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METHOD 524.4 MEASUREMENT OF PURGEABLE ORGANIC COMPOUNDS IN WATER BY GAS CHROMATOGRAPHY/MASS SPECTROMETRY USING NITROGEN PURGE GAS

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Foreword

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METHOD 524.4

MEASUREMENT OF PURGEABLE ORGANIC COMPOUNDS IN WATER BY GAS CHROMATOGRAPHY/MASS SPECTROMETRY USING NITROGEN PURGE GAS

1. SCOPE AND APPLICATION

1.1 This is a gas chromatography/mass spectrometry (GC/MS) method for the determination of purgeable organic compounds in finished drinking waters. Discontinuous scanning modes such as selected ion monitoring (SIM) and selected ion storage (SIS) are permitted for determining selected analytes that are monitored at levels too low for the full scan detection mode. Precision and accuracy data have been generated for the method analytes in reagent water, drinking water from a groundwater source and drinking water from a surface water source. The single laboratory Lowest Concentration Minimum Reporting Level (LCMRL) has also been determined in reagent water. The following compounds can be determined using this method:

Analyte	Chemical Abstract Services Registry Number (CASRN)
1,1,1,2-tetrachloroethane	630-20-6
1,1,1-trichloroethane	71-55-6
1,1,2,2-tetrachloroethane	79-34-5
1,1,2-trichloroethane	79-00-5
1,1-dichloroethane	75-34-3
1,1-dichloroethene	75-35-4
1,1-dichloropropene	563-58-6
1,2,3-trichlorobenzene	87-61-6
1,2,3-trichloropropane	96-18-4
1,2,4-trichlorobenzene	120-82-1
1,2,4-trimethylbenzene	95-63-6
1,2-dibromo-3-chloropropane	96-12-8
1,2-dibromoethane	106-93-4
1,2-dichlorobenzene	95-50-1
1,2-dichloroethane	107-06-2
1,2-dichloropropane	78-87-5
1,3,5-trimethylbenzene	108-67-8
1,3-butadiene	106-99-0
1,3-dichlorobenzene	541-73-1
1,3-dichloropropane	142-28-9
1,4-dichlorobenzene	106-46-7
1-chlorobutane	109-69-3
2-chlorotoluene	95-49-8
4-chlorotoluene	106-43-4

Analyte	Chemical Abstract Services Registry Number (CASRN)
4-isopropyltoluene	99-87-6
allyl chloride	107-05-1
benzene	71-43-2
bromobenzene	108-86-1
bromochloromethane	74-97-5
bromodichloromethane	75-27-4
bromoform	75-25-2
bromomethane	74-83-9
carbon disulfide	75-15-0
carbon tetrachloride	56-23-5
chlorobenzene	108-90-7
chlorodifluoromethane	75-45-6
chloroform	67-66-3
chloromethane	74-87-3
cis-1,2-dichloroethene	156-59-2
cis-1,3-dichloropropene	10061-01-5
dibromochloromethane	124-48-1
dibromomethane	74-95-3
dichlorodifluoromethane	75-71-8
diethyl ether	60-29-7
diisopropyl ether (DIPE)	108-20-3
ethyl methacrylate	97-63-2
ethylbenzene	100-41-4
hexachlorobutadiene	87-68-3
hexachloroethane	67-72-1
isopropylbenzene	98-82-8
methyl acetate	79-20-9
methyl iodide	74-88-4
methylene chloride	75-09-2
methyl-t-butyl ether (MtBE)	1634-04-4
m-xylene	108-38-3
naphthalene	91-20-3
n-butylbenzene	104-51-8
n-propylbenzene	103-65-1
o-xylene	95-47-6
pentachloroethane	76-01-7
p-xylene	106-42-3
sec-butylbenzene	135-98-8
styrene	100-42-5
t-amyl ethyl ether (TAEE)	919-94-8

Analyte	Chemical Abstract Services Registry Number (CASRN)
t-amyl methyl ether (TAME)	994-05-8
t-butyl alcohol (TBA)	75-65-0
t-butyl ethyl ether (ETBE)	637-92-3
t-butylbenzene	98-06-6
tetrachloroethene	127-18-4
tetrahydrofuran	109-99-9
toluene	108-88-3
trans-1,2-dichloroethene	156-60-5
trans-1,3-dichloropropene	10061-02-6
trichloroethene	79-01-6
trichlorofluoromethane	75-69-4
vinyl chloride	75-01-4

1.2 The ranges for purge-and-trap parameters specified in Section 9.1 are applicable to the use of nitrogen purge gas; helium may not be used. The mass spectrometry conditions described in this method were developed using a gas chromatograph (GC) interfaced to a quadrupole mass spectrometer (MS).

1.3 The single laboratory LCMRL is the lowest spiking concentration such that the probability of spike recovery in the 50% to 150% range is at least 99%. Single laboratory LCMRLs for the analytes in this method ranged from 0.10 to 0.62 microgram per liter (µg/L) in the full scan mode (Table 6). Single laboratory LCMRLs were also determined for selected analytes in the selected ion monitoring (SIM) mode (Table 10). The procedure used to determine the LCMRL is described elsewhere.[1]

1.4 Laboratories using this method are not required to determine LCMRLs, but they must demonstrate that the minimum reporting level (MRL) for each analyte meets the requirements described in Section 9.2.4.

1.5 Detection limit (DL) is defined as the statistically calculated minimum concentration that can be measured with 99% confidence that the reported value is greater than zero.[2] The DL is dependent on sample matrix, fortification concentration and instrument performance. Determining the DL for analytes in this method is optional (Sect. 9.2.6). DLs for method analytes fortified into reagent water ranged from 0.026 to 0.18 µg/L in the full scan mode. These values are presented in Table 6. DLs were also determined for selected analytes in SIM mode (Table 10).

1.6 This method is intended for use by analysts skilled in the technique of purge-and-trap concentration, the operation of GC/MS instrumentation and the interpretation of the associated data.

1.7 METHOD FLEXIBILITY – To accommodate technological advances in analytical instrumentation and techniques, the laboratory is permitted to modify purge-and-trap parameters and the GC/MS conditions. Because the purge-and-trap technique has a significant number of analyst-chosen parameters and because it employs a procedural

calibration, the authors have determined an acceptable range of purge-and-trap conditions that may be used (Sect. 9.1) and a means by which to evaluate method modifications (Sect. 9.4). **Changes may not be made to sample collection and preservation (Sect. 8) or to the quality control (QC) requirements (Sect. 9)**. Modifications that are introduced solely in the interest of reducing cost or sample processing time, but result in poorer method performance, may not be used. The option to operate the MS in SIM or SIS mode is restricted to analytes that cannot be effectively analyzed in full scan mode, e.g., 1,2-dibromoethane and 1,2-dibromo-3-chloropropane. The SIM detection mode should not be used to enhance analyte signal for instrumentation that is not properly optimized and maintained. Compliance monitoring for trihalomethanes (THMs) must be conducted in the full scan detection mode. In all cases where allowed method modifications are made, the analyst must perform the procedures outlined in the Initial Demonstration of Capability (IDC, Sect. 9.2), verify that all QC acceptance criteria in this method (Tables 12 and 13) are met and verify method performance in real sample matrices (Sect. 9.4.4).

NOTE: This description of method flexibility is a brief summary. Additional specific detail is provided throughout the method, which supersedes the above general guidance.

2. SUMMARY OF METHOD

Headspace-free samples are collected in amber, glass vials with polytetrafluoroethylene (PTFE)-faced septa. Samples are dechlorinated with ascorbic acid and the pH is adjusted with maleic acid. A 5.0-milliliter (mL) aliquot of the sample is transferred to a glass sparging vessel along with appropriate amounts of internal standard and quality control compounds. The method analytes are purged from the water using nitrogen and trapped on a sorbent material. After purging, the trap may be dry purged for a short period to remove water. The trap is then heated and backflushed with GC carrier gas to transfer the analytes directly into the gas chromatographic inlet. The inlet is operated in the split mode in order to achieve the desired desorb flow rates and further reduce water transmission. Analytes are transferred onto a capillary GC column, which is temperature programmed to optimize the separation of method analytes. Compounds eluting from the GC are directed into a mass spectrometer for detection and quantitation. The method analytes are identified by comparing the acquired mass spectra and retention times to reference spectra and retention times. The concentration of each analyte is calculated using the internal standard technique and response curves obtained via procedural calibration (Sect. 3.18).

3. DEFINITIONS

3.1 ANALYSIS BATCH – A sequence of samples, analyzed within a 24-hour period, including no more than 20 field samples. Each Analysis Batch must also include all required QC samples, which do not contribute to the maximum field sample total of 20. The required QC samples include:

Laboratory Reagent Blank (LRB),
Continuing Calibration Check (CCC) Standards,
Laboratory Fortified Sample Matrix (LFSM) and
Laboratory Fortified Sample Matrix Duplicate or Field Duplicate (LFSMD or FD).

3.2 CALIBRATION STANDARD – An aqueous solution of the method analytes prepared from the Primary Dilution Standard solution. The calibration standard solutions are used to calibrate the instrument response with respect to analyte concentration.

3.3 CONTINUING CALIBRATION CHECK (CCC) – A calibration standard containing the method analytes, internal standards and surrogate analytes, which is analyzed periodically to verify the accuracy of the existing calibration.

3.4 DESORB FLOW RATE – The rate at which gas is passed through the sorbent trap during the desorb cycle. The desorb flow rate is approximately equal to the total flow rate through the GC inlet (mL/min).

3.5 DETECTION LIMIT (DL) – The minimum concentration of an analyte that can be identified, measured and reported with 99% confidence that the analyte concentration is greater than zero. This is a statistical determination (Sect. 9.2.6) and accurate quantitation is not expected at this level.

3.6 DRY PURGE VOLUME – The total volume of purge gas (mL) bypassing the sparging vessel and passing through the sorbent trap during the dry purge cycle (used as a moisture control measure).

3.7 FIELD DUPLICATE (FD) – Separate samples collected at the same time, shipped and stored under identical conditions. Method precision, including the contribution from sample collection procedures, is estimated from the analysis of FDs. For the purposes of this method, FDs are necessary to conduct repeat analyses if the original field sample is lost or to conduct repeat analyses in the case of QC failures associated with the analysis of the original field sample. FDs are used to prepare Laboratory Fortified Sample Matrix (Sect. 3.11) and Laboratory Fortified Sample Matrix Duplicate (Sect. 3.12) QC samples.

3.8 FIELD REAGENT BLANK (FRB) – An aliquot of reagent water that is placed in a sample container in the laboratory and treated as a sample in all respects, including shipment to the sampling site, exposure to sampling site conditions, storage, preservation and all analytical procedures. The purpose of the FRB is to determine if method analytes or other interferences are introduced into the samples during transport and storage.

3.9 INTERNAL STANDARD (IS) – A pure compound added to all standard solutions, field samples and QC samples in a known amount. Each internal standard is assigned to a specific analyte or multiple analytes and is used to measure relative response.

3.10 LABORATORY FORTIFIED BLANK (LFB) – An aliquot of reagent water to which known quantities of the method analytes are added. The LFB is analyzed in the same manner as a sample, including the preservation procedures in Section 8. The LFB is used during the Initial Demonstration of Capability to verify method performance for precision and accuracy.

3.11 LABORATORY FORTIFIED SAMPLE MATRIX (LFSM) – A FD to which known quantities of the method analytes are added. The LFSM is processed and analyzed as a sample and its purpose is to determine whether the sample matrix contributes bias to the analytical results. For this method, separate field samples are required for preparing fortified matrix so that sampling error is included in the accuracy estimate.

3.12 LABORATORY FORTIFIED SAMPLE MATRIX DUPLICATE (LFSMD) – A second FD, of the same sample used to prepare the LFSM, which is fortified identically to the LFSM. The LFSMD is used instead of the FD to assess method precision and accuracy when the occurrence of the method analytes is infrequent. For this method, separate field samples are required for preparing fortified matrix so that sampling error is included in the precision estimate.

3.13 LABORATORY REAGENT BLANK (LRB) – An aliquot of reagent water containing the preservatives, internal standards and surrogate analytes. The LRB is used to determine if the method analytes or interferences are introduced from the laboratory environment, the reagents or glassware. The LRB is also used to test for cross contamination in the purge-and-trap system.

3.14 LOWEST CONCENTRATION MINIMUM REPORTING LEVEL (LCMRL) – The single laboratory LCMRL is the lowest spiking concentration such that the probability of spike recovery in the 50% to 150% range is at least 99%.[1]

3.15 MATERIAL SAFETY DATA SHEETS (MSDS) – Written information provided by vendors concerning a chemical's toxicity, health hazards, physical properties, fire and reactivity data, storage instructions, spill response procedures and handling precautions.

3.16 MINIMUM REPORTING LEVEL (MRL) – The minimum concentration that can be reported by a laboratory as a quantified value for the method analyte in a sample following analysis. This concentration must meet the criteria defined in Section 9.2.4 and must be no lower than the concentration of the lowest calibration standard for each method analyte.

3.17 PRIMARY DILUTION STANDARD (PDS) – A solution containing the method analytes (or internal standards and surrogate analytes) prepared in the laboratory from Stock Standard Solutions and diluted as needed to prepare calibration standards and sample fortification solutions.

3.18 PROCEDURAL CALIBRATION – A calibration technique in which calibration standards are processed through the entire method, including sample preparation, addition of preservatives, extraction and concentration.

3.19 PURGE FLOW RATE – The rate (mL/min) that the purge gas flows through the sparging vessel during the purge cycle.

3.20 PURGE VOLUME – The total volume of purge gas (mL) that flows through the sparging vessel during the purge cycle.

3.21 QUALITY CONTROL SAMPLE (QCS) – A solution containing the method analytes at a known concentration that is obtained from a source external to the laboratory and different from the source of calibration standards. The purpose of the QCS is to verify the accuracy of the primary calibration standards.

3.22 REAGENT WATER – Purified water that does not contain any measurable quantity of the method analytes or interfering compounds at or above ½ the MRL.

3.23 STOCK STANDARD SOLUTION (SSS) – A concentrated solution containing one or more of the method analytes that is prepared in the laboratory using assayed reference materials or purchased from a reputable commercial source, so that the concentration and purity of analytes are traceable to certificates of analysis.

3.24 SURROGATE ANALYTE – A pure analyte which is extremely unlikely to be found in any sample and which is added to a sample aliquot in a known amount before analysis. Surrogates are measured with the same procedures used to measure other sample components. Because surrogates are present in every sample, they provide a means of assessing method performance for a specific purge-and-trap analysis cycle.

4. INTERFERENCES

4.1 SAMPLE CONTAINERS, SHIPPING AND STORAGE – Volatile organic compounds (VOCs) present in ambient air, shipping containers and in the laboratory environment may permeate the PTFE-lined septa of the sample vials or be present at high concentrations in the headspace of the vial (especially if the vials were prepared in a laboratory). Contamination from these sources is evaluated by analyzing FRBs as described in Section 9.3.9.

4.2 PURGE-AND-TRAP SYSTEM – Commercially available purge-and-trap concentrators and autosamplers have complex sample paths that are subject to cross contamination, which is commonly referred to as "carryover." Carryover is controlled by minimizing the transfer line length from the autosampler to the sparging vessel and optimizing the bake cycle and rinse cycle parameters. The potential for carryover in the purge-and-trap system is evaluated during the Initial Demonstration of Capability by analyzing the highest concentration calibration standard followed by a LRB.

4.3 REAGENTS – All laboratory reagents must be routinely demonstrated to be free of interferences under the conditions of the analysis. This may be accomplished by analyzing LRBs and meeting the acceptance criterion as described in Section 9.3.1.

4.3.1 REAGENT WATER – Analysts may observe common laboratory contaminants, such as methylene chloride, in reagent water. Boiling and/or sparging reagent water with nitrogen is recommended. If possible, prepare aqueous standards and blanks in a laboratory environment isolated from ambient sources of VOCs.

4.3.2 METHANOL – Traces of ketones, methylene chloride and other organic solvents could be present in methanol. Use purge-and-trap-grade methanol with this method.

4.3.3 PRESERVATION REAGENTS – The potential exists for trace-level organic contaminants in the preservation reagents. Interferences from these sources must be monitored by analysis of LRBs when new lots of reagents are acquired.

4.3.4 SORBENT MATERIALS – Sorbent traps must be carefully evaluated because some traps, when heated, have been reported to produce small amounts of VOCs, particularly with extended use. For example, toluene may be detected the first time a trap is desorbed during a work shift. For this reason, a short bake cycle prior to beginning an analysis sequence is recommended. In addition, carbon-based traps,

recommended for use with nitrogen purge by this method (Section 6.8.2), commonly produce chloromethane and bromomethane when heated. This phenomenon is caused by the reaction of methanol with the adsorbent materials when the trap is heated in the desorb mode. The quantity of methanol used to prepare aqueous samples should be minimized and background levels of chloromethane and bromomethane should be carefully monitored in LRBs analyzed with each Analysis Batch. Background levels may preclude quantitation of these two analytes in SIM mode.

4.3.5 PURGE GAS SUPPLY – Nitrogen used to purge samples is a potential source of contamination. Trace VOCs in the purge gas, supply lines or the gas supply system (including the regulator) can concentrate on the sorbent trap. High-purity gas supplies and high-purity gas regulators are recommended to minimize contamination from these sources. Purge gas filters should be regenerated or replaced at the intervals specified by the manufacturers.

4.4 MATRIX INTERFERENCES – Matrix interferences are caused by contaminants that are present in the sample. The extent of matrix interferences will vary considerably from source to source depending upon the nature of the water. The analysis of LFSM (Sect. 9.3.7) provides evidence for the presence (or absence) of matrix effects.

5. SAFETY

5.1 The toxicity or carcinogenicity of each reagent used in this method has not been precisely defined. Each chemical should be treated as a potential health hazard and exposure to these chemicals should be minimized. Each laboratory is responsible for maintaining an awareness of OSHA regulations regarding safe handling of chemicals used in this method.[3] A reference file of MSDSs should be made available to all personnel involved in the analysis.

5.2 Pure standard materials and Stock Standard Solutions of the method compounds should be handled with suitable personal protection equipment.[4]

6. EQUIPMENT AND SUPPLIES

References to specific brands or catalog numbers are included as examples only and do not imply endorsement of the product. These references do not preclude the use of other vendors or supplies.

6.1 SAMPLE CONTAINERS – Clean, amber volatile organic analysis (VOA) vials fitted with PTFE-faced silicone septa and polypropylene screw caps (I-Chem Cat. No. S146–0040 or equivalent).

6.2 MICRO SYRINGES – Suggested sizes include 2.0, 5.0, 10 and 25 µL.

6.3 PURGE-AND-TRAP SYRINGES – 5-mL glass syringes with PTFE Luer-Lok fitting (Hamilton Model No. 1005 TLL or equivalent) for manual loading of samples into a sparging vessel.

6.4 SYRINGE VALVE – two-position syringe valves with Luer ends (Supelco Cat. No. 20926 or equivalent) for use in sealing purge-and-trap syringes (Sect. 6.3).

6.5 VOLUMETRIC FLASKS – Class A, suggested sizes include 50, 100 and 200 mL for preparation of calibration standards.

6.6 ANALYTICAL BALANCE – Capable of weighing to the nearest 0.0001 gram (g).

6.7 MICRO-REACTION VESSEL – 0.3-, 1.0-, 2.0-, 5.0-mL sizes (Supelco Cat Nos. 33291, 33293, 33295, 33299 or equivalent) equipped with Mininert Valves [Supelco Cat No. 33301 (15 millimeter (mm) for 0.3-, 1.0- and 2.0-mL vials) and Cat No. 33303 (20 mm for 5.0-mL vials)]. These vials are recommended for storage of Stock Standard Solutions and Primary Dilution Standards (PDS) prepared in methanol.

6.8 PURGE-AND-TRAP SYSTEM – Any purge-and-trap unit that is capable of being electronically interfaced to the GC and that is capable of meeting the method QC requirements outlined in Section 9 is permitted. The concentrator(s) may be equipped with an autosampler. Moisture control modules are permitted but not required.

6.8.1 SPARGING VESSEL – Instruments must be equipped with a sparging vessel specifically designed for purging a 5-mL sample volume. A glass frit should be installed at the base of the sample chamber so the purge gas passes through the water column as finely divided bubbles with a diameter of less than 3 mm at the origin.

