.005	9	0.027	0.006	0.050
81	1,2,4-Trimethyl benzene	7	0.006	0.005	0.007	7	0.028	0.008	0.040
82	1,3,5-Trimethylbenzene	5	0.004	0.003	0.005	9	0.019	0.004	0.030
	Vinyl acetate (10, 200) [1]	3	0.02	0.016	0.023	6	0.583	0.100	2.500
83	Vinyl bromide	0				0			
84	Vinyl chloride	0				1	0.003	0.003	0.003
85	*m*- and *p*-Xylene (2, 40)[1]	11	0.009	0.003	0.014	8	0.030	0.009	0.060
86	*o*-Xylene	4	0.007	0.004	0.009	6	0.020	0.010	0.030

[1]Some concentrations are higher than 1 and 20 µg/L. Differences are noted in parentheses.

Table 13. Mean percent recoveries from a 14-day preservation study, spiked at 2 micrograms per liter (except where noted in parentheses), and preserved at pH 2 and 4

[%, percent; µg/L, micrograms per liter; nd, not determined]

	Compound	Day 1		Day 7		Day 14	
		pH 4 (%)	pH 2 (%)	pH 4 (%)	pH 2 (%)	pH 4 (%)	pH 2 (%)
1	Acetone (20)	100.8	101.9	105.7	101.4	104.6	103.4
2	Acrolein [1] (8)	96.6	91.4	90.8	83.3	82.0	72.3
3	Acrylonitrile [1] (4)	93.4	100.0	99.9	97.2	96.8	92.8
4	Benzene	99.1	98.8	100.3	98.9	95.2	93.5
5	Bromobenzene	103.1	103.9	99.9	99.4	98.9	96.9
6	Bromochloromethane	101.5	102.5	102.0	101.1	95.6	94.9
7	Bromodichloromethane	102.6	103.3	104.4	102.3	97.3	96.6
8	Bromoform	98.2	99.5	98.2	93.4	90.5	89.9
9	Bromomethane	90.8	92.6	90.2	92.1	83.6	85.6
10	2-Butanone (20)	93.3	97.1	99.6	99.1	97.8	95.1
11	*n*-Butylbenzene	103.2	103.4	98.7	95.6	94.2	91.4
12	sec-Butylbenzene	103.0	103.4	101.0	99.5	98.2	96.2
13	*tert*-Butylbenzene	104.3	104.3	102.8	101.9	99.8	97.8
14	*tert*-Butyl ethyl ether [1]	100.4	102.6	104.9	103.6	101.9	99.9
	tert-Butyl formate[2]	nd	nd	nd	nd	nd	nd
15	*tert*-Butyl methyl ether	97.8	99.4	101.8	99.9	97.3	96.5
16	Carbon disulfide	91.5	93.4	94.1	88.0	81.8	81.6
	Chloroacetonitrile (20)	98.6	101.8	102.9	101.4	100.1	100.6
17	Chlorobenzene	101.9	102.1	100.9	99.3	100.8	98.2
	1-Chlorobutane	102.0	101.4	102.9	102.2	98.3	96.6
18	Chloroethane	90.7	91.4	90.1	91.0	84.9	85.1
	bis (2-Chloroethyl) ether[1] (10)	103.5	102.6	110.0	107.4	113.3	111.9
19	Chloroform	98.0	98.1	100.1	98.3	94.8	93.4
20	Chloromethane	87.5	92.8	90.1	92.7	84.1	89.5
21	3-Chloropropene	99.0	98.3	96.4	93.3	83.3	83.8
22	2-Chlorotoluene	105.1	105.4	103.4	101.4	101.4	98.9
23	4-Chlorotoluene	104.0	102.9	101.4	98.9	99.4	96.6
24	Dibromochloromethane	103.6	105.5	103.9	101.7	99.8	98.3
25	1,2-Dibromo-3-chloropropane	97.8	102.1	98.2	92.9	90.1	96.0
26	1,2-Dibromoethane	103.3	105.6	104.9	103.4	106.6	103.2
27	Dibromomethane	101.9	102.3	103.1	102.4	99.7	98.1
28	1,2-Dichlorobenzene	102.6	104.1	101.7	100.7	101.9	99.8
29	1,3-Dichlorobenzene	102.5	102.6	99.4	97.8	98.9	96.8
30	1,4-Dichlorobenzene	101.0	102.1	99.1	96.9	99.1	96.3
31	*trans*-1,4-Dichloro-2-butene (20)	103.1	107.4	95.0	95.0	81.9	84.9
32	Dichlorodifluoromethane	80.2	88.8	80.3	85.0	71.6	81.3
33	1,1-Dichloroethane	98.8	99.1	101.6	100.2	96.3	95.6
34	1,2-Dichloroethane	100.4	101.9	104.2	103.1	101.8	100.2

