Application Note 35000809

U.S. EPA Method 524.3 for Analysis of Volatile Organic Compounds (VOCs) in Finished Drinking Water: Optimized Instrument Parameters and Method Validation

Keywords

Drinking Water
Emerging Contaminants
Fuel Oxygenates
Method 524.2
Method 524.3
Minimum Reporting Levels (MRLs)
Purge & Trap (P&T)
Single Ion Mode (SIM)
Trihalomethanes (THMs)
U.S. EPA Office of Water
Volatile Organic Compounds (VOCs)

Introduction

The U.S. EPA Office of Groundwater and Drinking Water released Method 524.3 (1), "Measurement of Purgeable Organic Compounds in Water by Capillary Column Gas Chromatography/Mass Spectrometry, Revision 1.0," in the Federal Register (2), on August 3, 2009. The new method is used for determination of volatile organic compounds (VOCs) in finished drinking water, and includes several significant changes and improvements over its predecessor, U.S. EPA Method 524.2 (3).

This application note presents optimized instrument operating parameters, including a 6-minute purge time, and a complete set of method validation data. Quality control statistics shown here include calibration acceptance data, Minimum Reporting Levels (MRLs), Detection Limits (DLs) and Lowest Concentration Minimum Reporting Levels (LCMRLs); two precision and accuracy studies from the Initial Demonstration of Capability (IDC); and results from Laboratory Reagent Blanks (LRBs) and Continuing Calibration Check (CCC) samples.

Instrumentation

Instrumentation used for this project was the OI Analytical Eclipse 4660 Purge-and-Trap (P&T) Sample Concentrator equipped with an Infra-Sparge™ Sample heater, Model 4551A Water Autosampler, Standard Addition Module (SAM) (Figure 1), and an Agilent 7890/5975 GC-MS.

Figure 1. OI Analytical Eclipse 4660 Purge-and-Trap Sample Concentrator, 4551A Water Autosampler, and Standard Addition Module (SAM).

New Elements of Method 524.3

U.S. EPA Method 524.3 contains several noteworthy changes compared to previous protocols, which improve the performance of the method and allow the user greater latitude when optimizing instrument parameters. Some of the most important changes to the method are summarized below.

Compound List

U.S. EPA Method 524.3 includes a modified target compound list of 76 VOCs. Compounds that are not regulated and some of the poor performers in 524.2 have been removed from this new method. Two emerging contaminants of interest, 1,3-butadiene and chlorodifluoromethane, plus several oxygenates used as additives in reformulated gasoline have been added. The new method also increases the number of internal standards (IS) from 1 to 3, and the number of surrogate standards (SS) from 2 to 3.

Sample Preservation

The revised method includes a new sample-preservation scheme that does not require transporting hazardous materials to the field, and does not employ hydrochloric acid. Samples are now preserved with maleic and ascorbic acids. In addition, the method requires a procedural calibration, whereby both of the new preservatives are added to all calibration standards and other QC samples.

Purge-and-Trap Operating Parameters

Method 524.3 allows the analyst to use P&T operating conditions recommended by the instrument manufacturer, with five parameters restricted to prescribed ranges (Section 9.1). See Table 1 for a list of the five parameters and their prescribed ranges. If the instrument is operated within the "Recommended" ranges, no further steps are necessary and the operator may proceed with the Initial Demonstration of Capability (IDC) immediately after calibration. If the parameters are extended into the "Allowable" ranges, additional method modification QC requirements must be met (Section 9.4). Parameters outside the "Allowable" ranges may not be used.

Table 1. Purge-and-Trap Variables which may be Modified within Defined "Recommended" and "Allowable" Ranges

Parameter	Recommended		Allowable	
	Minimum	Maximum	Minimum	Maximum
Sample Temperature	Ambient	40 °C	Ambient	60 °C
Purge Flow Rate	40 mL/min	80 mL/min	20 mL/min	200 mL/min
Purge Volume	360 mL	520 mL	240 mL	680 mL
Desorb Time	1 min	2 min	0.5 min	4 min
Purge Volume + Dry Purge Volume	360 mL	720 mL	240 mL	880 mL

Instrument Operating Parameters

All other instrument operating parameters, including the remaining concentrator conditions, gas chromatograph (GC) conditions, and mass spectrometer (MS) conditions, may be varied without restriction. Single Ion Monitoring (SIM) mode is allowed for compounds which are regulated at concentrations below the normal instrument calibration range. Sample size may not be modified from the 5-mL volume required in the method.

Quality Control (QC) Requirements

Two significant changes to the QC requirements are the way the initial calibration curve is evaluated and the addition of Minimum Reporting Level (MRL) confirmation criteria. Determination of Detection Limits (DLs) is now optional and dependant on program-specific requirements. The Lowest Concentration Minimum Reporting Levels (LCMRLs) are not required, but are referenced in the method. Some of these new QC requirements are described in detail in the Results and Discussion section, below.

Experimental

Evaluation of several different P&T operating conditions has been described previously (4). For this study, the five variable P&T parameters and the sorbent trap were chosen as described below. Full instrument operating conditions are described in Table 2.

Sample Temperature

All standards and samples were purged at 40 °C to optimize purge efficiency of the hydrophilic and oxygenated compounds, while minimizing the amount of water transferred to the trap. Accurate and consistent heating of the sample with the Eclipse Infra-Sparge™ sample heater has the added advantage of purging every sample under precisely the same conditions, leading to improved sample-to-sample repeatability, and lower Relative Standard Deviations (RSDs).

Purge Flow Rate and Purge Volume

Several purge flow rates and volumes were evaluated and all resulted in exceptional method performance. For this study, all standards and samples were purged at 60 mL/minute for 6 minutes, for a total purge volume of 360 mL. These values fall within the "Recommended" range and minimize overall cycle time. These conditions shorten the P&T cycle time for each sample by 5 minutes (approximately 28%), significantly increasing the number of samples that can be analyzed in a given period of time.

Desorb Time

A desorb time of 1.0 minute was chosen because it has been shown to produce excellent desorb efficiency for all compounds, while minimizing the amount of water transferred to the GC/MS and shortening the P&T cycle time.

Purge Volume plus Dry Purge Volume

For this study, the total volume of purge gas plus dry purge gas stayed at the minimum recommended value of 360 mL because no dry purge step was used. The patented (5) Eclipse water management system is exceptionally efficient at removing water and eliminates the need for the dry purge. When the dry purge step is eliminated, the overall P&T cycle time can be shortened by 2 minutes or more.

Table 2. Instrument Operating Conditions for U.S. EPA Method 524.3

Purge-and-Trap	**Eclipse 4660 P&T Sample Concentrator**
Trap	Trap 524.3
Sample Size/ Temperature	5–mL sample, 40 °C during Purge
Purge Gas	Helium (He)
Purge Conditions	6 minutes at 60 mL/min (360–mL purge volume)
Desorb Preheat	ON, 230 °C
Desorb Conditions	1 minute at 240 °C
Bake Conditions	5 minutes at 250 °C *Note: The Bake time can be extended if necessary to balance the P&T cycle time with the GC cycle time.*
Six-port Valve and Transfer Line Temperatures	110 °C
Water Management Temperatures	110 °C during Purge 0 °C (ambient) during Desorb 240 °C during Bake
P&T Cycle Time	13 minutes (with 6–minute Purge)
Gas Chromatograph	**Agilent 7890**
Inlet	220 °C, split/splitless, 4–mm I.D. glass liner with single gooseneck, 35–to–1 spilt
Column	Restek Rtx–624, 30–meter x 0.25–mm I.D. x 1.4–μm film, 0.8 mL/minute He (constant flow mode)
Oven Program	45 °C for 4.5 minutes 12 °C/minute to 100 °C (0 minutes) 25 °C/minute to 240 °C (hold 1.3 minute)
GC Run Time	16 minutes plus cool down
Mass Spectrometer	**Agilent 5975 with Standard Turbo Pump**
Solvent Delay	1.75 minutes
Tune File	bfb.u (not modified)
MS Source Temperature MS Quad Temperature GC/MS Interface	230 °C 150 °C 230 °C
MS Scan Mode	m/z 35 to 260 Threshold 200
MS SIM Mode	100 msec dwell time on each ion 2 to 6 ions per window SIM mode used for selected compounds
SIM Compounds	Chlorodifluoromethane, m/z 51 1,3–Butadiene, m/z 54 Trichloroethylene, m/z 132 Tetrachloroethylene, m/z 166 1, 2 Dibromoethane, m/z 107 1,2–Dibromo-3-chloropropane, m/z 157

Sorbent Trap

The method states any trap design is acceptable provided the data meet all QC acceptance criteria. During the initial single-laboratory method validation at the U.S. EPA, a trap containing Tenax®, silica gel, and either coconut charcoal or carbon molecular sieve (CMS) exhibited at least partial breakthrough of chlorodifluoromethane; therefore, this type of trap is not permissible when chlorodifluoromethane is one of the target compounds.