NOTE: Larger sparging vessels are not allowed. While the larger sample volume could result in the transfer of more analyte to the trap, purging efficiency decreases unless the purge volume is increased proportionally. While the procedural calibration technique corrects for this, lower purging efficiency decreases method precision. In addition, larger purge volumes could result in the transfer of more water vapor to the trap, placing increased demand on moisture control strategies.

6.8.2 SORBENT TRAP – Purge-and-trap manufacturers typically recommend specific sorbent traps for use with their instruments. Any trap design is acceptable provided the data acquired meet all QC criteria described in Section 9.

During method development studies using nitrogen purge, traps containing Tenax, silica gel and coconut charcoal in series yielded lower recoveries for most of the method analytes when compared directly to the recoveries obtained using a helium purge. A trap containing Tenax, silica gel and carbon molecular sieve (CMS) exhibited similar poor performance. Thus, traps containing Tenax, silica gel and coconut charcoal or Tenax, silica gel and CMS may not be used in this method. Traps containing synthetic carbon adsorbent media (Supelco Vocarb® 3000 or equivalent) are recommended for use with this method.

6.8.3 TRANSFER LINE – Silcosteel® or equivalent heated transfer line used to transfer the desorbed analytes from the purge-and-trap concentrator to the injection port of the GC.

6.8.4 SAMPLE HEATER – A sparging vessel heater is optional. Resistance or infrared heaters may be used.

6.8.5 REFRIGERATED AUTOSAMPLER – Vial autosamplers must be capable of maintaining samples at a temperature of 10 °C or lower. Verify the temperature of field samples placed in the autosampler using an external thermocouple or thermometer (inserted into a vial containing water) during the IDC and at least quarterly. This temperature must not be altered after collecting the initial calibration because it may change analyte purging efficiencies.

6.8.6 STANDARD ADDITION MODULE – Automated device incorporated into vial autosamplers capable of fortifying internal standards and surrogate analytes directly into the sparging vessel. A standard addition module is recommended when vial autosamplers are used in the method.

6.8.7 TANDEM PURGE-AND-TRAP OPERATION – A technique allowing use of two purge-and-trap concentrators configured in tandem. The IDC procedure (Sect. 9.2) must be conducted for each concentrator. In addition, this option requires separate QC samples for each sample path (Sect. 9.3), separate calibrations (Sect. 10) and the use of a marker compound (Sect. 10, Note) to uniquely identify the sample path.

6.9 GAS CHROMATOGRAPHY MASS SPECTROMETRY SYSTEM/DATA SYSTEM (GC/MS/DS)

6.9.1 GC INJECTOR AND OVEN – The GC must be capable of temperature programming and must be equipped with a standard split/splitless injector and a flow controller that is compatible with purge-and-trap analysis. In this configuration, the purge-and-trap effluent is plumbed directly to the carrier gas inlet line of a split/splitless injection port. The injection port is operated in split mode to achieve the desired desorb flow rate and reduce water transmission. A deactivated glass liner (Restek Cat. No. 20972 or equivalent) is recommended to minimize dead volume and active sites within the GC inlet.

6.9.2 FUSED SILICA CAPILLARY GC COLUMN – Laboratories must use a column specifically designed for analysis of volatile organic compounds by purge-and-trap. The column must have an i.d. of 0.32 mm or less to be compatible with operation in the split mode (Sect. 6.9.1). The column must be capable of resolving the method analytes so that a unique quantitation ion is available for each analyte.

6.9.3 GC/MS INTERFACE – The mass spectrometer must have sufficient vacuum pumping capacity to allow the direct feed of the analytical column to the ion source.

6.9.4 MASS SPECTROMETER (MS) – The MS must be capable of electron ionization (EI) at a nominal energy of 70 electron volts (eV) and must be operated in the positive ion mode. An ion-trap mass spectrometer, tuned to produce mass spectra that approximate standard, library spectra obtained under EI conditions, may be used. The instrument must be capable of obtaining at least six scans during the elution of each chromatographic peak. Seven to ten scans across chromatographic peaks are recommended. The spectrometer must produce a mass spectrum that meets all criteria in Table 1 when 4-bromofluorobenzene (BFB) is introduced into the GC/MS (Sect. 10.1.1).

6.9.5 DATA SYSTEM – An interfaced data system is required to acquire, store, reduce and output mass spectral data. The computer software must have the capability of processing stored GC/MS data by recognizing a GC peak within any given retention time window, comparing the mass spectra from the GC peak with spectral data in a user-created data base and generating a list of tentatively identified compounds with their retention times and scan numbers. The software must allow integration of the ion abundance of any specific ion between specified time or scan number limits. The software must also allow construction of linear or second-order regression calibration curves and calculation of concentrations using the internal standard technique.

7. REAGENTS AND STANDARDS

7.1 REAGENTS AND SOLVENTS – Reagent grade or better chemicals must be used. Unless otherwise indicated, all reagents should conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society (ACS), when such specifications are available. Other grades may be used as long as the reagent is of sufficiently high purity to permit its use without negatively affecting data quality.

7.1.1 HELIUM – Ultra High Purity (99.999%) or equivalent, for use as GC carrier gas.

7.1.2 NITROGEN – Ultra High Purity (99.999%) or equivalent, for use as purge gas.

7.1.3 REAGENT WATER – Purified water which does not contain any measurable quantities of any method analytes or interfering compounds at or above ½ the MRL for each compound of interest.

7.1.4 METHANOL (CH_3OH, CAS# 67-56-1) – Purge-and-trap grade, demonstrated to be free of analytes and interferences (Burdick & Jackson Brand® for Purge-and-trap Analysis Cat. No. 232 or equivalent).

7.1.5 ASCORBIC ACID ($C_6H_8O_6$, CAS# 50-81-7) – Dechlorinating agent, demonstrated to be free of analytes and interferences (Alfa Aesar Cat. No. A15613 or equivalent).

7.1.6 MALEIC ACID ($C_4H_4O_4$, CAS# 110-16-7) – Used as a preservative and to lower pH for the purpose of preventing dehydrohalogenation of chlorinated analytes. High purity, demonstrated to be free of analytes and interferences (Sigma Cat. No. M0375 or equivalent).

7.1.7 SODIUM THIOSULFATE ($Na_2S_2O_3$, CAS# 7772-98-7) – Optional dechlorinating agent when sampling only for THMs (Sigma Cat. No. 563188 or equivalent).

7.2 STOCK STANDARD SOLUTIONS – Certified mixes of the 524.4 method analytes, the internal standards and the surrogate analytes are recommended. Users may prepare stock standards of the liquid and solid analytes, if not available as certified solutions, following the guidance provided in this section. After opening the sealed ampoules, store commercial mixes in micro-reaction vials with Mininert caps (Sect. 6.7) at a temperature of -10 °C or lower. After transfer replace vendor-supplied stock solutions within one month.

NOTE: Methyl iodide may degrade faster than other liquid analytes. Monitor the area of this compound relative to the internal standard, 1, 4-difluorobenzene. Replace the stock standard if methyl iodide shows evidence of degradation.

7.2.1 INTERNAL STANDARD STOCK SOLUTIONS (ISSS) (1000 to 2500 µg/mL) – This method uses three internal standards: 1,4-difluorobenzene (CAS# 540-36-3), chlorobenzene-d_5 (CAS# 3114-55-4) and 1,4-dichlorobenzene-d_4 (CAS# 3855-82-1).

7.2.2 SURROGATE STOCK STANDARDS (SURSS) (1000 to 2500 µg/mL) – This method uses three surrogate analytes: methyl-t-butyl-ether-d_3 (CAS# 29366-08-3), bromofluorobenzene (BFB) (CAS# 460-00-4) and 1,2-dichlorobenzene-d_4 (CAS# 2199-69-1).

7.2.3 ANALYTE STOCK STANDARD SOLUTIONS – Obtain the analytes listed in the table in Section 1.1 as certified mixes in methanol or as neat standards if necessary.

7.2.4 PREPARATION INSTRUCTIONS FOR LIQUID ANALYTES – Prepare the stock standards individually at 10 mg/mL. Using an analytical balance, obtain a tare weight for a VOA vial containing 20-mL of purge-and-trap-grade methanol. To achieve the 10 mg/L nominal concentration, calculate the volume of the liquid analyte corresponding to 200 mg. Carefully measure this volume with a 250-µL syringe and inject the entire quantity under the surface of the methanol. Subtract the tare weight from the final weight to calculate the exact solution concentration. When a compound's purity is assayed to be 96 percent or greater, the weight can be used without correction to calculate the concentration of the stock standard.

7.2.5 PREPARATION INSTRUCTIONS FOR SOLID ANALYTES - Prepare the stock standards individually at 10 mg/mL by weighing 200 mg of each solid analyte into a 40-mL VOA vial and diluting to 20 mL with purge-and-trap-grade methanol. For semi-solid and other difficult to transfer materials, insert the entire weigh boat into a VOA vial containing 20-mL of methanol. If the measured mass of analyte is not exactly 200 mg, adjust the volume of methanol to achieve a nominal concentration of 10 mg/mL. When a compound's purity is assayed to be 96 percent or greater, the weight can be used without correction to calculate the concentration of the stock standard.

7.2.6 STORAGE OF INDIVIDUAL STOCK STANDARDS - Store stock standards in the VOA vials in which they were prepared. Stock standard solutions of liquid and solid analytes prepared in-house are estimated to be stable for at least six months if stored at -10 °C or colder. However, such solutions may be stable for longer periods depending on the analyte. Laboratories must use accepted QC practices to determine when stock standards need to be replaced.

7.3 PRIMARY DILUTION STANDARDS (PDS) – Prepare Primary Dilution Standards by combining and diluting appropriate volumes of the stock standards with purge-and-trap-grade methanol.

7.3.1 INTERNAL STANDARD AND SURROGATE PRIMARY DILUTION STANDARD (IS/surrogate PDS) – Prepare a combined internal standard and

surrogate PDS from the ISSS and SURSS. Field samples and calibration standards must contain the same concentration of internal standards and surrogates and the quantity of methanol added should be minimized. Between one and 5 µL per 5-mL sample is recommended. An IS/surrogate PDS concentration that results in the aqueous concentration falling in the mid-range of the initial calibration, e.g., 5 µg/L in full scan mode and 0.5 µg/L in SIM mode is recommended. Store the IS/surrogate PDS in a glass vial with Teflon-lined septa at a temperature of -10 °C or colder. However, if the autosampler has a sealed reservoir on the standard addition module IS/surrogate PDS may be held at room temperature for extended periods (several months).

7.3.2 ANALYTE PRIMARY DILUTION STANDARD (analyte PDS) – The analyte PDS is used to prepare the calibration standards and to fortify LFBs, LFSMs and LFSMDs with the method analytes. The analyte PDS is prepared by combining appropriate volumes of the analyte stock standard solutions to achieve concentrations appropriate for preparing aqueous calibration standards and fortifying samples. Choose concentrations such that at least 2 µL of the PDS is transferred to achieve the desired aqueous concentration in the standard or QC samples; however, minimize the volume of methanol used. Methanol reacts to produce chloromethane and bromomethane when traps containing synthetic-carbon adsorbent materials are heated (Sect. 4.3.4). During method development, PDS solutions ranged in concentration from 10 µg/mL to 400 µg/mL. Lower concentrations of the analyte PDS may be necessary when conducting analyses in SIM mode. Store analyte PDS solutions in micro-reaction vials with Mininert caps at a temperature of -10 °C or colder. PDS solutions which contain gases must be replaced after one week; those which do not contain gases may be stored for up to one month.

7.4 CALIBRATION STANDARDS – Prepare procedural calibration standards by diluting the analyte PDS into reagent water containing the method preservatives (Sect. 8.1). A constant concentration of each internal standard and surrogate analyte is added to each calibration standard, either manually or by use of an automated standard addition module (Sect. 6.8.6). The lowest concentration calibration standard must be at or below the MRL. Additionally, these calibration standards may be used as CCCs. The dilution factors for calibration standards used to collect method performance data in Section 17 are provided in the tables below.

Typical concentrations for aqueous calibration standards used during method development in full scan mode

CAL[a] Level	Analyte PDS Conc. (µg/mL)	Analyte PDS Volume (µL)	Final CAL Std. Volume (L)	Final CAL Std. Conc. (µg/L)
1	10	5.0	0.100	0.50
2	10	10	0.100	1.0
3	100	2.0	0.100	2.0
4	100	5.0	0.100	5.0
5	400	2.5	0.100	10
6	400	5.0	0.100	20
7	400	10	0.100	40

[a] CAL = calibration standard.

Typical concentrations for aqueous calibration standards used during method development in SIM mode

CAL Level	Analyte PDS Conc. (µg/mL)	Analyte PDS Volume (µL)	Final CAL Std. Volume (L)	Final CAL Std. Conc. (ng/L)
1	0.1	10	0.100	10
2	1.0	2.5	0.100	25
3	1.0	5.0	0.100	50
4	1.0	10	0.100	100
5	10	2.0	0.100	200
6	10	5.0	0.100	500
7	10	10	0.100	1,000

7.5 GC/MS TUNE CHECK SOLUTION, BFB (CAS# 460-00-4) – Use the IS/surrogate analyte PDS (Sect. 7.3.1).

8. SAMPLE COLLECTION, PRESERVATION and STORAGE

8.1 SAMPLE COLLECTION

8.1.1 Prior to shipment to the field, ascorbic acid and maleic acid must be added to each sample bottle. Cap the vials tightly to avoid spillage of the preservation reagents. If using a 40-mL vial, add 25 mg of ascorbic acid and 200 mg of maleic acid. If other collection volumes are used, adjust the amount of the preservation reagents so that the final concentrations of ascorbic acid and maleic acid in the sample containers are 0.625 g/L and 5 g/L, respectively. Using narrow-range pH paper, periodically verify that sample pH is ~2 for each sample source.

8.1.2 If a sample foams vigorously when added to a VOA vial containing maleic and ascorbic acids, discard the sample. Collect another sample for that location, but do not add the method preservatives. Document these samples as “not acidified.” Unpreserved samples must be analyzed within 24 hours of collection.

8.1.3 If sampling only for the THMs, samples may be preserved with sodium thiosulfate. Add 3 mg to each 40-mL VOA vial prior to sample collection. Do not add ascorbic or maleic acid when employing this preservation option.

NOTE: If the residual chlorine is likely to be present at greater than 5 mg/L, a determination of the chlorine concentration may be necessary. Add an additional 25 mg of ascorbic acid or 3 mg of sodium thiosulfate per each 5 mg/L of residual chlorine for each 40-mL of sample.

8.1.4 Grab samples must be collected in accordance with standard sampling practices.[5] When sampling from a cold water tap, remove the aerator, open the tap and allow the system to flush until the water temperature has stabilized (approximately 3 to 5 minutes). Fill sample bottles to overflowing, but take care not to flush out the rapidly dissolving solid preservatives. No air bubbles should pass through the sample as the bottle is filled or be trapped in the sample when the bottle is sealed.

8.1.5 When sampling from an open body of water, fill a beaker with water collected from a representative area. Use this bulk sample to generate individual samples and Field replicates as needed.

8.2 FIELD REAGENT BLANK (FRB)

8.2.1 A FRB must accompany each sample set unless only THMs are being analyzed. At the laboratory, add the sample preservatives to the FRB sample bottle, fill with reagent water and ship the FRB with the sampling kits. Do not open the FRB in the field; the FRB must remain sealed until analysis. Since total THMs would be expected to be present in nearly all disinfected drinking water samples, field blank analysis is not required when reporting positive results for total THMs. This exception to the analysis of field blanks only applies to the analysis of total THMs as disinfection byproducts (DBPs). Positive results for all other chemicals observed must be accompanied by the analysis of a field blank to confirm that the positive result was not the result of contamination during sample handling or shipment.

8.2.2 Add the sample preservatives at the laboratory to prepare sample containers for the field samples. The same lots of ascorbic acid and maleic acid must be used for the FRB and the field samples.

8.3 FIELD DUPLICATES – At a minimum, collect all samples in duplicate. Adequate replicate samples in the analytical batch will need to be collected to fulfill QC requirements for LFSMs and LFSMDs or FDs.

8.4 SAMPLE SHIPMENT AND STORAGE – Samples must be chilled during shipment and must not exceed 10 °C during the first 48 hours after collection. Samples must be confirmed to be at or below 10 °C when they are received at the laboratory. In the laboratory, samples must be stored at or below 6 °C, protected from light and isolated from ambient sources of VOCs. When resident in the autosampler, samples must be held at 10 °C or lower. Samples must not be frozen.

8.5 SAMPLE HOLDING TIMES – Analyze samples as soon as possible. Samples that are collected and stored as described in Section 8.1 and 8.4 must be analyzed within 14 days of collection.

9. QUALITY CONTROL

QC requirements include the Initial Demonstration of Capability and ongoing QC requirements. This section describes each QC parameter, its required frequency and the performance criteria that must be met in order to satisfy EPA quality objectives. The QC criteria discussed in the following sections are summarized in Section 17, Tables 12 and 13. These QC requirements are considered the minimum acceptable QC criteria. Laboratories are encouraged to institute additional QC practices to meet their specific needs. Compliance with the requirements of the IDC must be demonstrated for each analyte that the laboratory intends to report using full scan MS and for each analyte that the laboratory intends to report in the SIM or SIS detection mode.

9.1 METHOD MODIFICATIONS – The analyst is permitted to select purge-and-trap and GC conditions appropriate for the available instrumentation. However, five key parameters are

restricted to prescribed ranges. These ranges are summarized in the table below. If the chosen parameters fall within the "recommended" ranges, the laboratory may proceed with the IDC. If values outside the "recommended" ranges are selected for any one of these five parameters, the laboratory must demonstrate equivalent performance in accordance with the guidelines provided in Section 9.4 and then the analyst must repeat the procedures of the IDC. However, values for the five key parameters must never exceed the "allowable" ranges listed in the table below. In addition, sample size cannot be varied from the 5-mL volume prescribed in this method. All other parameters including the remaining concentrator conditions, GC conditions and MS conditions may be varied without restriction.

Parameter	Recommended		Allowable	
	Minimum	**Maximum**	**Minimum**	**Maximum**
Sample temperature	Ambient	40 ºC	Ambient	60 °C
Purge flow rate	40 mL/min	55 mL/min	20 mL/min	80 mL/min
Purge volume	360 mL	520 mL	320 mL	520 mL
Desorb time	1 min	1 min	0.5 min	2 min
Purge volume + dry purge volume	360 mL	720 mL	320 mL	720 mL

NOTE: The "recommended" values provided equivalent response factors and internal standard areas compared to helium purge. The "allowable" limits resulted in a wider variation in response factors compared to helium purge; however, operation within this range may be appropriate for limited analyte lists and other concentrator designs. Sample temperature is limited to 60 ºC to avoid acid-catalyzed decomposition of method analytes. See Table 2 in Section 17 for typical values for purge-and-trap parameters.

9.2 INITIAL DEMONSTRATION OF CAPABILITY (IDC) – The IDC must be successfully performed prior to analyzing any field samples. Prior to conducting the IDC, the analyst must meet the calibration requirements outlined in Section 10. The IDC must be completed for each concentrator and trap. For example, if dual concentrators are interfaced to a single GC/MS, perform the IDC for each system. If a new trap is installed with sorbent materials different from the original trap, repeat the IDC. Requirements for the IDC are described in the following sections and are summarized in Table 12.

9.2.1 DEMONSTRATION OF LOW SYSTEM BACKGROUND – Analyze a LRB. Confirm that the blank is free of contamination as defined in Section 9.3.1.

NOTE: The system must be checked for carryover by analyzing a LRB immediately following the highest calibration standard. If this LRB does not meet the criteria outlined in Section 9.3.1, then carryover is present and the cause must be identified and eliminated.

9.2.2 DEMONSTRATION OF PRECISION – Prepare and analyze seven replicate LFBs. Fortify these samples near the midrange of the initial calibration curve. The method preservation reagents must be added to the LFBs as described in Section 8.1. The percent relative standard deviation (%RSD) of the concentrations of the replicate analyses must be ≤20% for all method analytes.

$$\% \text{ RSD} = \frac{\text{Standard Deviation of Measured Concentrations}}{\text{Average Concentration}} \times 100$$

9.2.3 DEMONSTRATION OF ACCURACY – Calculate the average percent recovery using the same set of replicate data generated for Section 9.2.2. The average recovery of the replicate analyses must be within ±20% of the true value.

$$\% \text{ Recovery} = \frac{\text{Average Measured Concentration}}{\text{Fortified Concentration}} \times 100$$

9.2.4 MINIMUM REPORTING LEVEL (MRL) CONFIRMATION – Establish a target concentration for the MRL based on the intended use of the data. The lowest calibration standard used to establish the initial calibration (as well as the low-level Continuing Calibration Check) must be at or below the concentration of the MRL. Establishing the MRL concentration too low may cause repeated failure of ongoing QC requirements. Confirm the MRL following the procedure outlined below.