Table 13. Mean percent recoveries from a 14-day preservation study, spiked at 2 micrograms per liter (except where noted in parentheses), and preserved at pH 2 and 4 — Continued

	Compound	Day 1		Day 7		Day 14	
		pH 4 (%)	pH 2 (%)	pH 4 (%)	pH 2 (%)	pH 4 (%)	pH 2 (%)
35	1,1-Dichloroethene	97.9	96.1	96.4	93.8	86.6	88.3
36	*cis*-1,2-Dichloroethene	99.4	99.0	99.4	99.0	93.3	91.8
37	*trans*-1,2-Dichloroethene	98.8	98.6	98.6	96.4	90.8	88.7
38	1,2-Dichloropropane	99.5	101.1	102.1	101.1	98.6	98.1
39	1,3-Dichloropropane	100.2	102.2	102.7	101.4	106.5	104.4
40	2,2-Dichloropropane	95.4	93.1	74.3	73.1	49.6	54.1
41	1,1-Dichloropropene	101.1	100.0	101.2	99.0	95.6	93.8
42	*cis*-1,3-Dichloropropene	102.6	104.0	96.1	94.4	83.6	83.9
43	*trans*-1,3-Dichloropropene	103.6	102.9	98.6	97.4	86.8	88.6
44	Diethyl ether	97.7	98.9	100.3	99.6	95.8	94.0
45	Diisopropyl ether [2]	nd	nd	nd	nd	nd	nd
	1,4-Dioxane [1] (80)	111.3	113.6	111.9	109.2	109.8	107.2
46	Ethyl benzene	102.9	102.7	101.5	100.1	100.0	97.1
47	Ethyl methacrylate	99.4	103.3	104.9	102.4	101.2	99.7
48	*o*-Ethyl toluene	103.7	104.5	102.6	102.1	100.4	98.8
49	Hexachlorobutadiene	101.1	101.1	95.0	92.5	89.9	87.2
50	Hexachloroethane [1]	107.1	105.6	104.9	102.0	99.8	99.2
51	2-Hexanone	98.9	103.8	104.7	103.5	109.6	105.3
52	Isopropylbenzene	102.6	102.8	100.9	99.1	98.5	95.8
53	p-Isopropyl toluene	104.9	104.6	101.6	99.4	97.9	94.9
54	Methyl acrylate (4)	102.2	104.8	104.7	104.8	103.0	100.5
55	Methyl acrylonitrile (4)	102.3	104.4	106.3	103.0	100.1	99.8
56	Methyl iodide	98.6	97.9	96.2	96.0	88.0	85.8
57	Methyl methacrylate	99.4	103.3	104.9	102.4	101.2	99.7
58	Methylene chloride	93.6	93.4	95.7	93.8	95.3	88.7
59	4-Methyl-2-pentanone (20)	102.3	105.1	106.8	105.6	105.4	103.2
60	Naphthalene	100.7	104.4	105.6	102.4	106.9	104.4
	Nitrobenzene (80)	73.9	69.9	69.3	62.6	59.9	60.4
	2-Nitropropane (20)	97.4	97.5	99.4	95.4	91.0	92.7
	Pentachloroethane	112.1	112.9	110.4	108.9	105.9	106.0
	Propionitrile	101.9	103.4	104.1	105.4	104.6	102.8
61	*tert*-Pentyl methyl ether [1]	98.1	100.2	101.1	99.7	97.7	97.0
62	*n*-Propylbenzene	104.4	103.6	100.2	98.5	97.2	93.9
63	Styrene	106.9	108.2	108.2	105.6	107.0	102.8
64	1,1,1,2-Tetrachloroethane	104.6	104.4	102.4	101.1	101.9	100.2
65	1,1,2,2-Tetrachloroethane	99.9	103.0	101.1	100.1	102.8	102.1
66	Tetrachloroethene	96.1	93.7	89.9	86.9	87.8	84.4
67	Tetrachloromethane	101.9	99.3	100.1	98.6	93.1	92.3
68	Tetrahydrofuran (20)	101.1	103.7	105.6	104.0	102.0	100.0
69	1,2,3 4-Tetramethylbenzene	102.4	106.2	105.5	103.2	104.4	101.0
70	1,2,3,5-Tetramethylbenzene	102.5	105.6	103.8	101.7	102.1	98.3