For studies which require reporting results for chlorodifluoromethane, the OI Trap 524.3 is recommended. Trap 524.3 is a proprietary trap specific to Method 524.3, and does not contain any of the materials expressly forbidden by the method. For studies which do not include chlorodifluoromethane any of the standard traps can be used including the Trap 524.3, the #11 Trap (VOCARB), or the #10 Trap (Tenax®, silica gel, CMS).

Study Outline

A procedural calibration curve was generated following method guidelines in Section 10.0, followed by an IDC. Performance of all 76 method compounds was evaluated using the MS full scan mode. Six of those compounds, including the two emerging contaminants, chlorodifluoromethane and 1,3-butadiene, were also evaluated using SIM mode. All compounds selected for SIM mode must have unique quantitation ions which can be baseline-resolved from other compounds so appropriate SIM windows can be defined. A typical chromatogram from a mid-point calibration standard is shown in Figure 2.

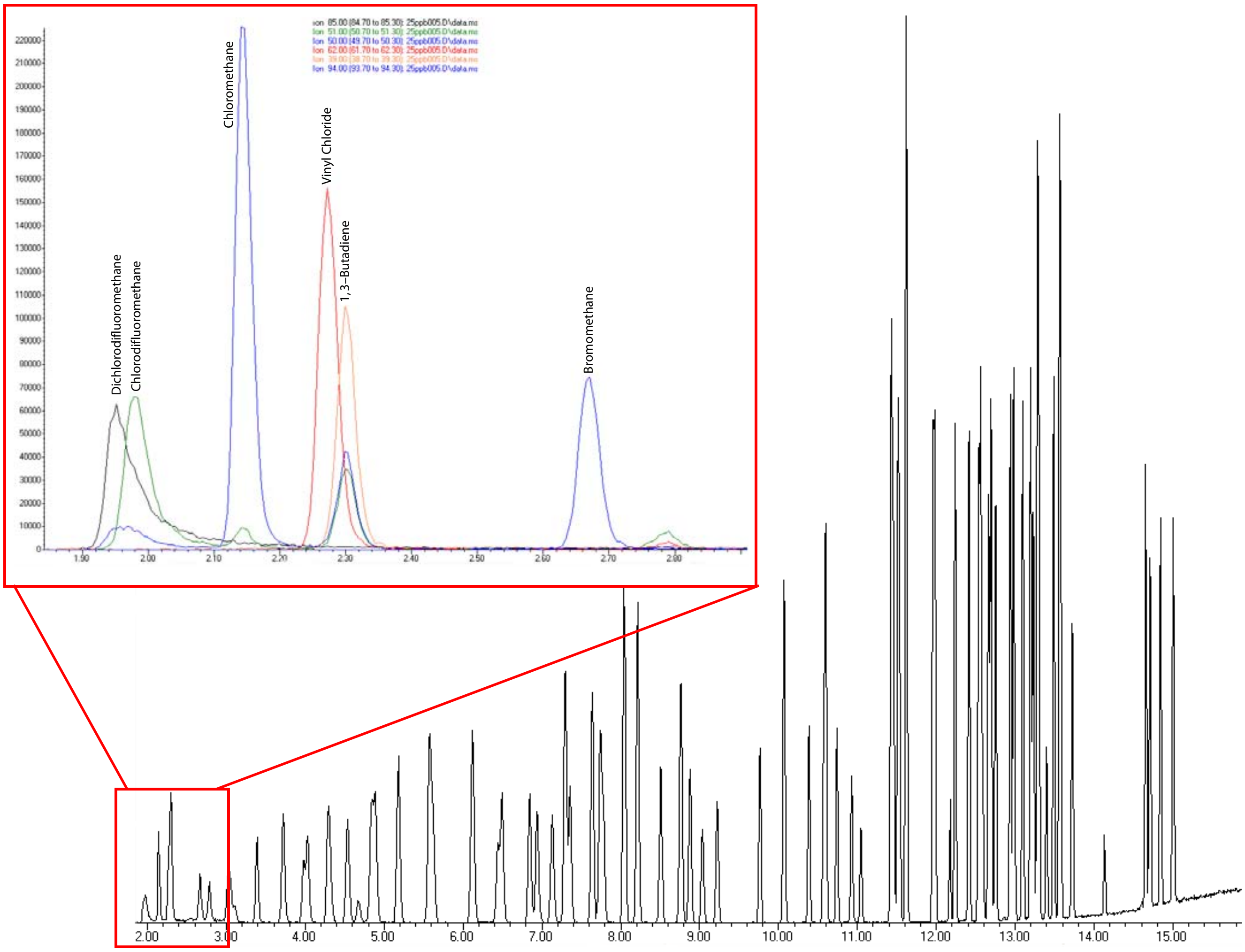

Figure 2. Representative chromatogram of a mid-point calibration standard for U.S. EPA Method 524.3. The insert illustrates typical chromatography of the six light gases.

Results and Discussion

Calibration

Seven procedural calibration standards were prepared from 0.5 to 40 ppb and analyzed using the instrument conditions shown in Table 2. Calibration curves were generated for all 76 compounds using a quadratic regression with inverse concentration weighting; the curves were not forced through zero. Average relative response factors were used for the surrogates because they were added at a single concentration level to the calibration standards.

This method introduces a new approach to validating the calibration curve. The initial calibration is validated by calculating the concentration of all analytes in each of the seven standards used to generate the calibration curve, and comparing the calculated concentrations to the acceptance criteria. Compounds at or below the MRL must be within ±50% of their true value, and compounds at all other concentrations must fall within ±30% of their true value.

For this study, the MRL was estimated at 0.5 ppb, the concentration of the lowest calibration standard. Calibration acceptance data for all 76 compounds (full scan mode) are shown in Table 3. All compounds met the acceptance criteria in all standards. Averages are not required, but have been included at the end of the table for informational purposes.

Table 3. Calibration acceptance data for U.S. EPA Method 524.3, full scan mode. Concentration of compounds at 0.5 ppb must be within ±50% of their true value. Concentration of compounds at all other levels must be within 30% of their true value. For this project, all compounds passed the acceptance criteria at all seven calibration levels.