NOTE: Method analytes that are consistently present in the background (e.g., methylene chloride, TBA, chloromethane and bromomethane) should be reported as detected in field samples only after careful evaluation of the background levels. In such cases, an MRL must be established at a value no less than three times the standard deviation of the mean LRB concentration or three times the mean LRB concentration, whichever is greater. This guidance is intended to minimize the occurrence of reporting false positive results.

9.2.4.1 Fortify and analyze seven replicate LFBs at or below the proposed MRL concentration. The LFBs must contain the method preservatives as specified in Section 8.1. Calculate the mean (*Mean*) and standard deviation (*S*) for these replicates. Determine the Half Range for the Prediction Interval of Results (HR_{PIR}) using the equation below

$$HR_{PIR} = 3.963S$$

where *S* is the standard deviation and 3.963 is a constant value for seven replicates.[1]

9.2.4.2 Confirm that the Upper and Lower limits for the Prediction Interval of Results ($PIR = Mean \pm HR_{PIR}$) meet the upper and lower recovery limits as shown below.

The Upper PIR Limit must be ≤150% recovery.

$$\frac{Mean + HR_{PIR}}{Fortified\,Concentration} \times 100 \leq 150\%$$

The Lower PIR Limit must be ≥50% recovery.

$$\frac{Mean - HR_{PIR}}{Fortified\,Concentration} \times 100 \geq 50\%$$

9.2.4.3 The MRL is validated if both the Upper and Lower PIR Limits meet the criteria described above. If these criteria are not met, the MRL has been set too low and must be confirmed again at a higher concentration.

NOTE: These equations are only valid for seven replicate samples.

9.2.5 QUALITY CONTROL SAMPLE (QCS) – Analyze a mid-level Quality Control Sample (Sect. 9.3.10) to confirm the accuracy of the primary calibration standards.

9.2.6 DETECTION LIMIT DETERMINATION (optional) – *While DL determination is not a specific requirement of this method, it may be required by various regulatory bodies associated with compliance monitoring. It is the responsibility of the laboratory to ascertain whether DL determination is required based upon the intended use of the data.*

Analyses for this procedure must be done over at least three days. Prepare at least seven replicate LFBs. Fortify the LFBs at a concentration estimated to be near the DL. This fortification level may be estimated by selecting a concentration at two to five times the noise level. The method preservatives must be added to the samples as described in Section 8.1. Process the seven replicates through all steps of Section 11.

NOTE: If a data set used for the MRL confirmation step of the IDC meets these requirements, a DL may be calculated from the MRL confirmation data and no additional analyses are necessary.

Calculate the DL using the following equation:

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

where

$t_{(n-1,1-\alpha = 0.99)}$ = Student's t value for the 99% confidence level with n-1 degrees of freedom (for seven replicate determinations, the Student's t value is 3.143 at a 99% confidence level),

n = number of replicates and

S = standard deviation of replicate analyses.

NOTE: Do not subtract blank values when performing DL calculations.

9.3 ONGOING QC REQUIREMENTS – This section describes the ongoing QC procedures that must be followed when processing and analyzing field samples. Table 13 summarizes these requirements.

9.3.1 LABORATORY REAGENT BLANK (LRB) – Analyze a LRB with each Analysis Batch. The LRB must contain the method preservatives, the internal standards and surrogate analytes at the same concentration used to fortify all field samples and

calibration standards. Background from method analytes or contaminants that interfere with the measurement of method analytes must be less than ½ the MRL. If the method analytes are detected in the LRB at concentrations equal to or greater than this level, then all data for the problem analyte(s) must be considered invalid for all samples that yielded a positive result. **Subtracting LRB values from sample results is not permitted.**

NOTE: Although quantitative data below the MRL may not be accurate enough for data reporting, such data are useful in determining the magnitude of background interference. Therefore, blank contamination levels may be estimated by extrapolation when the concentration is below the MRL.

NOTE: After analysis of a sample in which method analytes exceed the calibration range, one or more LRBs must be analyzed (to detect potential carryover) until the system meets the LRB acceptance criteria. If this occurs during an automated sequence, examine the results of samples analyzed following the sample that exceeded the calibration range. If the analytes that exceeded the calibration range in the previous sample are detected at or above the MRL, these samples are invalid. If the affected analytes do not exceed the MRL, these subsequent samples are valid. THMs are excluded from this requirement.

NOTE: The LRB test in the IDC may be particularly difficult to pass for compounds analyzed using the SIM detection mode. For analytes monitored in SIM mode, the laboratory should restrict the high calibration point to 1.0 or 2.0 µg/L and consider other techniques such as using a dedicated sparge vessel and more aggressive recycle parameters. If possible, select MRLs that allow monitoring goals to be achieved, but that are well above typical blank values.

9.3.2 CONTINUING CALIBRATION CHECK (CCC) – Analyze CCC standards at the beginning of each Analysis Batch, after every ten field samples and at the end of the Analysis Batch. See Section 10.2 for concentration requirements and acceptance criteria.

9.3.3 LABORATORY FORTIFIED BLANK (LFB) – Because this method utilizes procedural calibration standards, which are fortified reagent waters, there is no difference between the LFB and the CCC standards. Consequently, the analysis of a separate LFB is not required as part of the ongoing QC; however, the term “LFB” is used for clarity in the IDC.

9.3.4 MS TUNE CHECK – The procedure for conducting the MS Tune Check for BFB is found in Section 10.1.1. Acceptance criteria for the MS Tune Check are summarized in Section 17, Table 1. The MS Tune Check must be performed prior to establishing and/or re-establishing an initial calibration (Sect. 10.1) and each time a major change is made to the mass spectrometer. Daily BFB analysis is not required.

9.3.5 INTERNAL STANDARDS (IS) – The analyst must monitor the peak areas of the internal standards in all injections of the Analysis Batch. The IS responses (peak area) in any chromatographic run must not deviate from the response in the most recent CCC by more than ±30% and must not deviate by more than ±50% from the

average area measured during initial analyte calibration. If an IS area for a sample does not meet these criteria, check the corresponding IS area of the most recent CCC and proceed as follows.

9.3.5.1 If the IS criteria are met in the CCC but not the sample, reanalyze the sample (FD) in a subsequent Analysis Batch. If the IS area fails to meet the acceptance criteria in the FD, but passes in the most recent CCC, report the sample results as "suspect/matrix."

9.3.5.2 If both the original sample and the CCC fail the IS criteria, take corrective action beginning with an extended bake cycle for the GC column and the concentrator trap. Area counts may decrease as the rate of water entering the mass spectrometer exceeds the capacity of the pumping system to remove it. Additional measures such as clipping the inlet side of the GC column and cleaning the MS source may be indicated. Verify the integrity of the IS solution and the fortification technique. Perform the appropriate instrument maintenance and then reanalyze the sample (FD) in a subsequent Analysis Batch. If the IS area fails to meet the acceptance criteria in the FD, but passes in the most recent CCC, report the sample results as "suspect/matrix."

9.3.6 SURROGATE RECOVERY – The surrogate analytes are fortified into all calibration standards, field samples and QC samples prior to purge-and-trap analysis. Calculate the percent recovery (%R) for each surrogate using the following equation:

$$\%R = \left(\frac{A}{B}\right) \times 100$$

where
A = calculated surrogate concentration for the QC or field sample and
B = fortified concentration of the surrogate.

9.3.6.1 Surrogate recovery must be in the range of 70% to 130%. When surrogate recovery from a field sample, blank or QC sample is less than 70% or greater than 130% check: 1) calculations to locate possible errors, 2) the integrity of the surrogate analyte solution and the fortification technique, 3) contamination and 4) instrument calibration. Also, see corrective action options in Section 9.3.5.2. Correct the problem and reanalyze the sample in a subsequent Analysis Batch using the appropriate FD.

9.3.6.2 If the repeat analysis meets the surrogate recovery criterion, only report data for the FD.

9.3.6.3 If the FD fails the surrogate recovery criterion after corrective action has been taken, report all data for that sample as "suspect/surrogate recovery."

9.3.7 LABORATORY FORTIFIED SAMPLE MATRIX (LFSM) – Within each Analysis Batch, analyze a minimum of one LFSM. The native concentrations of the analytes

in the sample matrix must be determined in a separate aliquot and subtracted from the measured values in the LFSM. If a variety of different sample matrices are analyzed regularly, for example, drinking water from ground water and surface water sources, performance data must be collected for each source.

9.3.7.1 Prepare the LFSM by fortifying a FD with an appropriate amount of an analyte PDS (Sect. 7.3.2). Select a spiking concentration that is greater than or equal to the native background concentration, if known. Selecting a duplicate aliquot of a sample that has already been analyzed aids in the selection of an appropriate spiking level. If this is not possible, use historical data and rotate through low, medium and high calibration concentrations when selecting a fortifying concentration.

NOTE: If the presence of DBPs (e.g., THMs) precludes selection of an appropriate fortification level for the majority of the method analytes, the DBPs may be ignored. For example, if the analyst wishes to estimate accuracy and precision at 1.0 µg/L and chloroform is present in the native matrix at 10 µg/L, chloroform is fortified at only 10% of its native concentration. In such cases, recovery results for the DBPs may fail the acceptance criteria for LFSM. Appropriately qualify the QC result when this occurs. If the laboratory is analyzing specifically for DBPs or does not wish to exclude them, select a fortification level based on the DPB concentrations in the native sample such that the final DBP results fall within the calibration range.

9.3.7.2 Calculate the percent recovery (%R) using the equation:

$$\%R = \frac{(A - B)}{C} \times 100$$

where
A = measured concentration in the fortified sample
B = measured concentration in the unfortified sample and
C = fortification concentration.

9.3.7.3 Recoveries for samples fortified at concentrations near or at the MRL (within a factor of two times the MRL concentration) must be within ±50% of the true value. Recoveries for samples fortified at all other concentrations must be within ±30% of the true value. If the accuracy for any analyte falls outside the designated range and the laboratory performance for that analyte is shown to be in control in the CCCs, the recovery is judged matrix biased. The result for that analyte in the unfortified sample is labeled "suspect/matrix."

NOTE: In order to obtain meaningful percent recovery results, correct the measured values in the LFSM and LFSMD for the native levels in the unfortified samples, even if the native values are less than the MRL. This

situation and the LRB are the only permitted uses of analyte results below the MRL.

9.3.8 FIELD DUPLICATE OR LABORATORY FORTIFIED SAMPLE MATRIX DUPLICATE (FD or LFSMD) – Within each Analysis Batch, analyze a minimum of one FD or one LFSM Duplicate. If method analytes are not routinely observed in field samples, analyze an LFSMD rather than an FD.

9.3.8.1 Calculate the relative percent difference (RPD) for duplicate measurements (FD_1 and FD_2) using the equation:

$$\text{RPD} = \frac{|\text{FD}_1 - \text{FD}_2|}{(\text{FD}_1 + \text{FD}_2)/2} \times 100$$

9.3.8.2 RPDs for FDs must be ≤30%. Greater variability may be observed when FDs have analyte concentrations that are near or at the MRL (within a factor of two times the MRL concentration). At these concentrations, FDs must have RPDs that are ≤50%. If the RPD of an analyte falls outside the designated range and the laboratory performance for the analyte is in control in the CCC, the precision is judged matrix influenced. The result from the unfortified sample is labeled "suspect/matrix."

9.3.8.3 If an LFSMD is analyzed instead of a FD, calculate the RPD for the LFSM and LFSMD using the equation:

$$\text{RPD} = \frac{|\text{LFSM} - \text{LFSMD}|}{(\text{LFSM} + \text{LFSMD})/2} \times 100$$

9.3.8.4 RPDs for duplicate LFSMs must be ≤30%. Greater variability may be observed when fortified LFSMs have analyte concentrations that are near or at the MRL (within a factor of two times the MRL concentration). LFSMs at these concentrations must have RPDs that are ≤50%. If the RPD of an analyte falls outside the designated range and the laboratory performance for that analyte is in control in the CCC, the precision is judged matrix influenced. The result from the unfortified sample is labeled "suspect/matrix."

9.3.9 FIELD REAGENT BLANK (FRB) – FRBs must be analyzed if compounds other than commonly occurring DBPs, such as THMs, are detected in field samples. Qualify the result for any analyte that is detected in both a field sample and in the associated FRB as "probable contribution from shipping and storage." Subtracting FRB values from sample results is not permitted.

9.3.10 QUALITY CONTROL SAMPLE (QCS) – A QCS must be evaluated as part of the IDC and repeated at least quarterly. Fortify the QCS near the midpoint of the calibration range. The acceptance criteria for the QCS are the same as the mid-level and high-level CCCs (Sect. 10.2.1). If the accuracy for any analyte fails the recovery

criterion, check the standard preparation process, stock standard sources and the purity of neat materials used to prepare the stock standards to locate and correct the problem.

9.4 METHOD MODIFICATION QC REQUIREMENTS – The analyst is permitted to modify the five key purge-and-trap parameters (sample temperature, purge flow rate, purge volume, desorb time and dry purge volume). The analyst is not permitted to modify sample collection or preservation, change the QC requirements of the method or increase the sample volume above 5 mL. Do not add or delete QC compounds from the list prescribed in the method: ISs (Sect. 7.2.1) and surrogates (Sect. 7.2.2). If modified parameters fall outside of the "recommended" minimum and maximum for one of the five key parameters the laboratory must confirm that the new parameters provide acceptable method performance as defined in the following subsections.

9.4.1 The new parameters must fall within the "allowable" minimum and maximum limits specified in Section 9.1. Values outside these limits are not permitted.

9.4.2 Perform an initial calibration procedure (Sect. 10.1) for the method analytes that the laboratory intends to report using conditions that fall within the "recommended" ranges as presented in Section 9.1. Determine relative response factors (RRF) for each analyte averaged over the entire calibration range.

$$\text{RRF} = \frac{\text{Analyte}(\text{area}) \times \text{IS}(\mu\text{g/L})}{\text{IS}(\text{area}) \times \text{Analyte}(\mu\text{g/L})}$$

9.4.3 Optimize the purge-and-trap system using the proposed method modifications. Analyze three mid-level calibration standards and calculate mean RRFs for each method analyte. If all of the response factors observed using the modified conditions are ≥70% of the initial calibration response factors obtained using the "recommended" method conditions (Sect. 9.4.2), then the modified method parameters are permitted. Repeat the procedures of the IDC (Sect. 9.2) employing the modified parameters.

9.4.4 The analyst is also required to evaluate and document method performance for the proposed method modifications in real matrices that span the range of waters that the laboratory analyzes. This additional step is required because modifications that perform acceptably in the IDC, which is conducted in reagent water, could fail ongoing method QC requirements in real matrices. If, for example, the laboratory analyzes drinking water from both surface and ground water municipalities, this requirement can be accomplished by assessing precision and accuracy (Sects. 9.2.2 and 9.2.3) in a surface water with moderate to high total organic carbon (e.g., 2 mg/L or greater) and a hard ground water [e.g., 250 mg/L as calcium carbonate ($CaCO_3$) equivalent or greater].

9.4.5 The results of Sections 9.4.3 and 9.4.4 must be appropriately documented by the analyst and should be independently assessed by the laboratory's QA officer prior to analyzing field samples.

9.4.6 When implementing method modifications, it is the responsibility of the laboratory to closely review the results of ongoing QC and in particular, the results associated with the LFSM (Sect. 9.3.7), LFSMD (Sect. 9.3.8), CCCs (Sect. 9.3.2) and the IS area counts (Sect. 9.3.5). If repeated failures are noted, the modification must be abandoned.

10. CALIBRATION AND STANDARDIZATION

Demonstration and documentation of acceptable analyte calibration is required before performing the IDC (Sect. 9.2) and prior to analyzing field samples. Verification of the MS calibration and the initial calibration must be repeated each time a major instrument modification or maintenance is performed.

NOTE: For tandem concentrators or older systems that utilize multiple sparging vessels and/or traps, a separate calibration and all required QC samples must be analyzed on each sample path. In addition, a qualitative marker compound must be added to all samples to uniquely identify the sample path and ensure that samples are matched to the proper calibration and QC results. For example, fluorobenzene could be added to all samples analyzed on the second sample path of a tandem concentrator system.

10.1 PURGE-AND-TRAP GC/MS OPTIMIZATION AND INITIAL CALIBRATION – An initial calibration requires optimizing purge-and-trap and GC/MS conditions, confirming that the instrument meets the BFB tune check criteria and the preparation and analysis of at least seven calibration standards to determine the calibration curve. Calibration must be performed using peak areas and the internal standard technique. Calibration using peak heights and external standard calibration are not permitted.

10.1.1 MS TUNE/MS TUNE CHECK– Calibrate the mass and abundance scales of the MS utilizing calibration compounds and procedures recommended by the manufacturer with any modifications necessary to meet tuning requirements. Introduce BFB (Sect. 7.5) into the GC/MS system. Acquire a mass spectrum using the same scan range employed for full scan sample analyses. Use a single spectrum at the apex of the BFB peak, an average spectrum of the three highest points of the peak or an average spectrum across the entire peak to evaluate the performance of the system. Appropriate background subtraction is allowed; however, the background scan(s) must be chosen from the baseline prior to or after elution of the BFB peak. If the BFB mass spectrum does not meet all criteria in Table 1, the MS must be retuned to meet all criteria before proceeding with the initial calibration.

10.1.2 PURGE-AND-TRAP CONDITIONS – Establish purge-and-trap parameters following the manufacturer's recommendations. Make sure that the sample temperature, purge flow rate, purge volume, desorb time and dry purge volume are within the "allowable" ranges specified in section 9.1. Optimize purge-and-trap parameters to maximize purging efficiency and minimize the transmission of water to the GC/MS system.

10.1.3 GC CONDITIONS – Establish GC operating conditions appropriate for the GC column dimensions by optimizing the split ratio and temperature program. Generally, the required split ratio is inversely proportional to column diameter. The user must

balance the need to transfer enough of the method analytes to achieve the desired MRLs and the need to reduce water transmission from the purge-and-trap concentrator. The split ratio will also affect the chromatographic peak profile of the most volatile method analytes, commonly referred to as "gases." Sufficient resolution and symmetrical peak profiles with minimal tailing for these analytes must be achieved to enable accurate and precise integration. A mass chromatogram of the gases obtained during method development is provided in Figure 1. The GC program must be optimized to provide adequate resolution of the method analytes as defined in the following subsections.

10.1.3.1 If possible, optimize chromatographic conditions such that a unique quantitation ion is available for each analyte that is free from interference due to an identical fragment ion in any co-eluting (or overlapping) peak(s).

10.1.3.2 If a unique quantitation ion of sufficient intensity to set the desired MRL is not available, overlap with an identical ion from an overlapping analyte is permitted, providing that at least a 50% valley between the mass peaks is achieved.

10.1.4 FULL SCAN MS CONDITIONS – Select a scan range that allows the acquisition of a mass spectrum for each of the method analytes, which includes all of the major fragments mass-to-charge ratio (*m/z)* 35 and above. However, during elution of the water/carbon dioxide peak, the analyst is permitted to begin the scan at *m/z* 45 to eliminate the appearance of these matrix components in the baseline.

10.1.5 SIM MS CONDITIONS – In SIM mode, choose one primary quantitation ion and at least one secondary ion. If possible, select a second confirmation ion. Additional ions may be monitored that demonstrate a unique characteristic in the mass spectrum such as a halogen cluster. Verify that the primary ion is free from interference (Sect. 10.1.3.1 and Sect. 10.1.3.2) due to an identical fragment ion in any overlapping peak(s). If the chromatogram is divided into SIM windows (also termed segments or periods), the laboratory must ensure that each method analyte elutes entirely within the proper window during each Analysis Batch. Make this observation by viewing the mass chromatogram of the quantitation ion for each SIM analyte in the CCC analyzed at the beginning and end of each Analysis Batch. This requirement does not preclude continuous operation by sequencing multiple Analysis Batches; however, the entire Analysis Batch is invalid if one or more analyte peaks drift outside of designated SIM windows in either of these CCCs. For large analyte lists, minimize the number of ions monitored in each chromatographic window to ensure adequate sensitivity to meet the desired MRL. During method development, five SIM windows were used as indicated in Section 17, Table 5.