Table 13. Mean percent recoveries from a 14-day preservation study, spiked at 2 micrograms per liter (except where noted in parentheses), and preserved at pH 2 and 4 — Continued

	Compound	Day 1		Day 7		Day 14	
		pH 4 (%)	pH 2 (%)	pH 4 (%)	pH 2 (%)	pH 4 (%)	pH 2 (%)
71	Toluene	98.7	97.6	97.1	96.3	92.8	90.7
72	1,2,3-Trichlorobenzene	101.2	103.6	103.3	101.1	102.4	100.4
73	1,2,4-Trichlorobenzene	102.8	104.9	103.1	100.5	102.0	99.6
74	1,1,1-Trichloroethane	100.1	99.1	99.3	98.4	92.8	92.1
75	1,1,2-Trichloroethane	101.0	104.6	102.2	100.9	104.1	102.3
76	Trichloroethene	100.8	99.6	99.9	98.5	93.8	92.1
77	Trichlorofluoromethane	96.6	97.2	95.6	95.2	88.3	89.9
78	1,2,3-Trichloropropane	106.9	108.0	109.4	105.6	107.9	107.1
79	1,1,2-Trichloro-1,2,2-trifluoroethane	96.4	95.4	91.2	89.0	80.1	81.2
80	1,2,3-Trimethylbenzene	103.0	104.6	103.6	102.1	103.0	100.1
81	1,2,4-Trimethylbenzene	103.4	104.3	103.2	101.3	101.2	97.9
82	1,3,5-Trimethylbenzene	104.7	105.3	102.6	101.2	100.9	96.7
	Vinyl acetate (20)	103.1	103.1	105.8	92.9	98.9	75.9
83	Vinyl bromide [1]	98.7	97.3	97.5	96.0	89.1	87.5
84	Vinyl chloride	91.9	96.6	94.4	96.2	88.0	92.1
85	*m*- and *p*-Xylene (4)	102.9	102.7	101.5	100.1	100.0	97.1
86	*o*-Xylene	102.5	102.5	100.4	99.2	99.1	96.0

[1]This compound was selected by the National Water-Quality Assessment Program as a proposed compound for the volatile organic compound (VOC) method. These VOCs are not in USEPA Method 524.2, Revision 4.1 (Munch, 1995).

[2]After this test was completed, diisopropyl ether and *tert*-butyl formate were added to the selected compound list.

Table 14. Results of a 0.5-microgram-per-liter (or greater) preservation study in ground water from a well in Conifer, Colorado, preserved at pH 2

[µg/L, microgram per liter; %, percent; RSD, relative standard deviation; <, less than; E, estimated. Day 1 results are equivalent to 100 percent for all recovery calculations and include background concentrations listed in column 2. Recovery calculations represent the mean of five replicate spikes]