Compound	0.5 ppb		1.0 ppb		2.0 ppb		5.0 ppb		10 ppb		20 ppb		40 ppb	
	Conc.	*%Dev.*	Conc.	*%Dev.*	Conc.	*%Dev.*	Conc.	*%Dev.*	Conc.	*%Dev.*	Conc.	*%Dev.*	Conc.	*%Dev.*
Dichlorodifluoromethane	0.4	*-14.0*	1.0	*4.0*	2.1	*3.5*	6.0	*19.4*	10.8	*8.1*	17.6	*-12.1*	40.8	*1.9*
Chlorodifluoromethane	0.5	*-2.0*	1.1	*9.0*	1.8	*-9.0*	5.1	*2.6*	10.0	*-0.4*	20.0	*0.2*	40.0	*-0.1*
Chloromethane	0.4	*-12.0*	1.0	*-1.0*	2.1	*2.5*	5.8	*15.0*	10.3	*2.7*	18.4	*-8.1*	40.6	*1.6*
Vinyl chloride	0.4	*-20.0*	1.0	*4.0*	2.1	*4.5*	6.1	*21.0*	11.3	*13.0*	17.4	*-13.0*	40.9	*2.2*
1,3-Butadiene	0.5	*0.0*	1.1	*5.0*	1.9	*-4.0*	4.9	*-1.6*	10.2	*2.1*	19.9	*-0.5*	40.0	*0.0*
Bromomethane	0.5	*-2.0*	0.9	*-7.0*	1.9	*-6.5*	5.8	*16.4*	11.0	*9.5*	17.7	*-11.3*	40.7	*1.8*
Trichloromonofluoromethane	0.5	*-4.0*	1.1	*8.0*	2.1	*3.0*	5.3	*5.8*	10.6	*6.2*	17.1	*-14.3*	47.4	*18.5*
Ethyl ether	0.5	*-8.0*	1.0	*0.0*	2.1	*6.5*	4.9	*-1.2*	10.8	*8.3*	18.8	*-6.1*	40.4	*0.9*
1,1-Dichloroethene	0.4	*-22.0*	1.0	*-1.0*	2.2	*8.5*	5.9	*17.8*	11.0	*9.8*	16.9	*-15.4*	41.2	*3.1*
Methyl iodide	0.5	*-6.0*	1.0	*0.0*	2.1	*3.0*	5.1	*2.2*	11.1	*10.9*	17.3	*-13.5*	41.5	*3.7*
Carbon disulfide	0.5	*-4.0*	0.9	*-12.0*	2.0	*-2.5*	5.8	*15.6*	11.8	*17.7*	17.7	*-11.4*	40.9	*2.3*
Allyl chloride	0.5	*-2.0*	0.9	*-6.0*	2.0	*-2.5*	5.5	*9.2*	11.3	*12.9*	18.5	*-7.7*	40.5	*1.3*
Methyl acetate	0.4	*-24.0*	0.8	*-19.0*	2.0	*-1.0*	4.6	*-8.2*	11.7	*17.2*	19.1	*-4.6*	40.1	*0.3*
Methylene chloride	0.5	*-10.0*	0.9	*-12.0*	1.9	*-4.5*	5.4	*8.2*	10.6	*6.4*	18.5	*-7.4*	40.5	*1.3*
t-Butanol	0.6	*20.0*	1.2	*19.0*	1.8	*-9.0*	4.6	*-7.4*	11.4	*14.2*	17.8	*-10.9*	40.7	*1.7*
Methyl-*t*-butyl ether (MTBE)	0.5	*4.0*	1.0	*-5.0*	2.0	*0.5*	4.7	*-6.0*	11.3	*12.6*	18.7	*-6.5*	40.4	*0.9*
trans-1,2-Dichloroethene	0.4	*-14.0*	1.0	*3.0*	2.0	*0.0*	5.6	*11.2*	11.2	*12.1*	17.3	*-13.6*	41.0	*2.5*
Diisopropylether (DIPE)	0.5	*-2.0*	1.0	*1.0*	2.0	*-1.5*	5.1	*1.2*	10.3	*3.3*	19.5	*-2.6*	40.2	*0.4*
1,1-Dichloroethane	0.5	*-6.0*	1.0	*-4.0*	2.1	*2.5*	5.2	*4.0*	11.2	*12.1*	17.9	*-10.5*	40.7	*1.8*
t-Butyl ethyl ether (ETBE)	0.5	*2.0*	1.0	*0.0*	2.0	*-1.0*	4.9	*-1.4*	10.2	*2.3*	19.3	*-3.8*	40.6	*1.5*
cis-1,2-Dichloroethene	0.5	*0.0*	0.9	*-9.0*	2.0	*2.0*	5.2	*3.8*	11.1	*11.3*	18.1	*-9.5*	40.6	*1.6*
Tetrahydrofuran	0.6	*16.0*	0.8	*-20.0*	2.2	*7.5*	4.7	*-5.6*	12.0	*19.7*	17.5	*-12.7*	41.3	*3.4*
Bromochloromethane	0.5	*2.0*	0.9	*-8.0*	2.1	*3.5*	5.0	*-0.4*	11.0	*10.1*	18.5	*-7.3*	40.5	*1.2*
Chloroform	0.5	*-6.0*	1.0	*-2.0*	2.0	*1.0*	5.3	*5.2*	11.1	*10.7*	18.0	*-9.9*	40.7	*1.7*
1,1,1-Trichloroethane	0.4	*-12.0*	1.0	*-3.0*	2.0	*1.5*	5.5	*10.4*	11.7	*16.8*	16.6	*-17.0*	41.3	*3.2*
1-Chlorobutane	0.4	*-20.0*	1.0	*4.0*	2.1	*3.0*	5.5	*10.8*	11.7	*17.0*	16.5	*-17.7*	41.3	*3.3*
Carbon tetrachloride	0.4	*-18.0*	0.9	*-6.0*	2.2	*7.5*	5.9	*17.2*	12.6	*26.0*	15.9	*-20.5*	41.6	*3.9*
1,1-Dichloropropene	0.4	*-20.0*	1.0	*4.0*	2.1	*4.0*	5.5	*10.2*	11.6	*16.3*	16.6	*-17.2*	41.3	*3.2*
Benzene	0.4	*-14.0*	1.1	*5.0*	2.1	*2.5*	5.2	*3.6*	11.1	*11.1*	17.9	*-10.3*	40.8	*1.9*
t-Amyl methyl ether (TAME)	0.5	*4.0*	0.9	*-6.0*	2.0	*0.5*	5.0	*-0.4*	10.6	*5.9*	19.2	*-3.9*	40.2	*0.6*
1,2-Dichloroethane	0.5	*2.0*	0.9	*-8.0*	2.0	*2.0*	4.9	*-2.6*	11.2	*11.8*	18.5	*-7.6*	40.5	*1.2*
Trichloroethylene	0.5	*-8.0*	1.0	*0.0*	2.0	*-1.5*	5.5	*10.2*	10.8	*8.0*	18.0	*-9.9*	40.8	*2.0*
t-Amyl ethyl ether (TAEE)	0.5	*0.0*	1.0	*-1.0*	2.0	*-1.5*	5.0	*0.8*	10.4	*3.5*	19.5	*-2.4*	40.2	*0.4*
1,2-Dichloropropane	0.5	*-6.0*	1.0	*-1.0*	2.0	*-0.5*	5.2	*4.0*	11.0	*9.9*	18.2	*-8.9*	40.6	*1.5*
Dibromomethane	0.5	*4.0*	0.9	*-8.0*	2.1	*3.5*	4.7	*-6.8*	11.1	*11.4*	18.9	*-5.6*	40.3	*0.8*
Bromodichloromethane	0.5	*8.0*	0.9	*-14.0*	2.0	*-1.5*	5.0	*0.4*	11.6	*15.6*	17.9	*-10.7*	40.7	*1.7*
cis-1,3-Dichloropropene	0.5	*4.0*	0.9	*-7.0*	1.9	*-3.0*	4.9	*-1.6*	11.7	*16.6*	17.9	*-10.8*	40.7	*1.7*
Toluene	0.4	*-14.0*	1.0	*3.0*	2.0	*1.0*	5.5	*10.0*	10.9	*8.8*	17.9	*-10.6*	40.8	*1.9*
trans-1,3-Dichloropropene	0.5	*6.0*	1.0	*-2.0*	1.9	*-7.0*	4.7	*-5.8*	11.3	*12.7*	18.8	*-5.8*	40.3	*0.8*
Ethyl methacrylate	0.5	*2.0*	1.0	*-2.0*	2.0	*-1.0*	4.9	*-1.2*	10.5	*5.4*	19.4	*-3.1*	40.2	*0.4*
1,1,2-Trichloroethane	0.5	*-8.0*	0.9	*-6.0*	2.2	*7.5*	5.4	*7.2*	10.4	*4.2*	18.7	*-6.8*	40.5	*1.3*

Table 3 cont. Calibration acceptance data for U.S. EPA Method 524.3, full scan mode. Concentration of compounds at 0.5 ppb must be within ±50% of their true value. Concentration of compounds at all other levels must be within 30% of their true value. For this project, all compounds passed the acceptance criteria at all seven calibration levels.