10.1.6 ALTERNATING FULL AND SIM SCAN MODES – Alternating full and SIM scan functions during a single sample acquisition is permitted if the minimum number of scans across each GC peak acquired in this mode is maintained, i.e., six scans as specified in Section 6.9.4 in each full and SIM scan modes.

10.1.7 CALIBRATION STANDARDS – Prepare a set of at least seven calibration standards as described in Section 7.4. The lowest concentration of the calibration standards

must be at or below the MRL. The MRL must be confirmed using the procedure outlined in Section 9.2.4 after establishing the initial calibration. Additionally, field samples must be quantified using a calibration curve that spans the same concentration range used to collect the IDC data (Sect. 9.2), i.e., analysts are not permitted to use a restricted calibration range to meet the IDC criteria and then use a larger dynamic range during analysis of field samples.

10.1.8 CALIBRATION – Calibrate the GC/MS system using peak areas and the internal standard technique. Fit the calibration points with either a linear or a quadratic regression (response vs. concentration). Weighting may be used. The GC/MS instrument used during method development was calibrated using inverse concentration-weighted quadratic curves. Suggested internal standard assignments and quantitation ions for each method analyte evaluated in full scan mode are presented in Table 4. Suggested internal standard assignments and quantitation ions for each method analyte evaluated in SIM mode are presented in Table 5.

NOTE: Because the surrogate analytes are added at a single concentration level to the calibration standards, calibrate for each surrogate using an average response factor.

10.1.9 FORCING ZERO – Forcing the calibration curve through the origin is not recommended. However, zero must be forced for method analytes (e.g., common laboratory contaminants and for carbon-based traps, potentially chloromethane and bromomethane) if they are consistently detected in the Laboratory Reagent Blanks. Forcing zero allows for a better estimate of the background level of blank contaminants. An accurate estimate of background contamination is necessary to set MRLs for method analytes when blank levels are problematic (Sect. 9.2.4).

10.1.10 CALIBRATION ACCEPTANCE CRITERIA – The initial calibration is validated by calculating the concentration of the analytes for each of the analyses used to generate the calibration curve by use of the regression equations. Calibration points that are ≤MRL must calculate to be within ±50% of their true value. All other calibration points must calculate to be within ±30% of their true value. If these criteria cannot be met, the analyst will have difficulty meeting ongoing QC criteria. In this case, corrective action such as reanalyzing the calibration standards, restricting the range of calibration or performing instrument maintenance is recommended.

10.2 CONTINUING CALIBRATION CHECKS (CCCs) – Analyze a CCC to verify the initial calibration at the beginning of each Analysis Batch, after every tenth field sample and at the end of each Analysis Batch. The beginning CCC for each Analysis Batch must be at or below the MRL. This CCC verifies instrument sensitivity prior to the analysis of samples. Alternate subsequent CCCs between the remaining calibration levels.

10.2.1 Calculate the concentration of each analyte in the CCC. Each analyte in the CCC fortified at ≤MRL must calculate to be within ±50% of its true value. At all other levels, each analyte, including the surrogate analytes, must calculate to be within ±30%. If these limits are exceeded, then all data for the failed analytes must be considered invalid. Any field samples analyzed since the last acceptable CCC that

are still within holding time must be reanalyzed after an acceptable calibration has been restored.

10.2.2 REMEDIAL ACTION – Failure to meet QC performance criteria for CCCs requires remedial action. Acceptable method performance may be restored simply by recalibrating in accordance with the guidelines in Section 10.1 and verifying sensitivity by analyzing a CCC at or below the MRL. Because of the volatile nature of the method analytes, PDS have limited shelf life. Prepare a fresh PDS and repeat the CCC before contemplating instrument maintenance. If internal standard and calibration failures persist, maintenance such as extended bake cycles for both the purge-and-trap concentrator and the GC/MS, clipping the GC column, replacing the concentrator trap and cleaning the MS source may be required. Following major maintenance, the analyst must return to the initial calibration step (Sect. 10.1).

11. PROCEDURE

Important aspects of this analytical procedure include proper sample collection and storage (Section 8), ensuring that the instrument is properly calibrated (Section 10) and that all required QC elements are included (Section 9). This method is designed for a 5-mL sample volume. The concentration of the internal standards and surrogate analytes must be the same in the samples as in the calibration standards. In the laboratory, maintain field samples, QC samples and calibration standards at or below 6 °C at all times while in storage. While resident in the autosampler awaiting analysis, samples must be maintained at less than or equal to 10 °C. Do not store samples in the autosampler longer than the time required to complete the Analysis Batch.

11.1 SAMPLE PREPARATION: SYRINGE METHOD – For concentrators with a single sparging vessel and autosamplers with multiple sparging vessels, load the sample (or previously prepared calibration standard) by use of a 5-mL syringe. If the purge cycle will be initiated immediately after this step, warm the sample to room temperature. Remove the plunger from two syringes and attach a closed syringe valve. Open the VOA vial and carefully pour the sample into the syringe barrel to just short of overflowing. Replace the syringe plunger, invert the syringe and compress the sample. Open the syringe valve and vent any residual air while adjusting the sample volume to 5 mL. Add the internal standard/surrogate analyte PDS to the sample through the syringe valve. Immediately load the sample into the sparging vessel.

NOTE: Do not store samples in syringes or prepare QC samples by filling two syringes. A second VOA vial (i.e., a FD) is required as a means of ensuring that a back up sample is available and for preparing FD, LFSM and LFSMD QC samples.

11.1.1 PREPARATION OF LFSM and LFSMD: SYRINGE METHOD – Three 40-mL vials (FDs) are required for a sample and its associated LFSM and LFSMD. Fortify two of the samples using an analyte PDS of appropriate concentration by injecting through the syringe valve. Add the internal standards and surrogates as directed in Section 11.1.

11.1.2 FIELD DUPLICATE: SYRINGE METHOD – Fill a 5-mL syringe with the selected FD and fortify with internal standards and surrogates. Analyze FDs at the frequency specified in Section 9.3.8.

11.2 SAMPLE PREPARATION: VIAL AUTOSAMPLER METHOD – Activate the cooling mechanism of the refrigerated autosampler and allow it to reach the temperature set point. Remove samples from cold storage and immediately load them into the vial autosampler. Prepare the IS/surrogate fortification solution at a concentration appropriate for the automated standard addition device.

11.2.1 PREPARATION OF LFSM and LFSMD FOR VIAL AUTOSAMPLERS – Three 40-mL vials (FDs) are required for a sample and its associated LFSM and LFSMD. Fortify two of the samples using an analyte PDS of appropriate concentration by puncturing the septa of each vial with a syringe. Allow time for the compounds to disperse homogeneously within the sample. Assume that the sample volume is 40 mL or estimate the typical volume of a 40-mL vial in use at your laboratory. Fortification may be accomplished by use of a standard addition module if the autosampler is so equipped.

11.2.2 FDs FOR VIAL AUTOSAMPLERS – Load the appropriate FD vial into the autosampler. Analyze FDs at the frequency specified in Section 9.3.8.

11.3 PURGE-AND-TRAP ANALYSIS

11.3.1 Establish purge-and-trap and GC/MS operating conditions per the guidance in Section 10.1.

11.3.2 Bake the concentrator trap and GC column to remove contaminants that may have collected in the system. This step is especially important if the analytical system has been idle for more than a few hours.

11.3.3 Initiate the purge cycle and autosampler sequence. After the purge cycle, preheat the trap as recommended by the manufacturer. Start the data acquisition at the beginning of the desorb cycle. Bake the trap and rinse the sparging vessel and autosampler delivery lines using settings optimized to minimize sample carryover.

NOTE: The method preservatives cause the water column in the sparging vessel to appear effervescent during the purge cycle. This is normal and no adverse effects occur as a result of the effervescence.

11.4 THE ANALYSIS BATCH – Establish a valid initial calibration following the procedures outlined in Section 10.1 and confirm that the calibration is still valid by analyzing a CCC at or below the MRL as described in Section 10.2. Alternately, verify that an existing calibration, established for a previous Analysis Batch, is valid by analyzing a CCC at or below the MRL. Next, analyze a LRB. Continue the Analysis Batch by analyzing aliquots of field and QC samples at appropriate frequencies (Section 9.3), employing the optimized conditions used to acquire the initial calibration. Analyze a mid- or high-level CCC after every ten field samples and at the end each Analysis Batch.

NOTE: Each Analysis Batch must begin with the analysis of a CCC at or below the MRL for each analyte that the laboratory intends to report, followed by the analysis of a LRB. This is true whether or not an initial calibration is analyzed. After 20 field samples, the low-

level CCC and the LRB must be repeated to begin a new Analysis Batch. The acquisition start time of the mid-level CCC at the end of the Analysis Batch must be within 24 hours of the acquisition start time of the low-level CCC at the beginning of the Analysis Batch. Multiple Analysis Batches within a 24-hour period are permitted. Do not count QC samples (LRBs, FRBs, FDs, LFSMs, LFSMDs) when calculating the frequency of CCCs that are required during an Analysis Batch.

12. DATA ANALYSIS AND CALCULATIONS

12.1 COMPOUND IDENTIFICATION – Establish an appropriate retention time window for each analyte to identify them in QC and field sample chromatograms. Base this assignment on measurements of actual retention time variation for each compound in standard solutions analyzed on the GC/MS over the course of time. The suggested variation is plus or minus three times the standard deviation of the retention time for each compound for a series of injections. The injections from the initial calibration and from the IDC (Sect. 9.2) may be used to calculate the retention time window. However, the experience of the analyst should weigh heavily on the determination of an appropriate range.

12.1.1 At the conclusion of data acquisition, use the same software settings established during the calibration procedure to identify peaks of interest in the predetermined retention time windows. Initially, identify an analyte by comparison of its retention time with that of the corresponding analyte peak in a recent initial calibration standard or CCC.

12.1.2 Some GC/MS programs use spectra matching criteria when collecting data in full scan mode based on the comparison of field sample spectra (after background subtraction if necessary) to a reference spectrum in the user-created database. This database should be created prior to conducting the IDC from spectra obtained for a mid-level to high-level calibration standard and updated as necessary. If available, this feature may be utilized as a secondary identification routine; however, the primary criterion must be based on the analyte retention time.

12.2 COMPOUND CONFIRMATION FULL SCAN MODE – In general, all ions that are present above 30 percent relative abundance in the mass spectrum of the user-generated database must be present in the mass spectrum of the sample component and must agree within an absolute 20 percent of the relative abundance in the reference spectrum. For example, if an ion has a relative abundance of 30 percent in the standard spectrum, its abundance in the sample spectrum must be in the range of 10 to 50 percent. Some ions, particularly the molecular ion, are of special importance and should be evaluated even if they are below 30 percent relative abundance.

NOTE: Compound identification is more challenging when sample components are not resolved chromatographically and produce mass spectra containing ions contributed by more than one analyte. When GC peaks obviously represent more than one sample component (i.e., broadened peak with shoulder(s) or valley between two or more maxima), characteristic analyte spectra may be obtained by examining the spectra of individual scans across the peak and then applying appropriate background subtraction. When analytes co-elute (i.e., only one GC peak is apparent), the identification criteria may be met but each analyte spectrum will contain extraneous ions contributed by the co-eluting compound.

12.3 COMPOUND CONFIRMATION SIM MODE – In SIM mode, each confirmation ion should be present. For each analyte identified by retention time, the abundance of the confirmation ions relative to the quantitation ion should agree within an absolute 20 percent of the relative abundance in the spectrum taken from a recent calibration standard analyzed in SIM mode. For example, if an ion has a relative abundance of 30 percent in the calibration standard, its abundance in the sample spectrum should be in the range of 10 to 50 percent.

12.4 COMPOUND QUANTITATION – Calculate analyte concentrations using the multipoint calibration established in Section 10.1. Report only those values that fall between the MRL and the highest calibration standard.

12.4.1 Calculations must use all available digits of precision, but final reported concentrations should be rounded to an appropriate number of significant figures (one digit of uncertainty); this is typically two and not more than three, significant figures.

12.4.2 Prior to reporting data, the chromatograms must be reviewed for incorrect peak identification or improper integration.

12.4.3 Prior to reporting data, the laboratory is responsible for assuring that QC requirements have been met and that any appropriate qualifier is assigned.

12.5 EXCEEDING THE CALIBRATION RANGE – The analyst must not extrapolate beyond the established calibration range. If an analyte result exceeds the range of the initial calibration curve, dilute the FD using reagent water containing the method preservatives. Re-inject the diluted sample. Incorporate the dilution factor into final concentration calculations. The resulting data must be annotated as a dilution and the reported MRLs must reflect the dilution factor.

13. METHOD PERFORMANCE

References to specific brands or catalog numbers are included as examples only and do not imply endorsement of the product. These references do not preclude the use of other vendors or supplies.

13.1 PRECISION, ACCURACY AND DETECTION LIMITS – The method performance data presented in Section 17 were collected using a Tekmar Stratum Purge-and-trap Concentrator with a Tekmar AQUATek 70 Vial Autosampler interfaced to an Agilent 6890 Plus GC and an Agilent 5973 MS. Table 2 lists the purge-and-trap conditions used to gather the method performance data presented in Section 17. GC/MS conditions for the Agilent system are presented in Table 3. Table 4 presents the quantitation ions employed in full scan mode appropriate for the Restek Rtx®-VMS column (no interference from overlapping peaks) for each analyte, internal standard and surrogate analyte, suggested internal standard assignments and observed retention times associated with the method performance results. Table 5 lists the method analytes for which method performance data were collected in the SIM mode; primary quantitation ions, confirmation ions and internal standard references are provided. Single laboratory LCMRLs and DLs determined in full scan mode are listed in Table 6. Single laboratory precision and accuracy data obtained in full scan mode are presented for three water matrices: reagent water (Table 7), chlorinated (finished) ground water (Table 8) and chlorinated (finished) surface water (Table 9). LCMRLs and DLs obtained in SIM mode

for selected method analytes are presented in Table 10. Figure 1 depicts an extracted ion chromatogram of the method analytes that are gases at room temperature acquired in full scan mode. Figures 2 and 3 are total ion chromatograms of the method analytes in reagent water and drinking water obtained under the conditions employed during method development in full scan mode. Figure 4 depicts an extracted ion chromatogram of the method analytes that are gases at room temperature acquired in SIM mode. Figure 5 is a total ion chromatogram of the method analytes in reagent water obtained under the conditions employed during method development in SIM mode.

13.2 SAMPLE STORAGE STABILITY STUDIES – An analyte storage stability study was conducted during the development of EPA Method 524.3 by fortifying the analytes (20 µg/L of each analyte) into a chlorinated surface water that was collected, preserved and stored as described in Section 8. The average recovery of triplicate analyses, conducted on Days 0, 7 and 14 are presented in Table 11. These results are reproduced in Method 524.4 to document that storage stability for the method analytes has been demonstrated.

14. POLLUTION PREVENTION

For information about pollution prevention applicable to laboratory operations described in this method, consult: *Less is Better, Guide to Minimizing Waste in Laboratories*, a web-based resource available from the American Chemical Society website.

15. WASTE MANAGEMENT

The analytical procedures described in this method generate relatively small amounts of waste since only small amounts of reagents and solvents are used. The matrix of concern is finished drinking water. However, the Agency requires that laboratory waste management practices be conducted consistent with all applicable rules and regulations and that laboratories protect the air, water and land by minimizing and controlling all releases from fume hoods and bench operations. In addition, compliance is required with any sewage discharge permits and regulations, particularly the hazardous waste identification rules and land disposal restrictions.

16. REFERENCES

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17. TABLES, DIAGRAMS, FLOWCHARTS and VALIDATION DATA

The conditions listed in the tables of this section were used to collect method performance data at EPA. They do not represent any form of guidance for acceptable parameter settings. Refer to the relevant sections of the method for guidance on optimizing and selecting purge-and-trap and GC/MS conditions.

TABLE 1. 4-BROMOFLUOROBENZENE (BFB) MASS INTENSITY CRITERIA

m/z	Required Intensity (relative abundance)
95	Base peak, 100% relative abundance
96	5 to 9% of *m/z* 95
173	Less than 2% of *m/z* 174
174	Greater than 50% of *m/z* 95
175	5 to 9% of *m/z* 174
176	Greater than 95% but less than 105% of *m/z* 174
177	5 to 10% of *m/z* 176

TABLE 2. PURGE-AND-TRAP CONDITIONS USED FOR METHOD PERFORMANCE RESULTS

Parameter	Conditions[a]
Sample volume	5 mL
Sample purge temperature	40 ^{o}C
Trap	Supelco K-Trap (Vocarb® 3000)
Purge cycle	40 mL/min for 11 min
Condenser purge temperature	20 ^{o}C
Dry purge	100 mL/min for 3 min
Desorb preheat temperature	250 ^{o}C
Desorb cycle	260 ^{o}C for 1.0 min
Bake rinse cycles	Sparging vessel and autosampler sample path rinsed twice
Bake cycle	260 ^{o}C for 6 min @ 200 mL/min

[a] The chromatograms presented in Figures 2 and 3 were obtained under these conditions.

TABLE 3. GAS CHROMATOGRAPHY/MASS SPECTROMETRY (GC/MS) CONDITIONS FOR METHOD PERFORMANCE RESULTS

Parameter	Conditions[a]
Column	Restek Rtx®-VMS 30 meter, 0.25 mm i.d., 1.4 µm d_f
Inlet liner	1-mm i.d., deactivated glass
Inlet conditions	30:1 split ratio, 200 °C, helium carrier gas, column flow rate: 0.9 mL/min
GC temperature program	45 °C for 4.5 min, 12 ºC/min to 100 °C, hold 0 min, 25 °C to 240 °C, hold 3.32 min
Solvent delay	1.5 min before activating filaments in the electron impact source
MS source temperature	230 ºC
MS quadrupole temperature	150 °C
GC/MS interface	Direct, 240 ºC
Full scan window 1	*m/z* 47 to 150 (1.7 to 2.9 min)
Full scan window 2	*m/z* 35 to 260 (2.9 min to 18 min)
SIM parameters	multiple retention time windows; dwell times set to allow seven to 10 scans across chromatographic peaks

TABLE 4. RETENTION TIMES, RECOMMENDED QUANTITATION IONS and SUGGESTED INTERNAL STANDARD REFERENCES FOR FULL SCAN MODE[a]

Analyte	Peak no. Fig.'s 2a, 2b, 2c	RT	Q-Ion	IS[b] Reference
dichlorodifluoromethane	1	1.84	85	1
chlorodifluoromethane	2	1.90	51	1
chloromethane	3	2.05	50	1
vinyl chloride	4	2.10	62	1
1,3-butadiene	5	2.11	54	1
bromomethane	6	2.40	94	1
trichlorofluoromethane	7	2.66	101	1
diethyl ether	8	2.98	59	1
1,1-dichloroethene	9	3.18	96	1
carbon disulfide	10	3.23	76	1
methyl iodide	11	3.36	142	1
allyl chloride	12	3.74	76	1
methylene chloride	13	3.87	84	1
trans-1,2-dichloroethene	14	4.08	96	1
methyl acetate	15	4.10	43	1
methyl-t-butyl ether-d_3 (surrogate #1)	16	4.21	76	1
methyl-t-butyl ether (MtBE)	17	4.23	73	1
t-butyl alcohol (TBA)	18	4.38	59	1
diisopropyl ether (DIPE)	19	4.77	45	1
1,1-dichloroethane	20	4.94	63	1
t-butyl ethyl ether (ETBE)	21	5.29	59	1
cis-1,2-dichloroethene	22	5.68	96	1
bromochloromethane	23	5.95	128	1

Analyte	Peak no. Fig.'s 2a, 2b, 2c	RT	Q-Ion	IS[b] Reference
chloroform	24	6.05	83	1
carbon tetrachloride	25	6.22	117	1
tetrahydrofuran	26	6.26	72	1
1,1,1-trichloroethane	27	6.32	97	1
1,1-dichloropropene	28	6.48	110	1
1-chlorobutane	29	6.55	56	1
benzene	30	6.80	78	1
t-amyl methyl ether (TAME)	31	6.96	73	1
1,2-dichloroethane	32	7.06	62	1
trichloroethene	33	7.53	132	1
1,4-difluorobenzene (IS #1)	34	7.58	114	1
t-amyl ethyl ether (TAEE)	35	7.85	59	1
dibromomethane	36	8.05	93	1
1,2-dichloropropane	37	8.18	63	1
bromodichloromethane	38	8.26	83	1
cis-1,3-dichloropropene	39	9.06	75	1
toluene	40	9.32	92	2
tetrachloroethene	41	9.73	166	2
trans-1,3-dichloropropene	42	9.78	75	2
ethyl methacrylate	43	9.96	69	2
1,1,2-trichloroethane	44	9.94	83	2
dibromochloromethane	45	10.12	129	2
1,3-dichloropropane	46	10.21	76	2
1,2-dibromoethane	47	10.35	107	2
chlorobenzene-d_5 (IS #2)	48	10.82	117	2
chlorobenzene	49	10.84	112	2
ethylbenzene	50	10.86	91	2
1,1,1,2-tetrachloroethane	51	10.90	131	2
m-xylene	52	10.99	106	2
p-xylene	53	10.99	106	2
o-xylene	54	11.36	106	2
styrene	55	11.41	104	2
bromoform	56	11.43	173	2
isopropylbenzene	57	11.62	105	2
4-bromofluorobenzene (surrogate #2)	58	11.85	95	3
bromobenzene	59	11.94	156	3
n-propylbenzene	60	11.96	91	3
1,1,2,2-tetrachloroethane	61	12.01	83	3
2-chlorotoluene	62	12.08	126	3
1,3,5-trimethylbenzene	63	12.11	105	3
1,2,3-trichloropropane	64	12.12	110	3
4-chlorotoluene	65	12.21	91	3
t-butylbenzene	66	12.35	134	3
pentachloroethane	67	12.38	167	3

Analyte	Peak no. Fig.'s 2a, 2b, 2c	RT	Q-Ion	IS[b] Reference
1,2,4-trimethylbenzene	68	12.40	105	3
sec-butylbenzene	69	12.49	105	3
4-isopropyltoluene	70	12.59	119	3
1,3-dichlorobenzene	71	12.66	146	3
1,4-dichlorobenzene-d_4 (IS #3)	72	12.71	152	3
1,4-dichlorobenzene	73	12.72	146	3
n-butylbenzene	74	12.90	134	3
hexachloroethane	75	13.02	166	3
1,2-dichlorobenzene-d_4 (surrogate #3)	76	13.03	152	3
1,2-dichlorobenzene	77	13.04	146	3
1,2-dibromo-3-chloropropane	78	13.61	157	3
hexachlorobutadiene	79	14.05	225	3
1,2,4-trichlorobenzene	80	14.08	180	3
naphthalene	81	14.31	128	3
1,2,3-trichlorobenzene	82	14.44	180	3

[a] These quantitation ions are appropriate for the column used to generate method performance data. The user must verify that the quantitation ions selected for their column are unique and free from interference due to overlapping method analytes.