	Compound	Unspiked sample concentration (µg/L)	Day 1 (µg/L)	Day 1 % Recovery	Day 14 % Recovery	Day 28 % Recovery	Day 37 % Recovery	Day 47 % Recovery	Day 56 % Recovery	% RSD[1]
1	Acetone	<5	6.335	100	94	91	98	96	104	4.72
2	Acrolein	<2	31.820	100	70	51	70	70	57	16.89
3	Acrylonitrile	<2	15.583	100	107	95	74	75	88	13.30
4	Benzene	E0.01	0.567	100	101	103	100	104	108	3.16
5	Bromobenzene	<0.05	0.564	100	100	99	100	104	106	2.77
6	Bromochloromethane	<0.1	0.575	100	100	101	101	106	110	4.06
7	Bromodichloromethane	<0.1	0.560	100	105	98	105	113	108	5.40
8	Bromoform	<0.2	0.582	100	94	86	106	124	104	12.90
9	Bromomethane	<0.1	0.530	100	92	80	111	104	72	14.89
10	2-Butanone	<5	6.079	100	97	83	100	96	104	7.13
11	*n*-Butylbenzene	<0.05	0.496	100	91	93	80	88	87	6.68
12	*sec*-Butylbenzene	<0.05	0.565	100	96	96	90	94	97	3.37
13	*tert*-Butylbenzene	<0.05	0.535	100	100	100	96	99	104	2.52
14	*tert*-Butyl ethyl ether	<0.1	0.580	100	103	92	103	104	107	5.13
15	*tert*-Butyl methyl ether	<0.1	0.640	100	103	94	105	106	107	4.74
16	Carbon disulfide	<0.05	0.590	100	103	100	99	104	101	1.79
17	Chlorobenzene	<0.05	0.563	100	100	101	97	101	106	2.76
18	Chloroethane	<0.1	0.476	100	105	104	104	107	107	2.65
19	Chloroform	<0.05	0.577	100	103	104	100	105	105	2.53
20	Chloromethane	<0.2	0.515	100	102	101	94	97	107	4.57
21	3-Chloropropene	<0.1	1.048	100	98	93	91	94	93	3.30
22	2-Chlorotoluene	<0.05	0.558	100	98	98	94	97	102	2.84
23	4-Chlorotoluene	<0.05	0.559	100	98	96	94	98	100	2.59
24	Dibromochloromethane	<0.1	0.564	100	99	91	101	109	105	6.09
25	1,2-Dibromo-3-chloropropane	<0.5	0.567	100	95	93	100	106	98	4.38
26	1,2-Dibromoethane	<0.1	0.571	100	101	96	102	104	107	3.84
27	Dibromomethane	<0.1	0.559	100	103	100	104	107	110	3.88
28	1,2-Dichlorobenzene	<0.05	0.579	100	99	99	98	103	104	2.39
29	1,3-Dichlorobenzene	<0.05	0.577	100	98	95	94	97	99	2.17
30	1,4-Dichlorobenzene	<0.05	0.568	100	96	95	94	99	99	2.61
31	*trans*-1,4-Dichloro-2-butene	<5	5.684	100	86	67	77	83	74	11.51
32	Dichlorodifluoromethane	<0.2	0.476	100	102	104	88	90	92	7.02
33	1,1-Dichloroethane	<0.05	0.566	100	105	104	101	104	111	3.64
34	1,2-Dichloroethane	<0.05	0.580	100	101	95	99	101	107	4.01
35	1,1-Dichloroethene	<0.1	0.520	100	110	109	103	105	109	3.97
36	cis-1,2-Dichloroethene	<0.05	0.531	100	105	107	102	105	112	4.30
37	*trans*-1,2-Dichloroethene	<0.05	0.525	100	109	110	102	105	108	4.16
38	1,2-Dichloropropane	<0.05	0.571	100	99	95	97	98	106	3.57
39	1,3-Dichloropropane	<0.05	0.539	100	102	96	101	105	108	4.31

Table 14. Results of a 0.5-microgram-per-liter (or greater) preservation study in ground water from a well in Conifer, Colorado, preserved at pH 2 — Continued