Compound	0.5 ppb		1.0 ppb		2.0 ppb		5.0 ppb		10 ppb		20 ppb		40 ppb	
	Conc.	*%Dev.*	Conc.	*%Dev.*	Conc.	*%Dev.*	Conc.	*%Dev.*	Conc.	*%Dev.*	Conc.	*%Dev.*	Conc.	*%Dev.*
Tetrachloroethylene	0.4	*-26.0*	1.0	*4.0*	2.2	*8.5*	6.0	*19.4*	10.5	*4.8*	17.4	*-13.1*	41.1	*2.8*
1,3-Dichloropropane	0.5	*-2.0*	0.9	*-11.0*	2.1	*6.5*	5.3	*5.8*	10.6	*5.7*	18.6	*-6.9*	40.5	*1.3*
Dibromochloromethane	0.6	*12.0*	0.9	*-11.0*	1.9	*-7.0*	4.9	*-1.8*	11.7	*17.1*	18.0	*-10.3*	40.6	*1.6*
1,2-Dibromoethane	0.5	*-2.0*	1.0	*-5.0*	2.1	*3.0*	5.1	*1.8*	10.6	*6.2*	19.0	*-5.3*	40.4	*0.9*
Chlorobenzene	0.4	*-12.0*	1.0	*2.0*	2.1	*3.5*	5.3	*6.6*	10.8	*7.7*	18.2	*-9.1*	40.7	*1.8*
Ethylbenzene	0.4	*-12.0*	1.0	*1.0*	2.0	*-1.5*	5.6	*11.0*	11.2	*11.9*	17.4	*-13.2*	41.0	*2.4*
1,1,1,2-Tetrachloroethane	0.5	*0.0*	1.0	*0.0*	1.9	*-7.5*	5.1	*2.0*	11.2	*11.9*	18.3	*-8.5*	40.6	*1.4*
m,p-Xylene	0.5	*-10.0*	1.0	*-2.0*	2.0	*1.5*	5.4	*7.8*	11.3	*12.7*	17.5	*-12.8*	40.9	*2.3*
o-Xylene	0.5	*-10.0*	1.0	*1.0*	2.1	*2.5*	5.2	*3.8*	11.2	*11.5*	17.9	*-10.5*	40.8	*1.9*
Styrene	0.5	*2.0*	0.9	*-9.0*	2.0	*-1.5*	5.3	*6.8*	11.0	*9.9*	18.1	*-9.4*	40.7	*1.6*
Bromoform	0.5	*8.0*	0.9	*-10.0*	1.9	*-4.0*	4.6	*-8.0*	11.9	*18.7*	16.6	*-17.1*	41.2	*2.9*
Isopropylbenzene	0.5	*-10.0*	1.0	*-5.0*	2.0	*0.5*	5.6	*11.8*	11.4	*13.7*	17.0	*-14.8*	41.1	*2.7*
Bromobenzene	0.5	*-8.0*	1.0	*4.0*	2.0	*-2.5*	5.3	*6.6*	10.7	*6.9*	18.5	*-7.8*	40.6	*1.5*
1,1,2,2-Tetrachloroethane	0.5	*-8.0*	1.0	*2.0*	2.0	*1.5*	5.1	*1.2*	10.6	*6.3*	18.9	*-5.5*	40.4	*1.0*
n-Propylbenzene	0.4	*-16.0*	1.0	*0.0*	2.1	*3.5*	5.5	*9.6*	11.4	*14.3*	17.0	*-15.1*	41.1	*2.8*
1,2,3-Trichloropropane	0.4	*-12.0*	1.0	*3.0*	2.1	*5.0*	5.2	*4.6*	10.5	*4.8*	18.8	*-6.2*	40.5	*1.1*
2-Chlorotoluene	0.5	*-10.0*	1.0	*-5.0*	2.1	*5.0*	5.5	*9.2*	11.1	*10.6*	17.5	*-12.4*	41.0	*2.4*
1,3,5-Trimethylbenzene	0.4	*-14.0*	1.0	*2.0*	2.0	*2.0*	5.4	*8.2*	11.3	*13.2*	17.3	*-13.4*	41.0	*2.4*
4-Chlorotoluene	0.5	*-8.0*	1.0	*-1.0*	2.0	*0.0*	5.4	*7.0*	11.0	*10.4*	17.9	*-10.6*	40.8	*2.0*
t-Butylbenzene	0.4	*-22.0*	1.1	*11.0*	2.0	*-2.0*	5.5	*10.2*	11.5	*14.8*	17.0	*-15.2*	41.1	*2.7*
1,2,4-Trimethylbenzene	0.5	*-6.0*	1.0	*-4.0*	2.0	*0.0*	5.3	*6.8*	11.2	*11.9*	17.8	*-11.2*	40.8	*2.0*
Pentachloroethane	0.5	*8.0*	1.0	*-5.0*	1.8	*-10.5*	4.8	*-4.8*	11.4	*13.5*	17.3	*-13.3*	40.8	*1.9*
sec-Butylbenzene	0.4	*-18.0*	1.0	*-1.0*	2.1	*5.5*	5.6	*11.8*	11.8	*17.6*	16.3	*-18.6*	41.4	*3.5*
p-Isopropyltoluene	0.4	*-14.0*	1.0	*1.0*	2.0	*1.0*	5.5	*10.0*	11.7	*16.9*	16.7	*-16.8*	41.2	*3.1*
1,3-Dichlorobenzene	0.5	*-6.0*	1.0	*-3.0*	2.0	*1.0*	5.4	*8.0*	10.8	*8.2*	18.1	*-9.4*	40.7	*1.8*
1,4-Dichlorobenzene	0.5	*-8.0*	0.9	*-6.0*	2.1	*4.0*	5.4	*8.4*	10.9	*9.1*	18.0	*-10.1*	40.7	*1.8*
n-Butylbenzene	0.4	*-16.0*	1.0	*-3.0*	2.0	*2.0*	5.8	*15.8*	11.6	*16.2*	16.4	*-17.9*	41.2	*3.1*
1,2-Dichlorobenzene	0.4	*-14.0*	1.0	*-4.0*	2.2	*8.0*	5.5	*10.4*	10.7	*7.1*	18.0	*-10.1*	40.7	*1.9*
Hexachloroethane	0.5	*-2.0*	0.9	*-13.0*	2.4	*17.5*	4.9	*-2.8*	11.8	*18.4*	16.8	*-15.8*	40.9	*2.2*
1,2-Dibromo-3-chloropropane	0.4	*-14.0*	1.1	*8.0*	2.0	*-2.5*	5.2	*4.0*	11.5	*14.6*	17.7	*-11.6*	40.7	*1.8*
1,2,4-Trichlorobenzene	0.5	*-10.0*	1.0	*-4.0*	2.1	*6.0*	5.4	*8.6*	10.8	*8.3*	18.0	*-10.1*	40.7	*1.8*
Hexachlorobutadiene	0.5	*-10.0*	1.0	*-3.0*	2.2	*9.0*	5.9	*18.8*	11.6	*16.4*	15.8	*-21.3*	41.7	*4.1*
Naphthalene	0.5	*-10.0*	1.0	*-3.0*	2.1	*5.5*	5.4	*7.2*	10.5	*5.2*	18.6	*-6.8*	40.5	*1.2*
1,2,3-Trichlorobenzene	0.4	*-12.0*	1.0	*0.0*	2.1	*5.5*	5.3	*6.8*	10.7	*6.7*	18.3	*-8.4*	40.6	*1.5*
Averages	0.5	*-6.6*	1.0	*-2.3*	2.0	*1.2*	5.3	*5.7*	11.1	*10.9*	17.9	*-10.4*	40.8	*2.1*

Minimum Reporting Level (MRL) Confirmation

The second significant QC requirement added to the method is confirmation of the MRL. The MRL is defined as the minimum concentration of a given compound that can be reported as a quantified value, and must be no lower than the concentration of the lowest calibration standard.