[b] IS = internal standard.

TABLE 5. RETENTION TIMES, RECOMMENDED QUANTITATION IONS, CONFIRMATION IONS, SUGGESTED INTERNAL STANDARD REFERENCES, EXAMPLE CHROMATOGRAPHIC WINDOWS and DWELL TIMES FOR SIM MODE[a]

Analyte	Peak no. Fig.'s 5a, 5b, 5c	RT	Q-Ion	Confirmation Ions	IS[b] Reference	Window[c]
chlorodifluoromethane	1	1.87	51	67	1	1
chloromethane	2	2.03	50	52	1	
vinyl chloride	3	2.09	62	64	1	
1,3-butadiene	4	2.10	54	53	1	
bromomethane	5	2.39	94	96	1	
1,1-dichloroethene	6	3.18	96	61, 98	1	
methylene chloride	7	3.87	84	49	1	
trans-1,2-dichloroethene	8	4.07	96	61	1	2
methyl-t-butyl ether-d_3 (surrogate #1)	9	4.20	76	57	1	
methyl-t-butyl ether (MtBE)	10	4.22	73	57	1	
1,1-dichloroethane	11	4.94	63	65	1	
cis-1,2-dichloroethene	12	5.68	96	61	1	
bromochloromethane	13	5.96	128	130	1	
chloroform	14	6.05	83	85	1	
carbon tetrachloride	15	6.22	117	119	1	
1,1,1-trichloroethane	16	6.31	97	99	1	
benzene	17	6.79	78	77	1	
1,2-dichloroethane	18	7.06	62	64	1	3
trichloroethene	19	7.54	132	130, 95	1	

Analyte	Peak no. Fig.'s 5a, 5b, 5c	RT	Q-Ion	Confirmation Ions	IS[b] Reference	Window[c]
1,4-difluorobenzene (IS #1)	20	7.59	114	63	1	
1,2-dichloropropane	21	8.19	63	65	1	
bromodichloromethane	22	8.26	83	85	1	
toluene	23	9.32	92	91	2	
tetrachloroethene	24	9.74	166	164	2	
1,1,2-trichloroethane	25	9.95	83	97	2	
dibromochloromethane	26	10.12	129	127	2	
1,2-dibromoethane	27	10.35	107	109	2	
chlorobenzene-d_5 (IS #2)	28	10.83	117	-	2	
chlorobenzene	29	10.84	112	114	2	
ethylbenzene	30	10.86	91	106	2	
1,1,1,2-tetrachloroethane	31	10.90	131	133	2	4
m-xylene	32	11.00	106	91	2	
p-xylene	33	11.00	106	91	2	
o-xylene	34	11.36	106	91	2	
styrene	35	11.41	104	103, 78	2	
bromoform	36	11.43	173	175	2	
4-bromofluorobenzene (surrogate #2)	37	11.85	95	174	3	
n-propylbenzene	38	11.96	91	120	3	
1,2,3-trichloropropane	39	12.12	110	112, 75	3	
sec-butylbenzene	40	12.49	105	134	3	
1,4-dichlorobenzene-d_4 (IS #3)	41	12.71	152	-	3	
1,4-dichlorobenzene	42	12.73	146	148	3	5
1,2-dichlorobenzene-d_4 (surrogate #3)	43	13.03	152	-	3	
1,2-dichlorobenzene	44	13.04	146	148	3	
1,2-dibromo-3-chloropropane	45	13.61	157	155, 75	3	
1,2,4-trichlorobenzene	46	14.08	180	182	3	

[a] These quantitation ions are appropriate for the column used to generate method performance data. The user must verify that the quantitation ions selected for their column are unique and free from interference due to overlapping method analytes.

[b] IS = internal standard.

[c] Chromatographic window (also termed group number or period); dwell time for each ion is 10 milliseconds.

TABLE 6. LOWEST CONCENTRATION MINIMUM REPORTING LEVELS (LCMRLs) AND DETECTION LIMITS (DLs) FOR FULL SCAN MODE[a]

Analyte	LCMRL, µg/L	DL Fortification, µg/L	DL, µg/L
dichlorodifluoromethane	0.33	0.25	0.12
chlorodifluoromethane	0.16	0.25	0.059
chloromethane	0.16	0.10	0.077
vinyl chloride	0.15	0.25	0.063
1,3-butadiene	0.33	0.10	0.055
bromomethane	0.28	0.25	0.099
trichlorofluoromethane	0.23	0.25	0.083

Analyte	LCMRL, µg/L	DL Fortification, µg/L	DL, µg/L
diethyl ether	0.35	0.25	0.070
1,1-dichloroethene	0.18	0.25	0.14
carbon disulfide	0.20	0.10	0.078
methyl iodide	0.24	0.25	0.099
allyl chloride	0.26	0.25	0.12
methylene chloride	0.15	0.25	0.18
trans-1,2-dichloroethene	0.29	0.25	0.12
methyl acetate	0.21	0.25	0.12
methyl-t-butyl ether (MtBE)	0.17	0.10	0.042
t-butyl alcohol (TBA)	0.33	0.25	0.11
diisopropyl ether (DIPE)	0.10	0.10	0.029
1,1-dichloroethane	0.14	0.10	0.095
t-butyl ethyl ether (ETBE)	0.12	0.10	0.033
cis-1,2-dichloroethene	0.21	0.10	0.083
bromochloromethane	0.56	0.25	0.092
chloroform	0.16	0.10	0.070
carbon tetrachloride	0.14	0.10	0.073
tetrahydrofuran	0.49	0.10	0.063
1,1,1-trichloroethane	0.17	0.10	0.060
1,1-dichloropropene	0.50	0.25	0.14
1-chlorobutane	0.10	0.10	0.053
benzene	0.11	0.10	0.028
t-amyl methyl ether (TAME)	0.16	0.10	0.054
1,2-dichloroethane	0.23	0.10	0.027
trichloroethene	0.13	0.10	0.078
t-amyl ethyl ether (TAEE)	0.13	0.10	0.050
dibromomethane	0.18	0.25	0.13
1,2-dichloropropane	0.17	0.10	0.088
bromodichloromethane	0.19	0.25	0.081
cis-1,3-dichloropropene	0.13	0.10	0.050
toluene	0.13	0.10	0.031
tetrachloroethene	0.27	0.25	0.059
trans-1,3-dichloropropene	0.20	0.25	0.095
ethyl methacrylate	0.11	0.25	0.10
1,1,2-trichloroethane	0.38	0.10	0.048
dibromochloromethane	0.23	0.25	0.10
1,3-dichloropropane	0.12	0.10	0.098
1,2-dibromoethane	0.13	0.10	0.090
chlorobenzene	0.20	0.10	0.050
ethylbenzene	0.15	0.10	0.026
1,1,1,2-tetrachloroethane	0.18	0.10	0.081
m- and p-xylene	0.30	0.20	0.11
o-xylene	0.26	0.25	0.11
styrene	0.20	0.10	0.033
bromoform	0.26	0.25	0.14
isopropylbenzene	0.12	0.10	0.028
bromobenzene	0.19	0.10	0.066

Analyte	LCMRL, µg/L	DL Fortification, µg/L	DL, µg/L
n-propylbenzene	0.18	0.10	0.045
1,1,2,2-tetrachloroethane	0.15	0.10	0.067
2-chlorotoluene	0.26	0.10	0.088
1,3,5-trimethylbenzene	0.12	0.10	0.037
1,2,3-trichloropropane	0.42	0.25	0.13
4-chlorotoluene	0.23	0.10	0.082
t-butylbenzene	0.25	0.25	0.16
pentachloroethane	0.29	0.25	0.16
1,2,4-trimethylbenzene	0.18	0.10	0.055
sec-butylbenzene	0.24	0.10	0.052
4-isopropyltoluene	0.16	0.10	0.064
1,3-dichlorobenzene	0.20	0.10	0.049
1,4-dichlorobenzene	0.19	0.10	0.029
n-butylbenzene	0.30	0.10	0.094
hexachloroethane	0.62	0.25	0.14
1,2-dichlorobenzene	0.14	0.10	0.056
1,2-dibromo-3-chloropropane	0.44	0.25	0.15
hexachlorobutadiene	0.34	0.10	0.086
1,2,4-trichlorobenzene	0.15	0.10	0.071
naphthalene	0.14	0.10	0.044
1,2,3-trichlorobenzene	0.16	0.10	0.042

[a] LCMRLs calculated according to the procedure in reference 1 with the following modification: Instead of evaluating seven replicates at four concentration levels, LCMRLs are now obtained by analyzing four replicates at seven concentration levels.

TABLE 7. PRECISION AND ACCURACY OF METHOD ANALYTES FORTIFIED AT 0.50, 1.0 AND 10 µg/L IN REAGENT WATER FOR FULL SCAN MODE

Analyte	Fortified Conc. = 0.50 µg/L (n=7)		Fortified Conc. = 1.0 µg/L (n=7)		Fortified Conc. = 10 µg/L (n=7)	
	Mean % Recovery	RSD[a]	Mean % Recovery	RSD	Mean % Recovery	RSD
dichlorodifluoromethane	77.4	8.5	82.8	17	104	6.3
chlorodifluoromethane	127	4.1	122	4.7	110	7.1
chloromethane	88.8	14	102	3.3	108	5.5
vinyl chloride	103	8.7	106	6.0	109	6.5
1,3-butadiene	107	8.3	106	6.7	110	6.5
bromomethane	111	6.7	104	5.3	110	6.8
trichlorofluoromethane	105	9.0	104	8.2	111	6.9
diethyl ether	120	13	108	5.9	112	5.2
1,1-dichloroethene	108	7.9	93.2	5.3	103	6.0
carbon disulfide	93.6	6.4	92.3	6.0	98.9	6.6
methyl iodide	95.5	7.3	93.9	6.5	105	5.6
allyl chloride	76.1	5.6	84.2	6.1	100	8.0
methylene chloride	69.2	11	84.5	15	102	6.3
trans-1,2-dichloroethene	108	6.5	104	3.2	100	6.5
methyl acetate	88.9	11	89.6	12	103	4.3
methyl-t-butyl ether (MtBE)	97.5	8.9	97.6	3.5	103	5.2
t-butyl alcohol (TBA)	45.7	31	75.8	13	105	4.6
diisopropyl ether (DIPE)	90.5	3.5	96.2	2.5	103	5.2
1,1-dichloroethane	89.4	5.3	91.6	5.8	102	5.1
t-butyl ethyl ether (ETBE)	91.3	4.8	97.0	3.8	103	4.8
cis-1,2-dichloroethene	84.1	8.5	94.2	5.6	102	6.5
bromochloromethane	93.8	13	96.5	4.9	104	6.0
chloroform	90.1	4.5	97.3	4.3	103	5.5
carbon tetrachloride	83.0	9.7	92.4	3.9	100	5.2
tetrahydrofuran	86.6	21	93.5	8.9	100	5.1
1,1,1-trichloroethane	79.3	4.3	91.1	6.3	102	5.7
1,1-dichloropropene	99.7	6.6	95.6	6.7	97.6	8.1
1-chlorobutane	91.5	8.2	92.3	7.1	100	7.2
benzene	81.6	3.5	93.6	4.6	102	6.4
t-amyl methyl ether (TAME)	98.9	3.9	98.4	3.0	102	5.2
1,2-dichloroethane	105	4.0	102	4.5	104	4.3
trichloroethene	99.6	5.2	103	4.9	103	6.3
t-amyl ethyl ether (TAEE)	91.4	3.6	94.1	1.8	104	5.2
dibromomethane	89.0	12	93.8	6.1	104	5.4
1,2-dichloropropane	85.1	6.3	92.4	6.0	102	6.0
bromodichloromethane	87.3	8.5	97.1	3.7	104	4.7
cis-1,3-dichloropropene	83.9	3.9	92.7	3.5	102	5.9
toluene	85.6	3.4	92.0	6.5	102	4.4
tetrachloroethene	74.3	12	87.2	5.8	102	6.3
trans-1,3-dichloropropene	77.4	7.4	90.1	5.6	103	5.4
ethyl methacrylate	90.9	9.1	93.7	5.3	103	5.2
1,1,2-trichloroethane	97.6	7.0	101	8.5	104	3.7
dibromochloromethane	90.7	5.2	95.7	3.7	102	4.8
1,3-dichloropropane	93.0	2.7	96.4	4.0	105	3.9
1,2-dibromoethane	75.1	7.6	89.5	4.5	104	4.4
chlorobenzene	82.6	4.8	93.4	3.3	104	5.2
ethylbenzene	87.1	3.9	93.8	3.8	102	5.4

Analyte	Fortified Conc. = 0.50 µg/L (n=7)		Fortified Conc. = 1.0 µg/L (n=7)		Fortified Conc. = 10 µg/L (n=7)	
	Mean % Recovery	RSD[a]	Mean % Recovery	RSD	Mean % Recovery	RSD
1,1,1,2-tetrachloroethane	83.0	5.9	94.1	3.6	104	5.1
m- and p-xylene	82.6	7.0	93.3	2.9	102	4.5
o-xylene	77.3	5.6	94.3	2.7	103	5.6
styrene	88.2	8.1	95.3	3.3	102	5.3
bromoform	80.6	6.8	91.0	3.9	103	6.2
isopropylbenzene	83.1	2.8	93.6	3.0	103	5.3
bromobenzene	91.9	4.1	96.8	5.0	102	5.7
n-propylbenzene	89.7	4.1	96.3	2.1	100	6.1
1,1,2,2-tetrachloroethane	96.2	8.3	97.9	4.6	102	5.4
2-chlorotoluene	95.0	5.2	98.2	2.2	100	6.2
1,3,5-trimethylbenzene	87.4	4.4	94.9	1.8	102	5.8
1,2,3-trichloropropane	84.2	7.6	92.9	8.4	102	6.6
4-chlorotoluene	83.2	4.4	94.2	1.3	100	5.7
t-butylbenzene	86.9	8.7	92.4	6.9	102	6.0
pentachloroethane	87.6	12	89.9	5.8	100	5.8
1,2,4-trimethylbenzene	87.0	5.0	94.1	1.8	101	6.0
sec-butylbenzene	81.4	3.6	93.3	3.6	101	6.1
4-isopropyltoluene	84.5	5.9	95.5	2.4	102	6.6
1,3-dichlorobenzene	84.5	5.9	92.2	2.0	100	5.9
1,4-dichlorobenzene	86.6	4.2	97.2	3.3	102	5.7
n-butylbenzene	73.5	6.8	93.0	5.0	103	6.2
hexachloroethane	81.1	16	94.7	5.3	102	6.1
1,2-dichlorobenzene	83.0	6.2	96.6	3.4	103	5.6
1,2-dibromo-3-chloropropane	80.5	10	90.9	7.1	103	5.7
hexachlorobutadiene	64.2	6.0	85.7	6.6	100	6.9
1,2,4-trichlorobenzene	90.7	5.3	91.9	2.1	100	5.2
naphthalene	88.0	2.9	94.0	3.2	102	5.7
1,2,3-trichlorobenzene	86.8	8.7	92.4	4.0	101	5.5

[a] RSD = relative standard deviation.