	Compound	Unspiked sample concentration (µg/L)	Day 1 (µg/L)	Day 1 % Recovery	Day 14 % Recovery	Day 28 % Recovery	Day 37 % Recovery	Day 47 % Recovery	Day 56 % Recovery	% RSD[1]
40	2,2-Dichloropropane	<0.05	0.528	100	90	78	67	61	58	16.80
41	1,1-Dichloropropene	<0.05	0.521	100	110	110	104	107	109	4.08
42	cis-1,3-Dichloropropene	<0.1	0.553	100	99	89	88	91	89	5.33
43	*trans*-1,3-Dichloropropene	<0.1	0.542	100	99	90	92	94	92	4.15
44	Diethyl ether	<0.1	1.120	100	101	93	99	102	111	5.82
45	Diisopropyl ether	<0.1	0.609	100	99	92	102	103	112	6.43
46	Ethylbenzene	<0.05	0.558	100	100	99	96	99	104	2.53
47	Ethyl methacrylate	<1	2.892	100	95	82	92	94	98	6.18
48	*o*-Ethyl toluene	<0.05	0.618	100	98	97	96	100	99	1.80
49	Hexachlorobutadiene	<0.2	0.580	100	91	93	84	87	86	5.98
50	Hexachloroethane	<0.05	0.592	100	102	105	105	117	95	7.37
51	2-Hexanone	<5	5.861	100	99	82	99	101	103	7.43
52	Isopropylbenzene	<0.05	0.603	100	92	91	87	91	95	4.25
53	*p*-Isopropyltoluene	<0.05	0.539	100	94	96	86	91	92	4.73
54	Methyl acrylate	<2	2.722	100	98	82	96	99	99	6.73
55	Methyl acrylonitrile	<2	2.825	100	97	88	100	103	102	5.35
56	Methylene chloride	<0.138	0.613	100	103	102	103	105	112	3.98
57	Methyl iodide	<0.05	0.538	100	97	80	95	95	91	7.27
58	Methyl methacrylate	<1	3.002	100	95	82	91	94	92	6.14
59	4-Methyl-2-pentanone	<5	5.909	100	97	86	100	101	104	6.37
60	Naphthalene	<0.2	0.478	100	108	99	99	121	97	9.28
61	*tert*-Pentyl methyl ether	<0.1	0.579	100	103	92	102	103	105	4.66
62	*n*-Propylbenzene	<0.05	0.535	100	95	96	91	95	96	2.97
63	Styrene	<0.05	0.548	100	85	75	72	73	69	11.66
64	1,1,1,2-Tetrachloroethane	<0.05	0.545	100	100	99	98	104	105	2.90
65	1,1,2,2-Tetrachloroethane	<0.1	0.583	100	98	88	100	105	105	6.03
66	Tetrachloroethene	<0.05	0.553	100	99	101	94	94	100	2.98
67	Tetrachloromethane	<0.05	0.552	100	103	102	101	107	106	2.85
68	Tetrahydrofuran	<5	5.847	100	99	90	102	104	113	7.53
69	1,2,3,4-Tetramethylbenzene	<0.05	0.530	100	89	89	80	96	79	8.55
70	1,2,3,5-Tetramethylbenzene	<0.05	0.522	100	85	85	71	80	70	11.10
71	Toluene	<0.05	0.585	100	99	100	97	100	101	1.53
72	1,2,3-Trichlorobenzene	<0.2	0.543	100	101	102	97	110	109	5.29
73	1,2,4-Trichlorobenzene	<0.2	0.527	100	94	97	909	102	97	4.37
74	1,1,1-Trichloroethane	<0.05	0.552	100	104	106	101	104	108	3.12
75	1,1,2-Trichloroethane	<0.1	0.587	100	99	93	99	103	106	4.28
76	Trichloroethene	<0.05	0.539	100	104	104	100	102	109	3.30
77	Trichlorofluoromethane	<0.1	0.479	100	116	119	106	108	115	7.31
78	1,2,3-Trichloropropane	<0.2	0.563	100	101	92	103	105	112	6.38
79	1,1,2-Trichloro-1,2,2-trifluoroethane	<0.05	0.604	100	110	111	110	113	116	5.46
80	1,2,3-Trimethylbenzene	<0.05	0.558	100	94	94	91	98	94	3.22
81	1,2,4-Trimethylbenzene	<0.05	0.549	100	90	87	80	85	82	7.16
82	1,3,5-Trimethylbenzene	<0.05	0.524	100	94	92	87	91	92	4.14