For this study, the lowest calibration standard, 0.5 ppb was established as the MRL. Seven procedural LFBs were fortified at the MRL and analyzed using the conditions in Table 2. The MRLs were confirmed by comparing the average calculated concentration to the prediction interval following the procedure outlined in Section 9.2.4 of the method. The Lower and Upper limits for the Prediction Interval of Results (PIR) met the recovery limits of >50% and <150%, respectively. See Table 4 for MRL confirmation data.

Detection Limits

Determination of DLs is no longer a specific requirement of the method, but may be required by regulating agencies associated with compliance monitoring. For this study, the seven LFBs used in the MRL confirmation were used to establish the statistical DLs, using the procedure in Section 9.2.6. The DL is defined as the minimum concentration of a compound that can be identified, measured, and reported with 99% confidence the compound concentration is greater than zero. This is a statistical determination and accurate quantitation is not expected at this level. The statistical DLs calculated for this study are found in Table 4.

Lowest Concentration Minimum Reporting Level (LCMRL)

The single-laboratory LCMRL is defined as the lowest spiking concentration such that the probability of spike recovery in the 50 to 150% range is at least 99%. The LCMRL procedures and calculations are complex and are established using an on-line calculator available on the U.S. EPA web site(6, 7); they are not described in the method and are not required, but are referenced in the method validation. The LCMRLs listed in Table 4 were submitted to the EPA as part of the second laboratory validation study, and are shown here for reference.

Table 4. Minimum Reporting Level (MRL) confirmation, Detection Limits (DL), and Lowest Concentration Minimum Reporting Level (LCMRL), full scan mode. The Lower Prediction Interval Results (PIR) for the MRL must be greater than 50% recovery, and the Upper PIR must be less than 150% recovery (See U.S. EPA Method 524.3, Section 9.2.4, for details.). The DLs were determined following Section 9.2.6 of the method. The LCMRL data were determined using the U.S. EPA calculator; data shown here were reported for the second laboratory validation study.

Compound	MRL Confirmation Data for MRL at 0.5 ppb							Statistical DL, n=7 (ppb)	LCMRL (ppb)
	Mean Calculated Conc, n=7 (ppb)	Standard Deviation (ppb)	Half Range of Prediction Interval (ppb)	Lower PIR (%Recy)	*PASS/FAIL*	Upper PIR (%Recy)	*PASS/FAIL*		
Dichlorodifluoromethane	0.54	0.04	0.17	74.2	*PASS*	142.4	*PASS*	0.14	—
Chlorodifluoromethane	0.47	0.03	0.13	66.9	*PASS*	120.0	*PASS*	0.11	0.23
Chloromethane	0.59	0.04	0.16	85.5	*PASS*	148.8	*PASS*	0.13	—
Vinyl chloride	0.53	0.04	0.16	72.8	*PASS*	138.0	*PASS*	0.13	0.38
1,3-Butadiene	0.53	0.03	0.14	79.8	*PASS*	133.9	*PASS*	0.11	0.28
Bromomethane	0.56	0.06	0.22	79.4	*PASS*	142.8	*PASS*	0.18	—
Trichloromonofluoromethane	0.57	0.03	0.12	91.6	*PASS*	138.1	*PASS*	0.09	—
Ethyl ether	0.48	0.03	0.14	68.1	*PASS*	122.8	*PASS*	0.11	—
1,1-Dichloroethene	0.54	0.04	0.17	75.3	*PASS*	142.4	*PASS*	0.13	0.17
Methyl iodide	0.53	0.02	0.09	87.5	*PASS*	122.8	*PASS*	0.07	—
Carbon disulfide	0.48	0.06	0.23	50.7	*PASS*	141.3	*PASS*	0.18	—
Allyl chloride	0.42	0.06	0.23	52.9	*PASS*	116.3	*PASS*	0.18	—
Methyl acetate	0.48	0.05	0.20	55.1	*PASS*	135.8	*PASS*	0.16	—
Methylene chloride	0.49	0.03	0.10	77.1	*PASS*	117.7	*PASS*	0.08	0.43
t-Butanol	0.44	0.06	0.23	56.6	*PASS*	120.0	*PASS*	0.18	—
Methyl-*t*-butyl ether (MTBE)	0.49	0.01	0.04	89.9	*PASS*	107.8	*PASS*	0.04	—
trans-1,2-Dichloroethene	0.50	0.03	0.11	76.8	*PASS*	121.5	*PASS*	0.09	0.27
Diisopropylether (DIPE)	0.46	0.01	0.03	86.2	*PASS*	97.2	*PASS*	0.02	—
1,1-Dichloroethane	0.49	0.02	0.09	80.6	*PASS*	117.1	*PASS*	0.07	—
t-Butyl ethyl ether (ETBE)	0.48	0.02	0.06	83.1	*PASS*	108.9	*PASS*	0.05	—
cis-1,2-Dichloroethene	0.50	0.04	0.15	69.9	*PASS*	128.4	*PASS*	0.12	0.28
Tetrahydrofuran	0.40	0.04	0.17	56.5	*PASS*	104.1	*PASS*	0.13	—
Bromochloromethane	0.54	0.03	0.12	85.2	*PASS*	131.4	*PASS*	0.09	—
Chloroform	0.53	0.02	0.06	93.2	*PASS*	118.2	*PASS*	0.05	0.18
1,1,1-Trichloroethane	0.54	0.02	0.09	89.7	*PASS*	125.7	*PASS*	0.07	0.17
1-Chlorobutane	0.53	0.03	0.13	80.9	*PASS*	131.1	*PASS*	0.10	—
Carbon tetrachloride	0.54	0.04	0.16	77.3	*PASS*	139.8	*PASS*	0.12	0.21
1,1-Dichloropropene	0.55	0.06	0.24	78.3	*PASS*	141.7	*PASS*	0.19	—
Benzene	0.50	0.02	0.06	87.8	*PASS*	112.8	*PASS*	0.05	0.11
t-Amyl methyl ether (TAME)	0.48	0.01	0.05	85.5	*PASS*	105.4	*PASS*	0.04	—
1,2-Dichloroethane	0.52	0.02	0.08	88.1	*PASS*	119.9	*PASS*	0.06	0.14
Trichloroethylene	0.56	0.04	0.14	83.3	*PASS*	140.1	*PASS*	0.11	0.36
t-Amyl ethyl ether (TAEE)	0.46	0.03	0.10	71.5	*PASS*	111.9	*PASS*	0.08	—
1,2-Dichloropropane	0.51	0.02	0.10	81.6	*PASS*	121.2	*PASS*	0.08	0.26
Dibromomethane	0.50	0.04	0.17	65.6	*PASS*	132.7	*PASS*	0.13	—
Bromodichloromethane	0.48	0.05	0.20	56.1	*PASS*	134.2	*PASS*	0.16	0.27

Table 4 cont. Minimum Reporting Level (MRL) confirmation, Detection Limits (DL), and Lowest Concentration Minimum Reporting Level (LCMRL), full scan mode. The Lower Prediction Interval Results (PIR) for the MRL must be greater than 50% recovery, and the Upper PIR must be less than 150% recovery (See U.S. EPA Method 524.3, Section 9.2.4, for details.). The DLs were determined following Section 9.2.6 of the method. The LCMRL data were determined using the U.S. EPA calculator; data shown here were reported for the second laboratory validation study.