TABLE 8. PRECISION AND ACCURACY OF METHOD ANALYTES FORTIFIED AT 0.50, 1.0 AND 10 µg/L IN DRINKING WATER FROM A GROUND WATER SOURCE[a] FOR FULL SCAN MODE

Analyte	Native Conc., µg/L (n=3)	Fortified Conc. = 0.50 µg/L (n=7)		Fortified Conc. = 1.0 µg/L (n=7)		Fortified Conc. = 10 µg/L (n=7)	
		Mean % Recovery[b]	RSD[c]	Mean % Recovery[b]	RSD	Mean % Recovery[b]	RSD
dichlorodifluoromethane	N.D.	112	2.8	95.0	5.6	104	4.1
chlorodifluoromethane	N.D.	80.7	8.9	91.4	6.8	105	4.5
chloromethane	N.D.	90.7	4.5	92.3	9.2	105	2.5
vinyl chloride	N.D.	98.9	6.9	97.3	5.0	103	3.2
1,3-butadiene	N.D.	66.1	16	84.3	5.9	101	4.0
bromomethane	N.D.	115	7.3	115	8.4	127	10
trichlorofluoromethane	N.D.	101	5.4	101	5.8	103	3.6
diethyl ether	N.D.	101	5.6	103	9.0	103	1.4
1,1-dichloroethene	N.D.	89.6	11	91.1	12	97.8	3.1
carbon disulfide	N.D.	88.8	8.7	93.7	5.4	99.9	2.5
methyl iodide	N.D.	81.0	18	81.6	11	105	8.5
allyl chloride	N.D.	92.0	13	99.2	12	96.7	4.6
methylene chloride	0.39	73.7	10	97.8	11	100	3.4
trans-1,2-dichloroethene	N.D.	82.2	19	91.2	8.2	102	3.4
methyl acetate	N.D.	96.5	7.3	86.9	15	98.6	2.1
methyl-t-butyl ether (MtBE)	N.D.	80.6	12	86.2	5.1	97.9	1.5
t-butyl alcohol (TBA)	N.D.	92.3	9.7	97.9	9.4	91.3	2.0
diisopropyl ether (DIPE)	N.D.	95.3	3.6	97.8	7.4	98.9	1.9
1,1-dichloroethane	N.D.	86.0	10	93.9	5.7	99.8	2.9
t-butyl ethyl ether (ETBE)	N.D.	81.4	5.7	91.2	3.3	98.1	2.2
cis-1,2-dichloroethene	N.D.	87.3	9.4	94.8	4.3	97.1	2.5
bromochloromethane	N.D.	101	9.5	104	7.0	97.2	3.3
chloroform	3.48	[d]	3.5	[d]	1.9	97.4	1.7
carbon tetrachloride	N.D.	71.0	8.4	86.2	10	98.7	0.87
tetrahydrofuran	N.D.	127	8.3	128.5	4.4	98.3	2.7
1,1,1-trichloroethane	N.D.	90.2	8.5	98.7	5.5	99.9	2.8
1,1-dichloropropene	N.D.	100	6.6	97.4	8.2	99.6	3.3
1-chlorobutane	N.D.	94.7	9.1	98.9	4.7	101	3.2
benzene	N.D.	84.5	7.3	93.0	4.7	98.6	2.6
t-amyl methyl ether (TAME)	N.D.	97.3	4.2	92.3	8.7	94.5	2.4
1,2-dichloroethane	N.D.	95.2	7.4	103	7.1	99.6	2.3
trichloroethene	N.D.	83.6	6.8	91.9	6.3	98.3	2.7
t-amyl ethyl ether (TAEE)	N.D.	89.0	8.8	96.4	5.4	96.3	1.7
dibromomethane	N.D.	89.0	12	96.4	7.6	97.5	2.1
1,2-dichloropropane	N.D.	85.5	7.2	93.9	6.8	96.4	1.6
bromodichloromethane	5.09	78.4[d]	1.5	75.5[d]	1.5	97.4	1.9
cis-1,3-dichloropropene	N.D.	90.1	6.7	94.7	7.7	95.1	1.4
toluene	N.D.	91.1	5.8	94.3	4.9	97.7	1.8
tetrachloroethene	N.D.	93.5	12	95.3	11	97.3	2.9
trans-1,3-dichloropropene	N.D.	82.4	6.4	92.0	11	95.8	3.2
ethyl methacrylate	N.D.	94.0	8.8	91.9	8.3	94.4	1.7
1,1,2-trichloroethane	N.D.	100	7.0	98.5	8.5	96.0	2.7
dibromochloromethane	6.08	[d]	1.8	[d]	3.5	97.6	1.4
1,3-dichloropropane	N.D.	87.2	5.1	93.0	8.1	96.3	2.5
1,2-dibromoethane	N.D.	99.0	8.0	98.8	9.1	95.8	3.1

Analyte	Native Conc., µg/L (n=3)	Fortified Conc. = 0.50 µg/L (n=7)		Fortified Conc. = 1.0 µg/L (n=7)		Fortified Conc. = 10 µg/L (n=7)	
		Mean % Recovery[b]	RSD[c]	Mean % Recovery[b]	RSD	Mean % Recovery[b]	RSD
chlorobenzene	N.D.	89.3	2.5	96.0	6.0	94.8	1.4
ethylbenzene	N.D.	84.8	8.9	92.5	7.4	97.6	1.2
1,1,1,2-tetrachloroethane	N.D.	90.9	7.2	94.9	7.9	94.5	1.6
m- and p-xylene	N.D.	92.6	5.6	94.0	4.7	96.7	1.6
o-xylene	N.D.	93.7	5.5	99.1	8.2	96.8	2.4
styrene	N.D.	88.3	6.6	90.5	3.5	96.0	2.1
bromoform	2.17	[d]	4.5	[d]	4.5	92.1	2.6
isopropylbenzene	N.D.	85.9	3.6	93.7	5.6	98.2	1.8
bromobenzene	N.D.	78.2	11	94.0	6.4	92.7	2.5
n-propylbenzene	N.D.	85.9	5.0	96.2	7.3	96.9	3.6
1,1,2,2-tetrachloroethane	N.D.	96.4	6.8	99.2	7.2	92.6	1.8
2-chlorotoluene	N.D.	83.3	4.8	93.8	8.1	93.2	2.9
1,3,5-trimethylbenzene	N.D.	85.4	5.1	95.9	6.3	96.6	3.4
1,2,3-trichloropropane	N.D.	92.5	10	96.8	10	93.3	2.9
4-chlorotoluene	N.D.	84.5	6.1	93.1	8.6	93.6	2.5
t-butylbenzene	N.D.	76.7	11	89.8	6.5	97.6	4.1
pentachloroethane	N.D.	97.6	7.7	99.8	6.3	93.8	3.1
1,2,4-trimethylbenzene	N.D.	90.9	4.9	98.0	5.5	95.8	3.1
sec-butylbenzene	N.D.	85.9	1.8	97.6	4.7	97.3	3.3
4-isopropyltoluene	N.D.	85.1	5.6	97.0	4.7	96.7	3.4
1,3-dichlorobenzene	N.D.	88.6	4.5	98.0	7.0	93.6	2.0
1,4-dichlorobenzene	N.D.	86.5	2.9	94.9	7.3	92.7	2.3
n-butylbenzene	N.D.	87.0	3.6	95.8	5.9	95.2	3.1
hexachloroethane	N.D.	99.5	15	103	10	97.6	4.4
1,2-dichlorobenzene	N.D.	89.6	7.1	95.6	7.0	92.9	2.4
1,2-dibromo-3-chloropropane	N.D.	92.2	13	95.8	5.3	92.5	2.6
hexachlorobutadiene	N.D.	80.8	6.1	91.7	6.8	94.8	3.6
1,2,4-trichlorobenzene	N.D.	82.1	3.3	92.1	6.0	92.5	2.5
naphthalene	N.D.	95.4	4.1	93.2	5.2	92.8	2.0
1,2,3-trichlorobenzene	N.D.	101	5.0	95.6	6.8	91.4	2.6

[a] Ground water physical parameters: pH = 7.61; hardness = 350 milligrams/liter (mg/L) (as $CaCO_3$); free chlorine = 0.77 mg/L.

[b] Recoveries corrected for native levels in the unfortified matrix.

[c] RSD = relative standard deviation.

[d] Fortified at less than ½ the concentration in the native matrix.

TABLE 9. PRECISION AND ACCURACY OF METHOD ANALYTES FORTIFIED AT 0.50, 1.0 AND 10 µg/L IN DRINKING WATER FROM A SURFACE WATER SOURCE[a] FOR FULL SCAN MODE

Analyte	Native Conc., µg/L (n=3)	Fortified Conc. = 0.50 µg/L (n=7)		Fortified Conc. = 1.0 µg/L (n=7)		Fortified Conc. = 10 µg/L (n=7)	
		Mean % Recovery[b]	RSD[c]	Mean % Recovery[b]	RSD	Mean % Recovery[b]	RSD
dichlorodifluoromethane	N.D.	90.5	10	90.7	3.7	103	2.8
chlorodifluoromethane	N.D.	102	9.9	97.3	5.3	105	3.1
chloromethane	N.D.	96.7	7.1	94.0	6.4	102	3.0
vinyl chloride	N.D.	104	6.3	105	4.5	106	3.1
1,3-butadiene	N.D.	109	5.5	97.9	8.7	104	3.0
bromomethane	N.D.	108	8.5	104	9.1	116	5.3
trichlorofluoromethane	N.D.	94.4	4.8	94.7	4.7	106	2.9
diethyl ether	N.D.	104	8.3	104	4.7	104	3.7
1,1-dichloroethene	N.D.	97.9	10	97.7	6.8	98.2	3.2
carbon disulfide	N.D.	94.6	5.9	93.7	7.2	99.7	2.3
methyl iodide	N.D.	85.1	7.5	86.3	6.0	95.2	3.2
allyl chloride	N.D.	104	9.4	92.9	4.0	96.3	3.7
methylene chloride	N.D.	104	9.1	102	6.1	102	2.2
trans-1,2-dichloroethene	N.D.	100	11	89.8	12	97.7	3.0
methyl acetate	N.D.	110	8.6	104	9.4	107	2.8
methyl-t-butyl ether (MtBE)	N.D.	87.0	9.3	91.9	4.0	99.5	2.9
t-butyl alcohol (TBA)	N.D.	91.8	7.6	99.7	4.6	107	3.0
diisopropyl ether (DIPE)	N.D.	85.5	4.0	90.4	5.7	100	2.2
1,1-dichloroethane	N.D.	95.1	5.1	92.4	4.3	98.9	3.2
t-butyl ethyl ether (ETBE)	N.D.	84.2	4.1	87.6	3.6	99.4	2.0
cis-1,2-dichloroethene	N.D.	97.3	5.5	96.6	7.5	101	2.5
bromochloromethane	N.D.	90.8	16	98.3	8.3	103	2.1
chloroform	19.4	[d]	2.0	[d]	6.1	86.0	2.2
carbon tetrachloride	N.D.	86.0	8.6	89.4	5.1	101	1.4
tetrahydrofuran	N.D.	84.5	14	97.7	6.5	103	2.7
1,1,1-trichloroethane	N.D.	84.9	7.5	89.3	7.2	97.7	2.9
1,1-dichloropropene	N.D.	92.6	15	90.5	4.2	96.3	4.6
1-chlorobutane	N.D.	92.3	8.7	91.0	7.9	99.3	2.2
benzene	N.D.	94.6	7.8	96.2	4.6	99.4	2.1
t-amyl methyl ether (TAME)	N.D.	80.8	9.8	88.8	8.7	100	2.6
1,2-dichloroethane	N.D.	94.7	8.7	90.8	3.5	99.8	1.8
trichloroethene	N.D.	89.4	10	90.5	7.1	99.2	1.9
t-amyl ethyl ether (TAEE)	N.D.	59.5	7.1	83.1	3.4	104	2.3
dibromomethane	N.D.	91.4	7.9	93.6	7.1	99.5	2.9
1,2-dichloropropane	N.D.	86.3	7.3	90.9	7.6	99.3	2.1
bromodichloromethane	20.3	[d]	1.6	[d]	3.4	87.4	2.4
cis-1,3-dichloropropene	N.D.	97.1	8.3	93.1	6.5	98.6	2.1
toluene	N.D.	82.5	6.7	86.1	4.4	97.5	1.9
tetrachloroethene	N.D.	80.3	7.1	83.5	5.9	93.6	1.5
trans-1,3-dichloropropene	N.D.	91.3	7.1	92.3	5.1	97.2	3.9
ethyl methacrylate	N.D.	84.4	5.1	89.5	4.5	98.3	2.5
1,1,2-trichloroethane	N.D.	79.8	11	88.0	8.5	101	1.0
dibromochloromethane	16.1	[d]	1.3	[d]	3.0	99.6	2.7
1,3-dichloropropane	N.D.	87.6	8.5	91.6	4.3	98.5	2.3
1,2-dibromoethane	N.D.	80.8	4.9	83.9	5.6	97.7	3.0

Analyte	Native Conc., µg/L (n=3)	Fortified Conc. = 0.50 µg/L (n=7)		Fortified Conc. = 1.0 µg/L (n=7)		Fortified Conc. = 10 µg/L (n=7)	
		Mean % Recovery[b]	RSD[c]	Mean % Recovery[b]	RSD	Mean % Recovery[b]	RSD
chlorobenzene	N.D.	73.9	6.6	86.0	3.1	97.2	2.1
ethylbenzene	N.D.	79.8	4.9	84.7	4.6	96.3	2.2
1,1,1,2-tetrachloroethane	N.D.	75.5	6.2	83.3	5.9	95.9	3.8
m- and p-xylene	N.D.	80.1	4.2	86.8	3.3	98.3	2.0
o-xylene	N.D.	75.6	7.2	81.0	4.3	97.0	1.3
styrene	N.D.	82.3	7.0	89.2	3.2	96.5	2.7
bromoform	3.63	[d]	3.5	[d]	4.0	96.0	2.4
isopropylbenzene	N.D.	73.6	6.0	82.4	5.7	97.7	2.1
bromobenzene	N.D.	79.0	11	86.1	7.5	95.7	3.7
n-propylbenzene	N.D.	64.9	6.9	82.2	3.6	97.0	3.1
1,1,2,2-tetrachloroethane	N.D.	74.1	8.0	86.3	4.7	96.9	4.6
2-chlorotoluene	N.D.	81.7	6.2	86.0	4.1	95.8	2.8
1,3,5-trimethylbenzene	N.D.	74.3	8.4	85.5	4.1	97.8	3.2
1,2,3-trichloropropane	N.D.	86.3	8.0	87.4	7.7	96.6	5.1
4-chlorotoluene	N.D.	69.9	11	79.7	5.8	97.2	2.8
t-butylbenzene	N.D.	69.4	13	84.8	9.1	97.4	4.1
pentachloroethane	N.D.	72.0	10	84.3	8.2	96.4	3.7
1,2,4-trimethylbenzene	N.D.	77.8	4.8	86.0	6.1	97.8	2.9
sec-butylbenzene	N.D.	64.5	5.5	80.7	5.7	99.1	2.6
4-isopropyltoluene	N.D.	64.0	3.8	79.6	6.9	98.4	2.8
1,3-dichlorobenzene	N.D.	77.3	10	84.4	8.8	97.3	2.5
1,4-dichlorobenzene	N.D.	70.5	4.2	86.2	5.5	97.4	2.4
n-butylbenzene	N.D.	69.4	12	80.9	9.5	99.1	3.7
hexachloroethane	N.D.	89.3	14	93.3	10	99.7	2.9
1,2-dichlorobenzene	N.D.	71.3	5.5	82.4	5.5	97.3	4.1
1,2-dibromo-3-chloropropane	N.D.	73.2	11	87.8	8.6	95.9	4.0
hexachlorobutadiene	N.D.	59.2	14	75.7	8.4	98.5	3.6
1,2,4-trichlorobenzene	N.D.	70.9	8.2	83.2	3.0	97.0	3.6
naphthalene	N.D.	68.3	4.5	83.1	6.0	101	4.5
1,2,3-trichlorobenzene	N.D.	72.3	10	82.8	4.6	97.0	5.1

[a] Surface water physical parameters: pH = 7.20; hardness = 152 milligrams/liter (mg/L) (as $CaCO_3$); free chlorine = 1.85 mg/L.

[b] Recoveries corrected for native levels in the unfortified matrix.

[c] RSD = relative standard deviation.

[d] Fortified at less than ½ the concentration in the native matrix.

TABLE 10. LOWEST CONCENTRATION MINIMUM REPORTING LEVELS (LCMRLs) AND DETECTION LIMITS (DLs) FOR SIM MODE[a]

Analyte	LCMRL, µg/L	DL Fortification, µg/L	DL, µg/L
chlorodifluoromethane	0.027	0.025	0.006
chloromethane	Not determined: significant background levels from trap materials (See Section 4.3.4)		
vinyl chloride	0.048	0.025	0.007
1,3-butadiene	0.028	0.025	0.008
bromomethane	Not determined: significant background levels from trap materials (See Section 4.3.4)		
1,1-dichloroethene	0.061	0.050	0.009
methylene chloride	Not determined: significant background levels from ambient sources		
trans-1,2-dichloroethene	0.028	0.025	0.014
methyl-t-butyl ether (MtBE)	0.012	0.025	0.009
1,1-dichloroethane	0.011	0.025	0.007
cis-1,2-dichloroethene	0.040	0.040	0.037
bromochloromethane	0.060	0.040	0.013
chloroform	0.032	0.025	0.015
carbon tetrachloride	0.033	0.025	0.008
1,1,1-trichloroethane	0.039	0.025	0.009
benzene	0.022	0.025	0.012
1,2-dichloroethane	0.029	0.025	0.012
trichloroethene	0.037	0.025	0.012
1,2-dichloropropane	0.043	0.040	0.011
bromodichloromethane	0.027	0.025	0.011
toluene	0.034	0.025	0.009
tetrachloroethene	0.025	0.025	0.011
1,1,2-trichloroethane	0.029	0.025	0.010
dibromochloromethane	0.016	0.025	0.006
1,2-dibromoethane	0.048	0.025	0.023
chlorobenzene	0.036	0.025	0.009
ethylbenzene	0.013	0.025	0.009
1,1,1,2-tetrachloroethane	0.059	0.025	0.011
m-xylene and p-xylene	0.17	0.025	0.020
o-xylene	0.037	0.025	0.016
styrene	0.018	0.025	0.012
bromoform	0.021	0.025	0.008
n-propylbenzene	0.022	0.025	0.010
1,2,3-trichloropropane	0.033	0.040	0.028
sec-butylbenzene	0.019	0.025	0.011
1,4-dichlorobenzene	0.026	0.025	0.012
1,2-dichlorobenzene	0.025	0.025	0.013
1,2-dibromo-3-chloropropane	0.069	0.040	0.033
1,2,4-trichlorobenzene	0.030	0.025	0.013

[a] LCMRLs calculated according to the procedure in reference 1 with the following modification: Instead of evaluating seven replicates at four concentration levels, LCMRLs are now obtained by analyzing four replicates at seven concentration levels.

TABLE 11. SAMPLE HOLDING TIME DATA FOR METHOD ANALYTES FORTIFIED AT 20 µg/L IN A CHLORINATED SURFACE WATER[a] (n=3 SAMPLES)

Analyte	Day 0		Day 7		Day 14	
	Mean % Recovery	RSD[b]	Mean % Recovery	RSD	Mean % Recovery	RSD
dichlorodifluoromethane	110	2.2	107	2.5	111	3.9
chlorodifluoromethane	112	2.0	109	0.63	107	0.87
chloromethane	114	0.88	110	1.1	112	2.0
vinyl chloride	117	0.99	113	1.6	116	0.87
1,3-butadiene	116	1.3	106	1.9	105	4.6
bromomethane	117	6.9	116	3.5	114	2.5
trichlorofluoromethane	114	0.54	116	2.9	117	2.4
diethyl ether	110	1.2	106	1.5	113	1.0
1,1-dichloroethene	106	0.94	107	0.62	111	2.3
carbon disulfide	108	0.58	106	1.9	107	3.0
methyl iodide	106	1.3	106	0.33	101	0.93
allyl chloride	108	0.57	100	0.73	101	1.0
methylene chloride	106	0.17	106	0.55	108	0.92
trans-1,2-dichloroethene	107	0.89	103	1.8	107	1.5
methyl acetate	105	3.4	101	0.32	83.2	4.0
methyl-t-butyl ether (MtBE)	104	0.92	101	0.049	105	0.79
t-butyl alcohol (TBA)	105	3.2	104	2.9	105	1.8
diisopropyl ether (DIPE)	107	0.71	109	0.72	109	0.65
1,1-dichloroethane	109	1.0	108	0.82	111	0.74
t-butyl ethyl ether (ETBE)	105	0.30	107	0.53	107	0.89
cis-1,2-dichloroethene	106	0.66	105	0.67	108	0.71
bromochloromethane	104	0.64	104	1.4	105	0.45
chloroform	102	0.56	100	0.91	107	0.97
carbon tetrachloride	108	1.4	109	1.2	116	2.2
tetrahydrofuran	102	1.4	98.4	1.5	101	1.7
1,1,1-trichloroethane	109	0.70	109	0.89	115	0.94
1,1-dichloropropene	110	0.24	107	1.5	108	1.5
1-chlorobutane	114	0.25	111	1.1	115	0.90
benzene	108	0.63	106	1.2	109	0.57
t-amyl methyl ether (TAME)	105	0.56	107	0.45	107	0.59
1,2-dichloroethane	108	2.1	105	0.59	108	1.2
trichloroethene	105	0.28	105	0.85	107	0.16
t-amyl ethyl ether (TAEE)	107	0.31	108	0.73	107	0.69
dibromomethane	106	1.5	105	0.42	107	0.33
1,2-dichloropropane	108	0.48	106	0.21	109	0.78
bromodichloromethane	105	0.85	104	1.2	109	1.2
cis-1,3-dichloropropene	106	0.33	98.5	1.0	96.7	1.2
toluene	109	1.3	108	0.46	110	1.2
tetrachloroethene	110	2.4	106	1.1	111	2.7
trans-1,3-dichloropropene	106	1.9	99.1	0.94	96.4	0.30
ethyl methacrylate	108	1.4	104	0.56	105	1.5
1,1,2-trichloroethane	105	1.8	103	0.93	106	2.1
dibromochloromethane	104	0.99	104	0.98	107	0.98
1,3-dichloropropane	108	1.0	104	0.10	106	1.2
1,2-dibromoethane	104	1.7	104	1.3	106	0.72
chlorobenzene	108	1.4	106	0.36	109	1.1
ethylbenzene	115	1.1	110	0.33	116	1.4
1,1,1,2-tetrachloroethane	106	1.6	106	0.35	110	0.92
m- and p-xylene	114	1.3	110	0.70	114	2.3

Analyte	Day 0		Day 7		Day 14	
	Mean % Recovery	RSD[b]	Mean % Recovery	RSD	Mean % Recovery	RSD
o-xylene	113	0.83	109	0.87	115	0.79
styrene	111	1.3	106	0.62	108	1.7
bromoform	103	1.8	101	1.7	108	1.5
isopropylbenzene	118	1.2	114	0.81	123	1.5
bromobenzene	109	0.38	104	1.9	107	1.8
n-propylbenzene	122	1.3	111	2.0	119	2.1
1,1,2,2-tetrachloroethane	108	0.63	100	1.5	103	0.83
2-chlorotoluene	115	0.65	107	1.9	112	2.1
1,3,5-trimethylbenzene	121	1.2	111	1.4	120	1.7
1,2,3-trichloropropane	106	1.6	102	2.5	102	1.4
4-chlorotoluene	113	4.1	106	1.8	110	2.0
t-butylbenzene	123	0.84	115	1.3	129	0.38
pentachloroethane	109	2.2	103	3.0	112	0.47
1,2,4-trimethylbenzene	120	0.99	110	2.0	118	1.5
sec-butylbenzene	125	1.5	115	1.8	129	1.9
4-isopropyltoluene	123	1.3	112	2.4	123	2.6
1,3-dichlorobenzene	113	0.85	105	1.7	109	1.5
1,4-dichlorobenzene	113	1.1	104	2.0	107	1.7
n-butylbenzene	122	1.3	106	3.6	111	6.5
hexachloroethane	123	0.42	115	0.82	132	1.6
1,2-dichlorobenzene	111	0.82	104	1.7	108	1.0
1,2-dibromo-3-chloropropane	105	1.9	99.1	1.9	103	2.4
hexachlorobutadiene	122	2.5	112	3.6	124	2.1
1,2,4-trichlorobenzene	114	1.3	102	2.3	105	3.0
naphthalene	112	0.77	103	1.0	107	2.1
1,2,3-trichlorobenzene	114	0.53	103	1.7	108	2.0

[a] Surface water physical parameters: pH = 7.43; hardness = 154 milligrams/liter (mg/L) (as $CaCO_3$); free chlorine = 2.7 mg/L; total chlorine = 3.7 mg/L.