Table 14. Results of a 0.5-microgram-per-liter (or greater) preservation study in ground water from a well in Conifer, Colorado, preserved at pH 2 — Continued

	Compound	Unspiked sample concentration (µg/L)	Day 1 (µg/L)	Day 1 % Recovery	Day 14 % Recovery	Day 28 % Recovery	Day 37 % Recovery	Day 47 % Recovery	Day 56 % Recovery	% RSD[1]
	Vinyl acetate	<5	6.992	100	78	53	89	125	52	28.15
83	Vinyl bromide	<0.1	0.495	100	106	110	118	125	131	11.72
84	Vinyl chloride	<0.1	0.492	100	107	108	104	106	98	3.83
85	*m*- and *p*-Xylene	<0.05	1.097	100	98	95	92	95	99	3.05
86	*o*-Xylene	<0.05	0.564	100	100	98	96	100	105	2.75
	[2]*p*-Bromofluorobenzene (surrogate)	97	101	100	99	95	100	103	99	2.44
	[2]1,2-Dichloroethane-d_4	99	103	100	96	92	97	97	97	2.60
	[2]Toluene-d_8	99	100	100	99	101	98	100	100	0.88

[1]Represents the %RSD of these 30 replicate spikes.

[2]Surrogate compound spiked at 1 µg/L and reported in percent recovery in column 2.

Table 15. Results of a 0.5-microgram-per-liter (or greater) preservation study in surface water from Bear Creek, Morrison, Colorado, preserved at pH 2

[µg/L, microgram per liter; %, percent; RSD, relative standard deviation; <, less than; E, estimated. Day 1 results are equivalent to 100 percent for all recovery calculations and include background concentrations listed in column 2. Recovery calculations represent the mean of five replicate spikes]