Compound	MRL Confirmation Data for MRL at 0.5 ppb							Statistical DL, n=7 (ppb)	LCMRL (ppb)
	Mean Calculated Conc, n=7 (ppb)	Standard Deviation (ppb)	Half Range of Prediction Interval (ppb)	Lower PIR (%Recy)	*PASS/FAIL*	Upper PIR (%Recy)	*PASS/FAIL*		
cis-1,3-Dichloropropene	0.47	0.03	0.12	70.3	*PASS*	118.3	*PASS*	0.10	—
Toluene	0.49	0.01	0.04	91.1	*PASS*	106.6	*PASS*	0.03	0.11
trans-1,3-Dichloropropene	0.48	0.03	0.11	74.6	*PASS*	118.0	*PASS*	0.09	—
Ethyl methacrylate	0.43	0.02	0.06	72.3	*PASS*	98.0	*PASS*	0.05	—
1,1,2-Trichloroethane	0.51	0.03	0.10	80.8	*PASS*	121.5	*PASS*	0.08	0.24
Tetrachloroethylene	0.55	0.04	0.18	74.1	*PASS*	145.3	*PASS*	0.14	0.21
1,3-Dichloropropane	0.51	0.02	0.08	85.4	*PASS*	116.9	*PASS*	0.06	—
Dibromochloromethane	0.47	0.04	0.18	59.5	*PASS*	130.3	*PASS*	0.14	0.27
1,2-Dibromoethane	0.53	0.03	0.11	82.7	*PASS*	128.2	*PASS*	0.09	0.19
Chlorobenzene	0.50	0.01	0.04	91.8	*PASS*	109.4	*PASS*	0.04	0.06
Ethylbenzene	0.50	0.01	0.04	91.8	*PASS*	108.8	*PASS*	0.03	0.05
1,1,1,2-Tetrachloroethane	0.51	0.04	0.16	69.8	*PASS*	133.0	*PASS*	0.13	—
m,p-Xylene	0.50	0.01	0.06	88.8	*PASS*	111.2	*PASS*	0.04	0.13
o-Xylene	0.48	0.04	0.15	65.2	*PASS*	126.2	*PASS*	0.12	0.08
Styrene	0.48	0.02	0.08	79.5	*PASS*	113.1	*PASS*	0.07	0.12
Bromoform	0.46	0.05	0.21	50.1	*PASS*	133.9	*PASS*	0.17	0.36
Isopropylbenzene	0.53	0.02	0.09	87.7	*PASS*	123.7	*PASS*	0.07	—
Bromobenzene	0.51	0.02	0.09	84.1	*PASS*	121.6	*PASS*	0.07	—
1,1,2,2-Tetrachloroethane	0.50	0.02	0.07	85.5	*PASS*	114.5	*PASS*	0.06	—
n-Propylbenzene	0.52	0.02	0.07	89.2	*PASS*	117.7	*PASS*	0.06	—
1,2,3-Trichloropropane	0.52	0.06	0.22	58.6	*PASS*	147.7	*PASS*	0.18	—
2-Chlorotoluene	0.53	0.03	0.12	83.1	*PASS*	130.6	*PASS*	0.09	—
1,3,5-Trimethylbenzene	0.51	0.02	0.09	82.9	*PASS*	119.4	*PASS*	0.07	—
4-Chlorotoluene	0.52	0.02	0.07	89.9	*PASS*	116.9	*PASS*	0.05	—
t-Butylbenzene	0.51	0.03	0.10	82.0	*PASS*	123.8	*PASS*	0.08	—
1,2,4-Trimethylbenzene	0.50	0.02	0.07	87.0	*PASS*	113.6	*PASS*	0.05	—
Pentachloroethane	0.47	0.03	0.12	68.9	*PASS*	118.5	*PASS*	0.10	—
sec-Butylbenzene	0.53	0.02	0.08	89.6	*PASS*	121.8	*PASS*	0.06	—
p-Isopropyltoluene	0.54	0.01	0.06	96.1	*PASS*	118.2	*PASS*	0.04	—
1,3-Dichlorobenzene	0.51	0.02	0.08	85.5	*PASS*	118.5	*PASS*	0.07	—
1,4-Dichlorobenzene	0.49	0.02	0.09	79.5	*PASS*	114.8	*PASS*	0.07	0.16
n-Butylbenzene	0.52	0.03	0.12	78.9	*PASS*	128.5	*PASS*	0.10	—
1,2-Dichlorobenzene	0.47	0.02	0.07	79.5	*PASS*	108.5	*PASS*	0.06	0.14
Hexachloroethane	0.53	0.06	0.23	75.2	*PASS*	138.6	*PASS*	0.19	—
1,2-Dibromo-3-chloropropane	0.49	0.06	0.23	52.2	*PASS*	144.9	*PASS*	0.18	0.55
1,2,4-Trichlorobenzene	0.47	0.03	0.12	71.1	*PASS*	118.6	*PASS*	0.09	0.11

Table 4 cont. Minimum Reporting Level (MRL) confirmation, Detection Limits (DL), and Lowest Concentration Minimum Reporting Level (LCMRL), full scan mode. The Lower Prediction Interval Results (PIR) for the MRL must be greater than 50% recovery, and the Upper PIR must be less than 150% recovery (See U.S. EPA Method 524.3, Section 9.2.4, for details.). The DLs were determined following Section 9.2.6 of the method. The LCMRL data were determined using the U.S. EPA calculator; data shown here were reported for the second laboratory validation study.

Compound	MRL Confirmation Data for MRL at 0.5 ppb							Statistical DL, n=7 (ppb)	LCMRL (ppb)
	Mean Calculated Conc, n=7 (ppb)	Standard Deviation (ppb)	Half Range of Prediction Interval (ppb)	Lower PIR (%Recy)	*PASS/FAIL*	Upper PIR (%Recy)	*PASS/FAIL*		
Hexachlorobutadiene	0.51	0.03	0.13	76.8	*PASS*	128.3	*PASS*	0.10	—
Naphthalene	0.49	0.02	0.08	82.3	*PASS*	114.9	*PASS*	0.06	—
1,2,3-Trichlorobenzene	0.49	0.03	0.11	76.5	*PASS*	119.5	*PASS*	0.09	—

Precision and Accuracy

Before samples can be analyzed, the IDC requires a demonstration of precision and accuracy. Seven replicate Laboratory Fortified Blanks (LFBs) were fortified at 0.5, 1.0, and 10 ppb and analyzed using the conditions in Table 2. A second series of samples was prepared by spiking seven aliquots of tap water at 0.5, 1.0, and 10 ppb.

Precision is measured as the %RSD for the seven calculated concentrations, and must be below 20%. Accuracy is measured as the average percent recovery, and must fall between 80 and 120%. Precision and accuracy for all three fortification levels in reagent water and tap water are shown in Tables 5 and 6, respectively. One aliquot of blank tap water was analyzed and found to contain concentrations of trihalomethanes (THMs) that interfered with the analyses. Precision and accuracy for those compounds could not be reported, and are listed in the table with an asterisk (*). Except as noted above, all compounds met the precision and accuracy acceptance criteria at all three fortification levels in both matrices.