[b] RSD = relative percent deviation.

TABLE 12. INITIAL DEMONSTRATION OF CAPABILITY (IDC) QUALITY CONTROL REQUIREMENTS

Method Reference	Requirement	Specification and Frequency	Acceptance Criteria
Section 9.2.1	Demonstration of low system background	Analyze a Laboratory Reagent Blank (LRB) prior to any other IDC steps.	Demonstrate that all method analytes are <½ of the Minimum Reporting Level (MRL) and that possible interferences from reagents and glassware do not prevent the identification and quantitation of method analytes.
Section 9.2.1	Test for system carryover	Analyze a LRB after the high calibration standard during the IDC calibration.	Demonstrate that the method analytes are <½ of the MRL.
Section 9.2.2	Demonstration of precision	Analyze 7 replicate Laboratory Fortified Blanks (LFBs) fortified near the midrange concentration.	Percent relative standard deviation must be ≤20%.
Section 9.2.3	Demonstration of accuracy	Calculate average recovery for replicates used in Section 9.2.2.	Mean recovery within ±20% of the true value.
Section 9.2.4	MRL confirmation	Fortify and analyze 7 replicate LFBs at the proposed MRL concentration. Confirm that the Upper Prediction Interval of Results (PIR) and Lower PIR (Sect. 9.2.4.2) meet the recovery criteria.	Upper PIR ≤150% Lower PIR ≥50%
Section 9.2.5	Quality Control Sample (QCS)	Analyze mid-level QCS.	Results must be within ±30% of the true value.

TABLE 13. ONGOING QUALITY CONTROL REQUIREMENTS

Method Reference	Requirement	Specification and Frequency	Acceptance Criteria
Section 10.1	Initial calibration	Use the internal standard calibration technique to generate a linear or quadratic calibration curve. Use at least 7 standard concentrations. Validate the calibration curve as described in Section 10.1.10.	When each calibration standard is calculated as an unknown using the calibration curve, the lowest level standard must be within ±50% of the true value. All other points must be within ±30% of the true value.
Section 9.3.1	Laboratory Reagent Blank (LRB)	Analyze one LRB with each Analysis Batch.	Demonstrate that all method analytes are below ½ the Minimum Reporting Level (MRL) and that possible interference from reagents and glassware do not prevent identification and quantitation of method analytes.
Section 10.2	Continuing Calibration Check (CCC)	Verify initial calibration by analyzing a low-level CCC at the beginning of each Analysis Batch. Subsequent CCCs are required after every 10 field samples and after the last field sample in a batch.	The lowest level CCC must be within ±50% of the true value. All other points must be within ±30% of the true value. Results for field samples that are not bracketed by acceptable CCCs are invalid.
Section 9.3.5	Internal standard (IS)	Internal standards are added to all standards and samples.	Peak area counts for each IS must be within ±30% of the area in the most recent CCC and ±50% of the average peak area in the initial calibration.
Section 9.3.6	Surrogate analytes	Surrogates are added to all field samples and QC samples prior to analysis.	70% to 130% recovery
Section 9.3.7	Laboratory Fortified Sample Matrix (LFSM)	Analyze one LFSM per Analysis Batch. Fortify the LFSM with method analytes at a concentration close to but greater than the native concentrations (if known).	For analytes fortified at concentrations ≤2 x the MRL, the result must be within ±50% of the true value. All other analytes must be within ±30% of the true value.
Section 9.3.8	Laboratory Fortified Sample Matrix Duplicate (LFSMD) or Field Duplicate (FD)	Analyze at least one LFSMD or FD with each Analysis Batch.	For LFSMDs or FDs, relative percent differences must be ≤30% (≤50% if concentration ≤2 x the MRL.).
Section 9.3.9	Field Reagent Blank (FRB)	Analyze FRB if method analytes are detected in field samples (except disinfection byproducts).	Qualify results of any analyte detected in both field samples and the FRB.
Section 9.3.10	Quality Control Sample (QCS)	Analyze mid-level QCS at least quarterly.	Results must be ±30% of the true value.

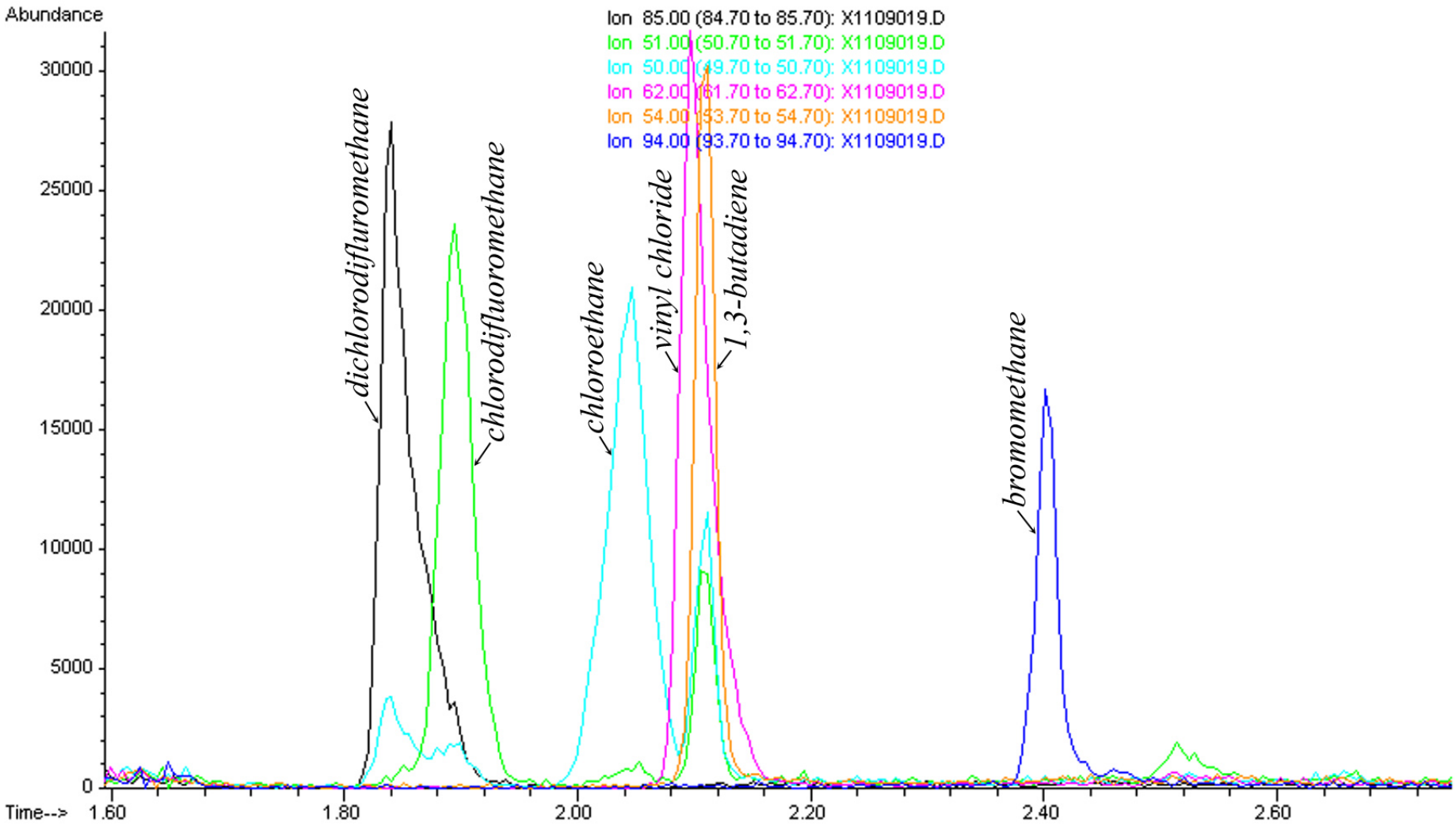

Figure 1. Mass chromatograms of "gases" in full scan mode @ 10 µg/L.

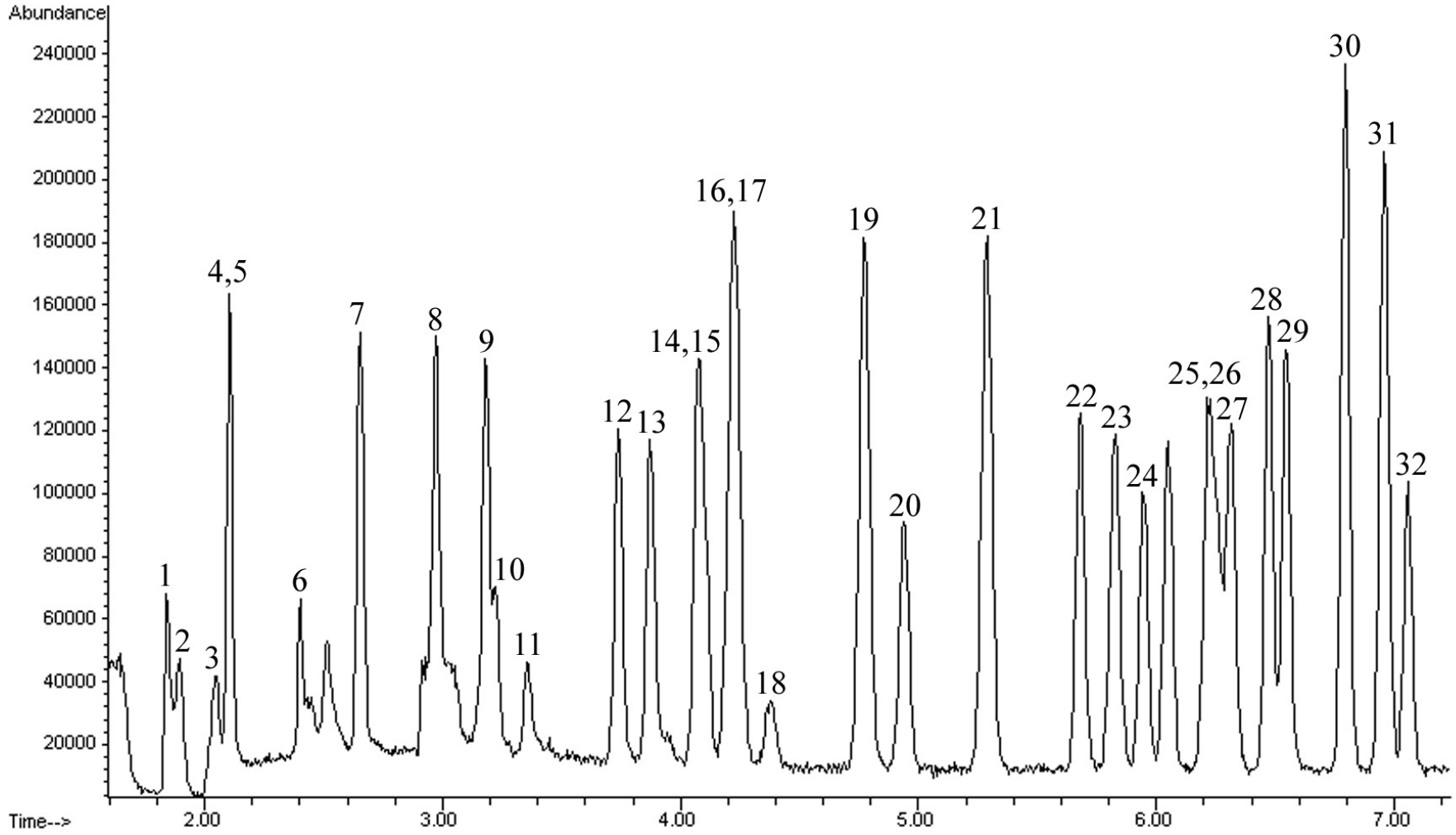

Figure 2a. Reconstructed total ion chromatogram full scan mode: 10-µg/L procedural calibration standard. See Table 4 for peak number to peak name cross reference.

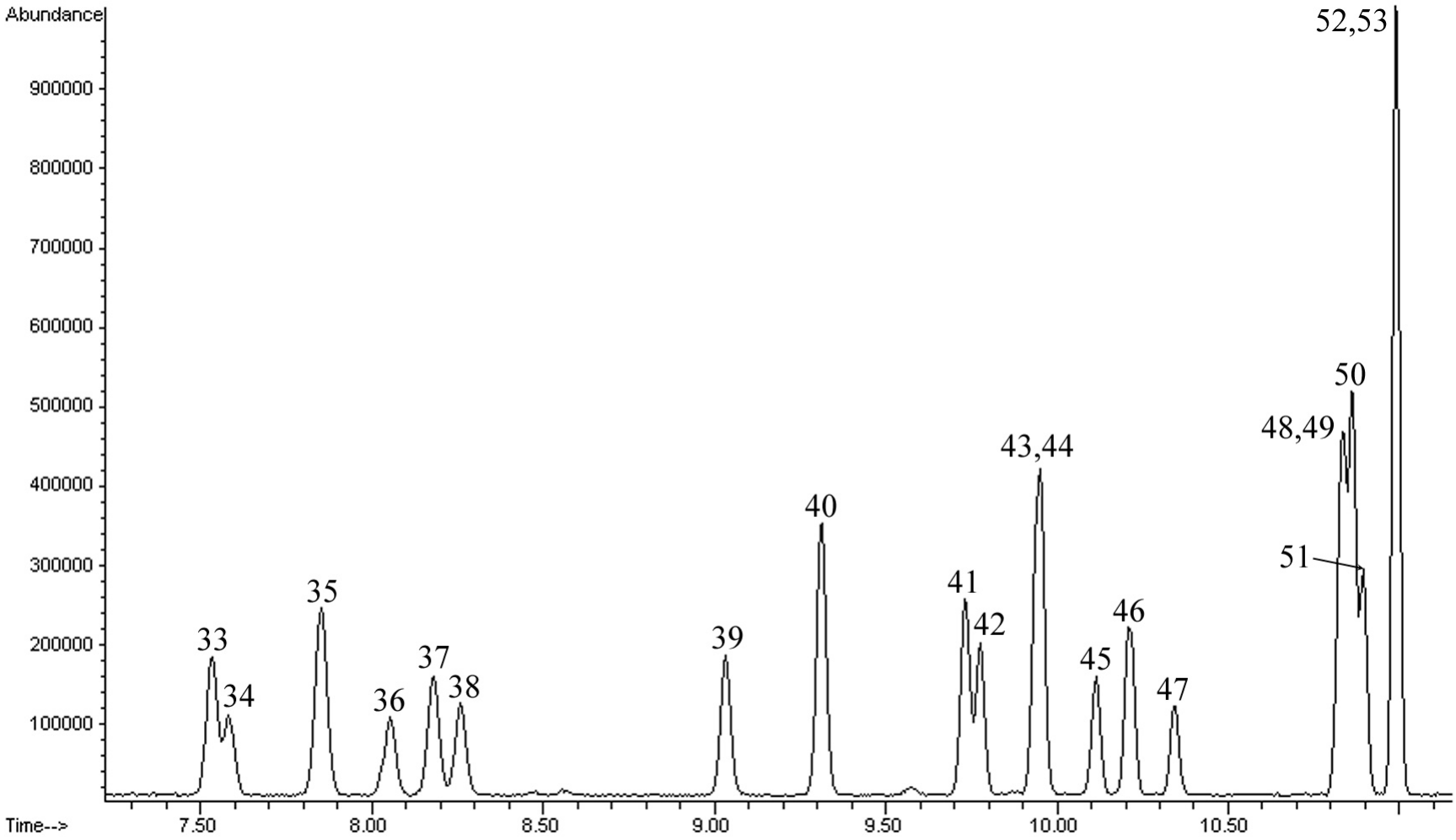

Figure 2b. Reconstructed total ion chromatogram full scan mode: 10-µg/L procedural calibration standard. See Table 4 for peak number to peak name cross reference.

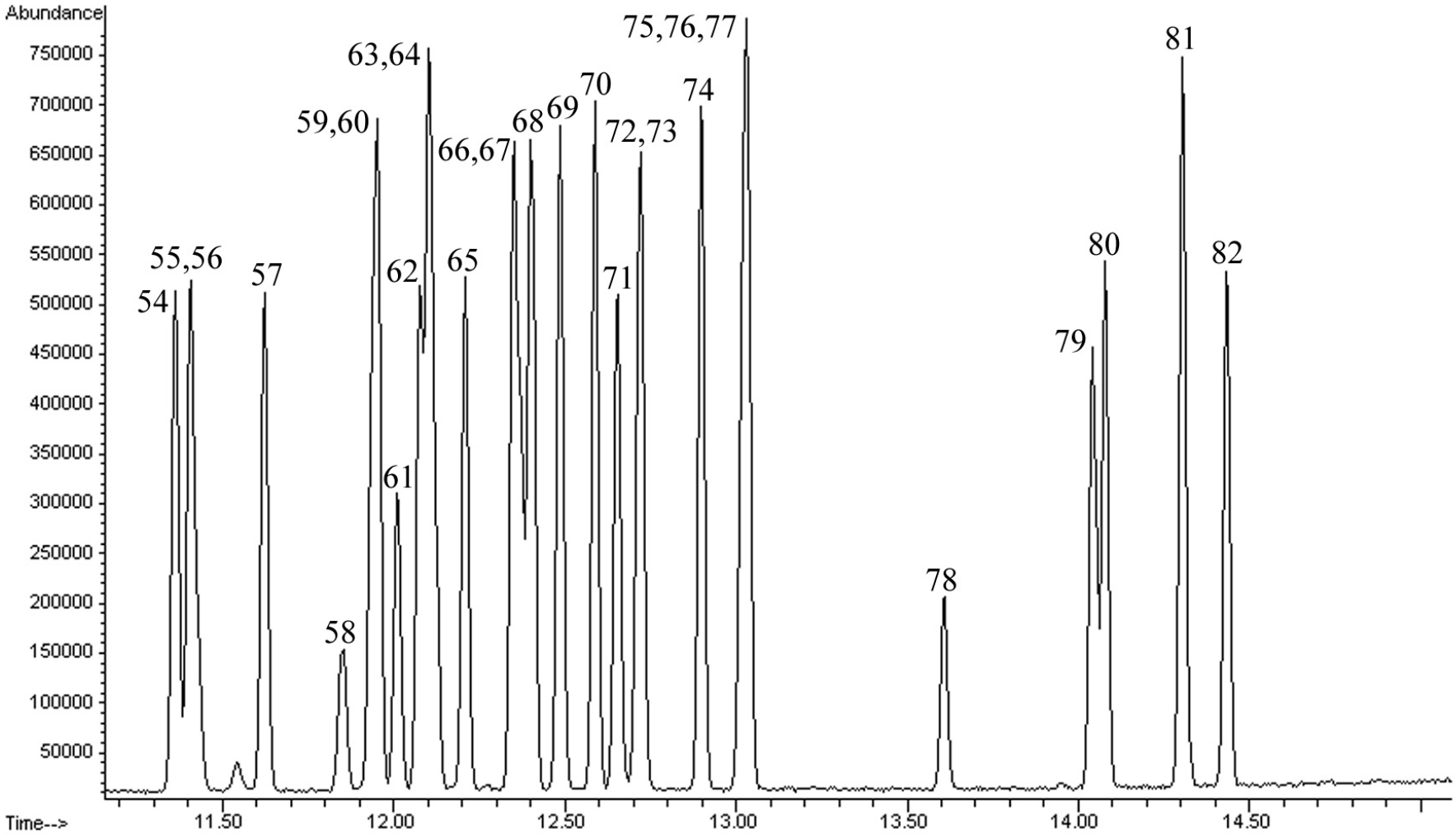

Figure 2c. Reconstructed total ion chromatogram full scan mode: 10-µg/L procedural calibration standard. See Table 4 for peak number to peak name cross reference.