	Compound	Unspiked sample concentration (µg/L)	Day 1 (µg/L)	Day 1 % Recovery	Day 14 % Recovery	Day 28 % Recovery	Day 37 % Recovery	Day 47 % Recovery	Day 56 % Recovery	% RSD[1]
1	Acetone	<5	7.083	100	104	99	109	107	121	7.42
2	Acrolein	<2	30.190	100	55	13	6	0	0	139.67
3	Acrylonitrile	<2	15.187	100	113	99	79	79	96	14.32
4	Benzene	E0.06	0.611	100	101	103	102	104	110	3.47
5	Bromobenzene	<0.05	0.549	100	104	101	104	107	111	4.00
6	Bromochloromethane	<0.1	0.570	100	104	101	1035	105	112	3.98
7	Bromodichloromethane	<0.1	0.548	100	107	100	109	115	115	6.43
8	Bromoform	<0.2	0.584	100	99	87	112	123	105	11.84
9	Bromomethane	<0.1	0.517	100	87	76	98	99	69	14.99
10	2-Butanone	<5	6.031	100	104	88	106	102	89	7.65
11	*n*-Butylbenzene	<0.05	0.504	100	93	92	81	90	86	6.96
12	*sec*-Butylbenzene	<0.05	0.573	100	96	95	92	95	98	2.92
13	*tert*-Butylbenzene	<0.05	0.537	100	99	98	97	100	104	2.53
14	*tert*-Butyl ethyl ether	<0.1	0.561	100	107	96	107	108	115	6.21
15	*tert*-Butyl methyl ether	1.504	2.109	100	109	99	110	111	117	6.47
16	Carbon disulfide	<0.05	0.592	100	101	97	99	105	101	2.60
17	Chlorobenzene	<0.05	0.561	100	101	100	98	101	108	3.44
18	Chloroethane	<0.1	0.456	100	109	108	105	109	112	3.87
19	Chloroform	E0.02	0.595	100	105	107	103	107	108	2.93
20	Chloromethane	<0.2	0.503	100	97	99	93	96	115	7.46
21	3-Chloropropene	<0.1	1.054	100	98	94	93	98	98	2.77
22	2-Chlorotoluene	<0.05	0.552	100	98	98	97	100	105	2.91
23	4-Chlorotoluene	<0.05	0.560	100	97	96	94	98	100	2.42
24	Dibromochloromethane	<0.1	0.556	100	103	91	103	112	110	7.24
25	1,2-Dibromo-3-chloropropane	<0.5	0.545	100	104	98	110	116	109	6.48
26	1,2-Dibromoethane	<0.1	0.553	100	107	99	108	108	116	5.67
27	Dibromomethane	<0.1	0.551	100	107	102	105	109	114	4.81
28	1,2-Dichlorobenzene	<0.05	0.567	100	104	101	101	105	111	3.77
29	1,3-Dichlorobenzene	<0.05	0.566	100	100	98	97	99	104	2.41
30	1,4-Dichlorobenzene	<0.05	0.557	100	98	93	97	99	103	3.33
31	*trans*-1,4-Dichloro-2-butene	<5	5.476	100	93	73	84	92	83	10.89
32	Dichlorodifluoromethane	<0.2	0.404	100	103	105	89	93	93	6.60
33	1,1-Dichloroethane	<0.05	0.560	100	105	105	103	104	113	4.26
34	1,2-Dichloroethane	<0.05	0.564	100	104	100	104	104	111	4.12
35	1,1-Dichloroethene	<0.1	0.522	100	110	113	107	111	119	5.80
36	*cis*-1,2-Dichloroethene	<0.05	0.528	100	105	106	102	104	112	3.84
37	*trans*-1,2-Dichloroethene	<0.05	0.520	100	110	112	103	109	113	4.84
38	1,2-Dichloropropane	<0.05	0.560	100	102	98	99	100	110	4.27

Table 15. Results of a 0.5-microgram-per-liter (or greater) preservation study in surface water from Bear Creek, Morrison, Colorado, preserved at pH 2 — Continued