Table 5. Precision and accuracy of method compounds in DI water fortified at 0.5, 1.0, and 10 μg/L (ppb), full scan mode. The Relative Standard Deviation (RSD) must be less than 20% (Precision), and the average recovery must be between 80 and 120% of the expected concentration (Accuracy).

Compound	Fortification Conc. 0.5 µg/L (n = 7)		Fortification Conc. 1.0 µg/L (n = 7)		Fortification Conc. 10 µg/L (n = 7)	
	Precision as %RSD	Accuracy as Average %Recovery	*Precision as %RSD*	Accuracy as Average %Recovery	*Precision as %RSD*	Accuracy as Average %Recovery
Dichlorodifluoromethane	*7.9*	108.3	*3.9*	80.4	*6.9*	103.9
Chlorodifluoromethane	*7.2*	93.4	*4.2*	89.1	*4.5*	100.6
Chloromethane	*6.8*	117.1	*6.0*	96.1	*5.2*	101.9
Vinyl chloride	*7.8*	105.4	*3.9*	94.1	*8.6*	106.5
1,3-Butadiene	*6.4*	106.9	*1.9*	100.1	*5.9*	97.6
Bromomethane	*10.2*	111.1	*7.6*	97.9	*5.3*	112.7
Trichloromonofluoromethane	*5.1*	114.9	*5.1*	106.9	*13.0*	97.8
Ethyl ether	*7.2*	95.4	*3.8*	92.9	*2.0*	109.1
1,1-Dichloroethene	*7.8*	108.9	*3.5*	98.0	*10.6*	106.5
Methyl iodide	*4.2*	105.1	*6.0*	97.3	*4.6*	108.8
Carbon disulfide	*11.9*	96.0	*7.8*	89.7	*13.4*	103.7
Allyl chloride	*13.6*	84.6	*5.9*	87.4	*8.3*	114.5
Methyl acetate	*10.7*	95.4	*5.2*	102.1	*3.4*	119.7
Methylene chloride	*5.3*	97.4	*5.3*	96.9	*3.0*	98.7
t-Butanol	*14.0*	89.4	*11.7*	111.3	*7.3*	119.0
Methyl-*t*-butyl ether (MTBE)	*2.3*	98.9	*1.7*	99.0	*1.8*	108.1
trans-1,2-Dichloroethene	*5.7*	99.1	*3.6*	102.4	*7.4*	109.2
Diisopropylether (DIPE)	*1.5*	91.7	*1.8*	93.4	*1.3*	104.6
1,1-Dichloroethane	*4.7*	98.9	*2.7*	99.0	*5.5*	109.6
t-Butyl ethyl ether (ETBE)	*3.4*	96.0	*2.4*	95.3	*1.9*	103.8
cis-1,2-Dichloroethene	*7.4*	99.1	*5.2*	97.0	*4.9*	110.1
Tetrahydrofuran	*10.4*	80.3	*15.1*	88.7	*19.3*	109.2
Bromochloromethane	*5.4*	108.3	*4.3*	99.3	*5.4*	104.2
Chloroform	*3.0*	105.7	*1.9*	103.4	*4.7*	109.0
1,1,1-Trichloroethane	*4.2*	107.7	*18.3*	101.3	*10.1*	108.8
1-Chlorobutane	*6.0*	106.0	*4.8*	101.7	*8.9*	108.6
Carbon tetrachloride	*7.3*	108.6	*5.1*	103.0	*12.8*	111.9
1,1-Dichloropropene	*11.1*	110.0	*6.3*	99.1	*9.6*	112.3
Benzene	*3.1*	100.3	*3.5*	100.9	*5.0*	109.0
t-Amyl methyl ether (TAME)	*2.6*	95.4	*2.3*	94.3	*1.7*	107.8
1,2-Dichloroethane	*3.8*	104.0	*2.6*	105.4	*2.1*	108.1
Trichloroethylene	*6.4*	111.7	*3.6*	107.1	*6.0*	104.5
t-Amyl ethyl ether (TAEE)	*5.5*	91.7	*3.0*	91.6	*2.3*	105.1
1,2-Dichloropropane	*4.9*	101.4	*3.2*	99.3	*3.8*	106.9
Dibromomethane	*8.5*	99.1	*3.9*	99.4	*3.6*	108.2
Bromodichloromethane	*10.4*	95.1	*5.4*	99.9	*8.6*	108.2

Table 5 cont. Precision and accuracy of method compounds in DI water fortified at 0.5, 1.0, and 10 µg/L (ppb), full scan mode. The Relative Standard Deviation (RSD) must be less than 20% (Precision), and the average recovery must be between 80 and 120% of the expected concentration (Accuracy).

Compound	Fortification Conc. 0.5 µg/L (n = 7)		Fortification Conc. 1.0 µg/L (n = 7)		Fortification Conc. 10 µg/L (n = 7)	
	Precision as %RSD	Accuracy as Average %Recovery	*Precision as %RSD*	Accuracy as Average %Recovery	*Precision as %RSD*	Accuracy as Average %Recovery
cis-1,3-Dichloropropene	*6.4*	94.3	*4.3*	91.7	*5.7*	110.6
Toluene	*2.0*	98.9	*3.9*	98.1	*5.0*	106.9
trans-1,3-Dichloropropene	*5.7*	96.3	*3.5*	92.0	*5.7*	108.5
Ethyl methacrylate	*3.8*	85.1	*5.0*	89.6	*2.4*	105.6
1,1,2-Trichloroethane	*5.1*	101.1	*6.8*	97.3	*3.0*	106.0
Tetrachloroethylene	*8.2*	109.7	*4.3*	104.9	*9.0*	107.4
1,3-Dichloropropane	*3.9*	101.1	*3.5*	100.3	*2.4*	104.6
Dibromochloromethane	*9.4*	94.9	*7.3*	92.1	*9.6*	107.5
1,2-Dibromoethane	*5.4*	105.4	*2.2*	105.6	*3.1*	107.0
Chlorobenzene	*2.2*	100.6	*2.8*	100.9	*4.8*	107.4
Ethylbenzene	*2.1*	100.3	*2.8*	100.9	*6.0*	110.5
1,1,1,2-Tetrachloroethane	*7.9*	101.4	*3.6*	101.4	*6.1*	108.0
m,p-Xylene	*2.8*	100.0	*2.9*	98.6	*6.2*	110.0
o-Xylene	*8.0*	95.7	*3.0*	97.3	*5.2*	107.8
Styrene	*4.4*	96.3	*2.7*	98.3	*4.2*	108.0
Bromoform	*11.5*	92.0	*11.6*	90.1	*10.2*	111.8
Isopropylbenzene	*4.3*	105.7	*2.6*	102.7	*6.7*	111.1
Bromobenzene	*4.6*	102.9	*1.8*	100.1	*3.3*	106.9
1,1,2,2-Tetrachloroethane	*3.7*	100.0	*5.4*	98.6	*2.3*	107.2
n-Propylbenzene	*3.5*	103.4	*1.9*	99.3	*7.3*	111.8
1,2,3-Trichloropropane	*10.9*	103.1	*4.9*	104.4	*3.1*	106.9
2-Chlorotoluene	*5.6*	106.9	*3.4*	100.3	*5.3*	108.3
1,3,5-Trimethylbenzene	*4.5*	101.1	*2.1*	99.7	*6.1*	111.6
4-Chlorotoluene	*3.3*	103.4	*1.7*	98.4	*4.5*	108.5
t-Butylbenzene	*5.1*	102.9	*3.9*	100.0	*6.8*	114.0
1,2,4-Trimethylbenzene	*3.3*	100.3	*2.4*	97.0	*4.9*	110.3
Pentachloroethane	*6.7*	93.7	*6.0*	95.6	*7.1*	113.4
sec-Butylbenzene	*3.9*	105.7	*2.2*	98.6	*7.3*	113.4
p-Isopropyltoluene	*2.6*	107.1	*4.1*	101.9	*6.9*	113.0
1,3-Dichlorobenzene	*4.1*	102.0	*2.6*	100.1	*4.0*	109.4
1,4-Dichlorobenzene	*4.6*	97.1	*3.6*	98.3	*3.9*	110.1
n-Butylbenzene	*6.0*	103.7	*5.4*	99.1	*8.1*	115.6
1,2-Dichlorobenzene	*3.9*	94.0	*2.4*	99.3	*3.0*	108.0
Hexachloroethane	*11.0*	106.9	*10.0*	102.3	*7.3*	119.4
1,2-Dibromo-3-chloropropane	*11.9*	98.6	*8.9*	97.3	*6.1*	118.1
1,2,4-Trichlorobenzene	*6.3*	94.9	*3.6*	100.4	*3.1*	112.6

Table 5 cont. Precision and accuracy of method compounds in DI water fortified at 0.5, 1.0, and 10 μg/L (ppb), full scan mode. The Relative Standard Deviation (RSD) must be less than 20% (Precision), and the average recovery must be between 80 and 120% of the expected concentration (Accuracy).