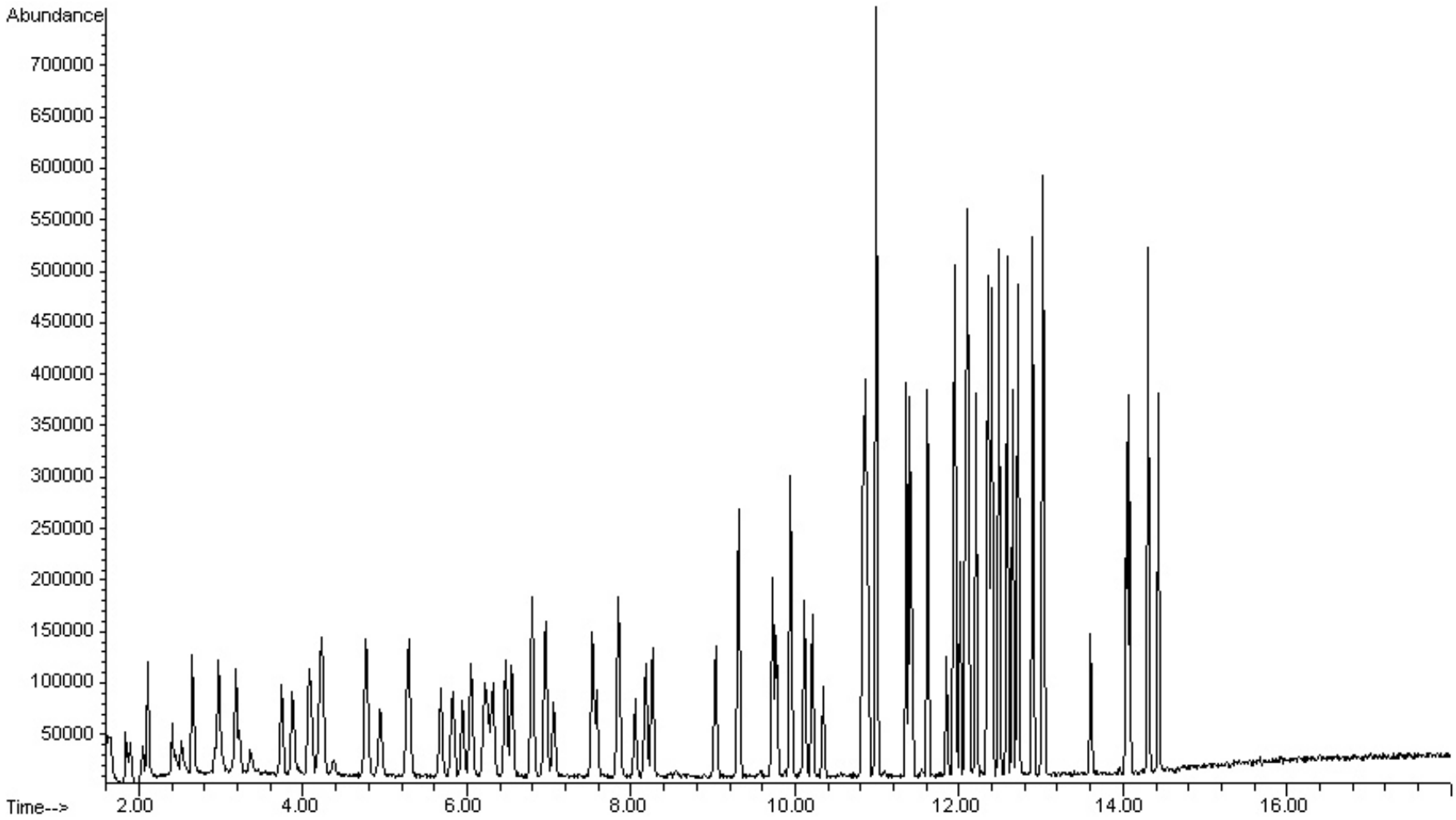

Figure 3. Reconstructed total ion chromatogram full scan mode: method analytes fortified into drinking water @ 10 µg/L.

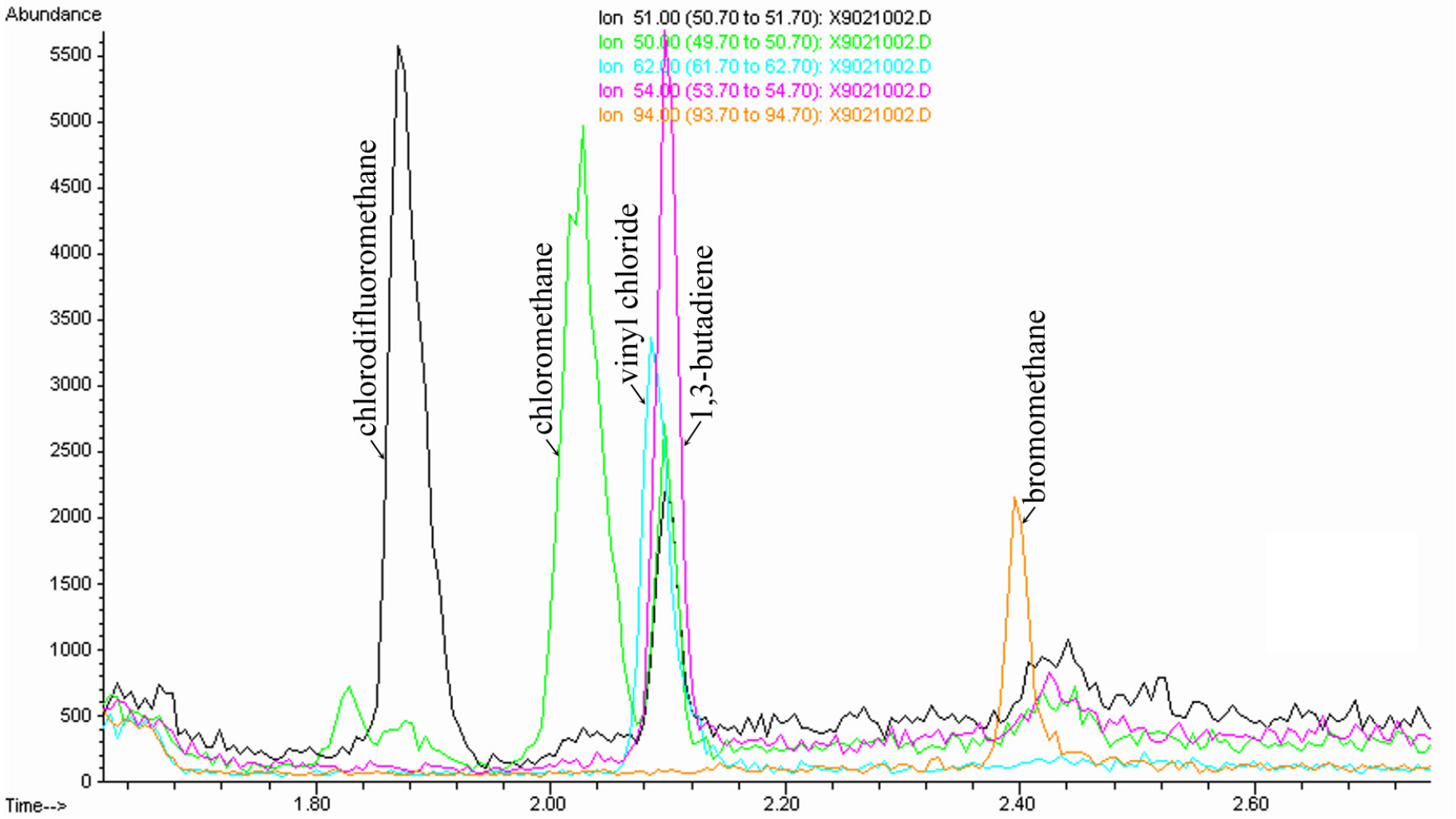

Figure 4. Mass chromatograms of "gases" in SIM mode @ 1.0 µg/L.

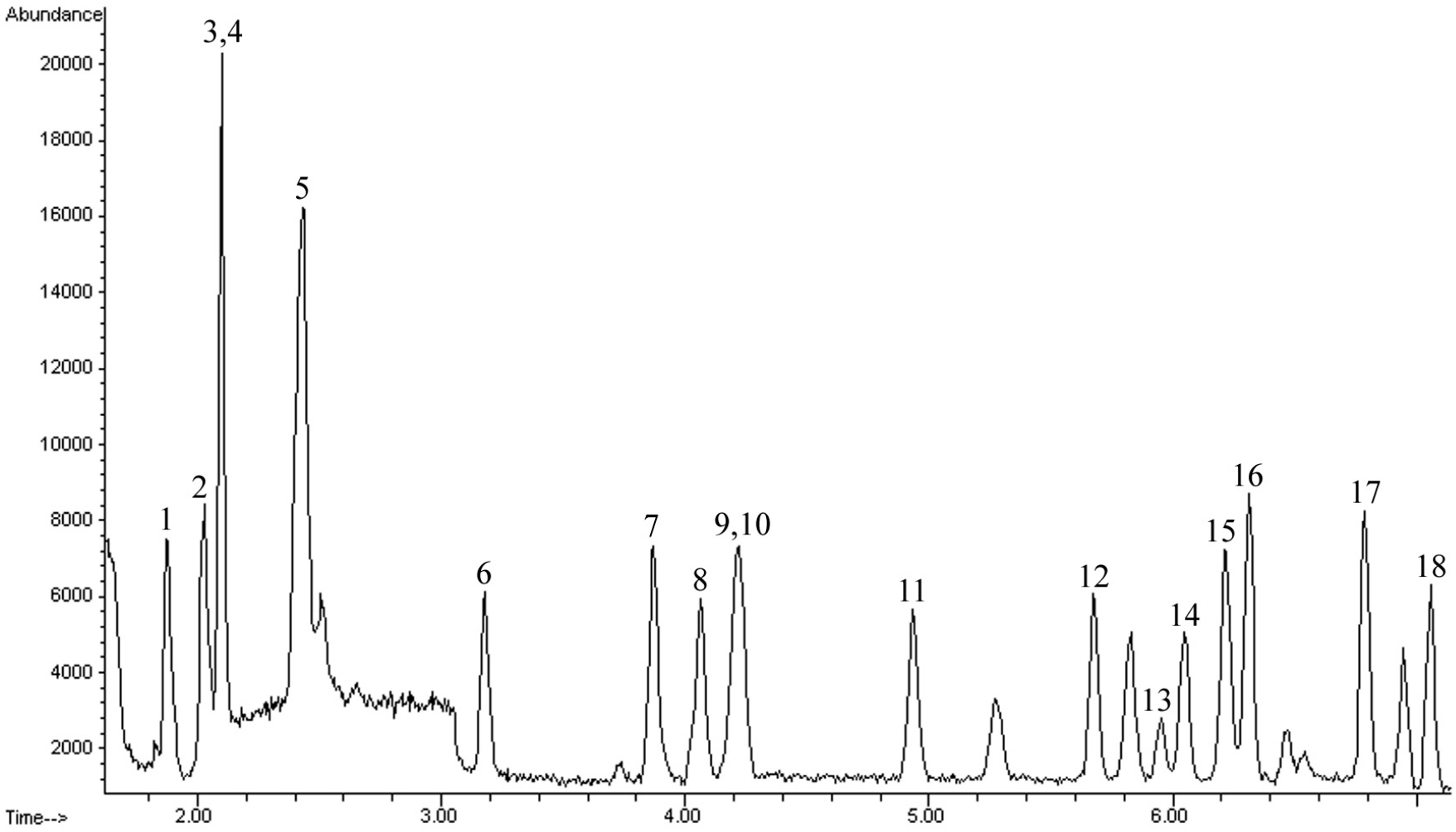

Figure 5a. Reconstructed total ion chromatogram SIM mode: 1.0-µg/L procedural calibration standard. See Table 5 for peak number to peak name cross reference.

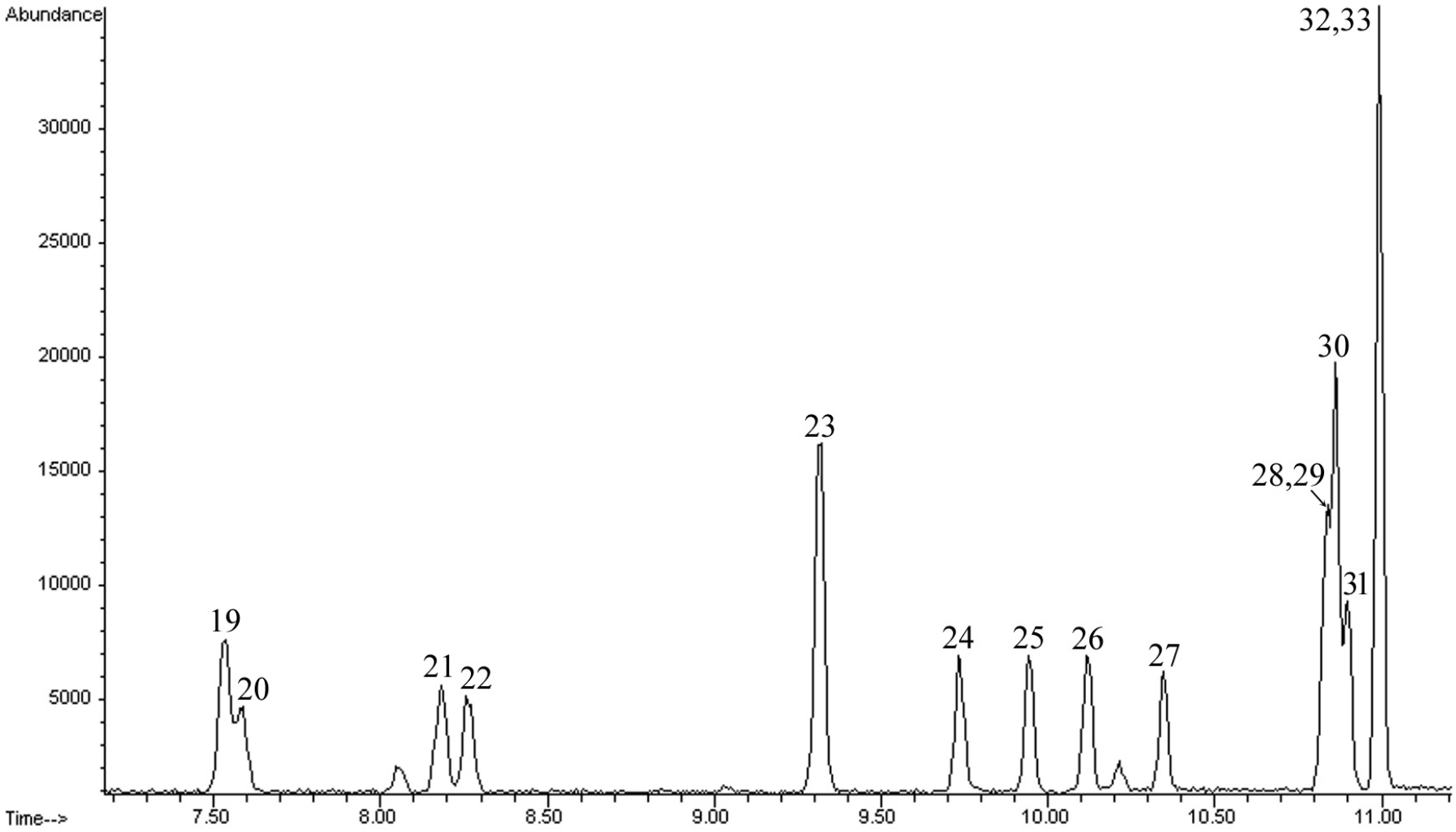

Figure 5b. Reconstructed total ion chromatogram SIM mode: 1.0-µg/L procedural calibration standard. See Table 5 for peak number to peak name cross reference.

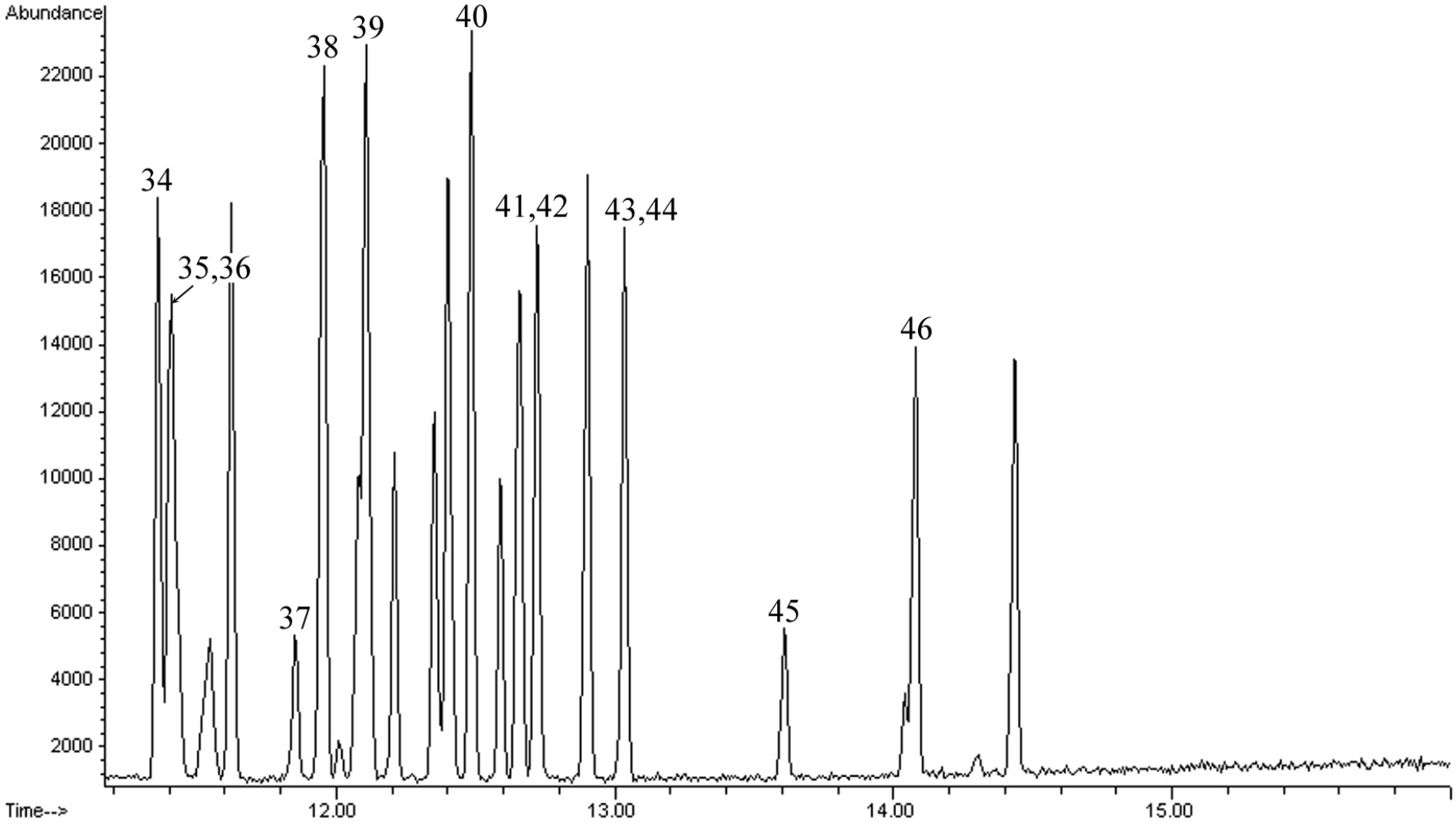

Figure 5c. Reconstructed total ion chromatogram SIM mode: 1.0-µg/L procedural calibration standard. See Table 5 for peak number to peak name cross reference.