	Compound	Unspiked sample concentration (µg/L)	Day 1 (µg/L)	Day 1 % Recovery	Day 14 % Recovery	Day 28 % Recovery	Day 37 % Recovery	Day 47 % Recovery	Day 56 % Recovery	% RSD[1]
39	1,3-Dichloropropane	<0.05	0.530	100	105	99	106	106	112	4.48
40	2,2-Dichloropropane	<0.05	0.525	100	92	84	71	67	63	18.56
41	1,1-Dichloropropene	<0.05	0.515	100	113	113	109	111	117	5.19
42	*cis*-1,3-Dichloropropene	<0.1	0.547	100	102	92	92	91	96	5.03
43	*trans*-1,3-Dichloropropene	<0.1	0.538	100	105	94	98	97	96	4.07
44	Diethyl ether	<0.1	1.083	100	107	98	105	104	120	7.25
45	Diisopropyl ether	<0.1	0.604	100	99	93	104	104	120	8.76
46	Ethylbenzene	E0.009	0.565	100	100	99	98	100	105	2.33
47	Ethyl methacrylate	<1	2.797	100	105	71	58	33	21	53.03
48	*o*-Ethyl toluene	<0.05	0.620	100	98	97	98	103	102	2.27
49	Hexachlorobutadiene	<0.2	0.590	100	90	91	84	88	89	5.87
50	Hexachloroethane	<0.05	0.604	100	101	103	104	116	94	7.20
51	2-Hexanone	<5	5.636	100	107	80	81	58	45	30.19
52	Isopropylbenzene	<0.05	0.607	100	91	91	89	91	96	4.51
53	*p*-Isopropyltoluene	<0.05	0.545	100	94	83	65	52	40	33.16
54	Methyl acrylate	<2	2.620	100	102	64	52	28	16	59.34
55	Methyl acrylonitrile	<2	2.759	100	103	94	107	108	111	6.06
56	Methylene chloride	<0.1	0.608	100	105	102	103	106	115	5.08
57	Methyl iodide	<0.05	0.529	100	94	82	94	94	80	8.65
58	Methyl methacrylate	<1	2.925	100	107	103	126	126	124	10.90
59	4-Methyl-2-pentanone	<5	5.775	100	106	90	101	92	91	6.94
60	Naphthalene	<0.2	0.495	100	138	124	125	151	132	13.28
61	*tert*-Pentyl methyl ether	<0.1	0.568	100	107	97	106	107	113	5.38
62	*n*-Propylbenzene	<0.05	0.534	100	97	96	93	97	99	2.55
63	Styrene	<0.05	0.537	100	96	92	93	94	99	3.51
64	1,1,1,2-Tetrachloroethane	<0.05	0.542	100	101	100	101	105	108	3.23
65	1,1,2,2-Tetrachloroethane	<0.1	0.571	100	104	93	105	108	111	6.00
66	Tetrachloroethene	<0.05	0.546	100	100	101	96	96	103	2.98
67	Tetrachloromethane	<0.05	0.556	100	104	101	102	110	109	4.04
68	Tetrahydrofuran	<5	5.643	100	110	98	112	112	122	8.15
69	1,2,3,4-Tetramethylbenzene	<0.05	0.535	100	109	109	102	120	107	6.57
70	1,2,3,5-Tetramethylbenzene	<0.05	0.529	100	103	106	94	106	101	4.49
71	Toluene	E0.05	0.621	100	99	100	98	101	103	1.65
72	1,2,3-Trichlorobenzene	<0.2	0.543	100	107	105	103	116	114	5.81
73	1,2,4-Trichlorobenzene	<0.2	0.528	100	99	99	94	105	103	3.80
74	1,1,2-Trichloroethane	<0.1	0.567	100	105	99	104	105	114	5.15
75	1,1,1-Trichloroethane	<0.05	0.555	100	103	106	101	104	110	3.57
76	Trichloroethene	<0.05	0.543	100	105	105	101	104	111	3.80
77	Trichlorofluoromethane	<0.1	0.459	100	114	117	106	106	114	5.95
78	1,2,3-Trichloropropane	<0.2	0.539	100	108	99	109	112	127	9.21
79	1,1,2-Trichloro-1,2,2-trifluoroethane	<0.05	0.603	100	109	109	108	115	116	5.23
80	1,2,3-Trimethylbenzene	<0.05	0.555	100	99	98	99	105	104	2.60

Table 15. Results of a 0.5-microgram-per-liter (or greater) preservation study in surface water from Bear Creek, Morrison, Colorado, preserved at pH 2 — Continued

	Compound	Unspiked sample concentration (µg/L)	Day 1 (µg/L)	Day 1 % Recovery	Day 14 % Recovery	Day 28 % Recovery	Day 37 % Recovery	Day 47 % Recovery	Day 56 % Recovery	% RSD[1]
81	1,2,4-Trimethylbenzene	<0.05	0.563	100	96	96	93	98	99	2.66
82	1,3,5-Trimethylbenzene	<0.05	0.523	100	97	96	94	97	101	2.86
	Vinyl acetate	<5	6.658	100	74	17	15	7	0	115.61
83	Vinyl bromide	<0.1	0.489	100	107	111	121	125	136	11.32
84	Vinyl chloride	<0.1	0.469	100	107	109	106	107	103	3.02
85	*m*- and *p*-Xylene	E0.02	1.114	100	99	97	95	98	103	2.64
86	*o*-Xylene	<0.05	0.571	100	101	98	99	101	109	3.81
	[2]*p*-Bromofluorobenzene	98	100	100	102	98	105	105	103	2.98
	[2]1,2-Dichloroethane-d_4	103	101	100	102	94	101	100	102	3.16
	[2]Toluene-d_8	100	100	100	99	99	100	99	101	0.59

[1]Represents the % RSD of these 30 replicate spikes.

[2]Surrogate compound spiked at 1 µg/L and reported in percent recovery in column 2.