Compound	Fortification Conc. 0.5 µg/L (n = 7)		Fortification Conc. 1.0 µg/L (n = 7)		Fortification Conc. 10 µg/L (n = 7)	
	Precision as %RSD	Accuracy as Average %Recovery	*Precision as %RSD*	Accuracy as Average %Recovery	*Precision as %RSD*	Accuracy as Average %Recovery
Hexachlorobutadiene	*6.3*	102.6	*2.3*	101.1	*6.3*	118.9
Naphthalene	*4.2*	98.6	*2.0*	101.1	*1.5*	111.0
1, 2, 3–Trichlorobenzene	*5.5*	98.0	*5.1*	102.4	*2.3*	112.2

Table 6. Precision and accuracy of method compounds in tap water fortified at 0.5, 1.0, and 10 μg/L, full scan mode. The Relative Standard Deviation (RSD) must be less than 20% (Precision), and the average recovery must be between 80 and 120% of the expected concentration (Accuracy). Cells with an asterisk (*) indicate that the compound was found in the blank water at a concentration that interfered with the analysis.

Compound	Fortification Conc. 0.5 µg/L (n = 7)		Fortification Conc. 1.0 µg/L (n = 7)		Fortification Conc. 10 µg/L (n = 7)		Blank Tap Water
	Precision as %RSD	Accuracy as Average %Recovery	*Precision as %RSD*	Accuracy as Average %Recovery	*Precision as %RSD*	Accuracy as Average %Recovery	Conc. (ppb)
Dichlorodifluoromethane	*7.3*	102.6	*5.4*	85.9	*3.6*	109.4	—
Chlorodifluoromethane	*3.3*	96.3	*5.3*	90.3	*4.5*	102.4	—
Chloromethane	*8.1*	118.3	*2.4*	99.7	*4.9*	100.2	0.2
Vinyl chloride	*10.0*	105.7	*6.8*	93.9	*8.5*	114.5	—
1,3-Butadiene	*5.8*	112.3	*2.7*	95.3	*14.5*	94.3	—
Bromomethane	*11.7*	108.9	*8.0*	99.1	*4.0*	114.3	—
Trichloromonofluoromethane	*3.8*	114.9	*5.7*	106.3	*15.4*	105.0	—
Ethyl ether	*7.4*	95.4	*5.8*	100.1	*1.6*	107.1	—
1,1-Dichloroethene	*6.4*	106.3	*7.8*	98.1	*6.7*	113.9	—
Methyl iodide	*2.8*	107.1	*2.6*	101.7	*6.0*	114.0	—
Carbon disulfide	*14.7*	111.4	*7.2*	113.7	*14.1*	116.1	—
Allyl chloride	*8.4*	84.0	*8.9*	91.9	*10.8*	116.6	—
Methyl acetate	*6.1*	108.9	*10.3*	100.3	*3.9*	119.2	—
Methylene chloride	*6.8*	93.1	*4.4*	98.4	*8.2*	93.3	—
t-Butanol	*16.6*	99.7	*13.1*	118.0	*7.3*	113.1	—
Methyl-*t*-butyl ether (MTBE)	*3.3*	101.7	*3.0*	101.6	*2.5*	108.3	—
trans-1,2-Dichloroethene	*6.2*	103.1	*7.1*	105.1	*2.5*	113.0	—
Diisopropylether (DIPE)	*2.9*	94.6	*1.7*	94.1	*2.3*	102.8	—
1,1-Dichloroethane	*6.2*	102.9	*3.9*	102.0	*2.0*	111.8	—
t-Butylethylether (ETBE)	*2.6*	97.4	*1.0*	96.6	*1.7*	102.5	—
cis-1,2-Dichloroethene	*6.2*	100.0	*5.7*	103.4	*1.5*	109.8	—
Tetrahydrofuran	*	*	*	*	*	*	91.7
Bromochloromethane	*15.5*	106.0	*4.4*	109.9	*11.8*	98.6	—
Chloroform	*	*	*	*	*	*	1.1
1,1,1-Trichloroethane	*5.7*	114.3	*4.4*	114.1	*2.0*	119.0	—
1-Chlorobutane	*4.1*	108.9	*3.3*	103.6	*3.6*	117.9	—
Carbon tetrachloride	*6.1*	113.1	*6.2*	110.4	*4.2*	115.3	—
1,1-Dichloropropene	*8.0*	105.1	*9.6*	99.9	*3.1*	119.1	—
Benzene	*4.1*	100.6	*2.6*	101.1	*2.4*	111.0	—
t-Amyl methyl ether (TAME)	*3.6*	98.3	*2.0*	94.0	*2.6*	106.0	—
1,2-Dichloroethane	*4.3*	109.1	*4.1*	112.4	*2.0*	107.3	—
Trichloroethylene	*4.7*	110.3	*3.6*	104.4	*3.8*	109.2	—
t-Amy ethyl ether (TAEE)	*4.1*	94.3	*3.6*	95.4	*2.6*	102.8	—
1,2-Dichloropropane	*5.3*	101.4	*5.4*	102.4	*1.4*	108.1	—
Dibromomethane	*2.7*	106.0	*5.3*	106.0	*0.9*	108.8	—
Bromodichloromethane	*	*	*	*	*	*	5.7

Table 6 cont. Precision and accuracy of method compounds in tap water fortified at 0.5, 1.0, and 10 μg/L, full scan mode. The Relative Standard Deviation (RSD) must be less than 20% (Precision), and the average recovery must be between 80 and 120% of the expected concentration (Accuracy). Cells with an asterisk (*) indicate that the compound was found in the blank water at a concentration that interfered with the analysis.

Compound	Fortification Conc. 0.5 µg/L (n = 7)		Fortification Conc. 1.0 µg/L (n = 7)		Fortification Conc. 10 µg/L (n = 7)		Blank Tap Water
	Precision as %RSD	Accuracy as Average %Recovery	*Precision as %RSD*	Accuracy as Average %Recovery	*Precision as %RSD*	Accuracy as Average %Recovery	Conc. (ppb)
cis-1,3-Dichloropropene	*7.9*	98.3	*5.3*	97.4	*3.8*	108.8	—
Toluene	*4.4*	97.1	*4.7*	100.0	*3.1*	108.4	—
trans-1,3-Dichloropropene	*5.6*	97.4	*5.3*	99.1	*3.4*	106.0	—
Ethyl methacrylate	*6.0*	80.3	*3.4*	89.6	*3.5*	104.6	—
1,1,2-Trichloroethane	*6.1*	100.0	*5.1*	97.7	*3.6*	104.4	—
Tetrachloroethylene	*4.1*	112.9	*5.6*	103.1	*5.0*	109.4	—
1,3-Dichloropropane	*6.6*	104.6	*3.4*	103.9	*2.8*	104.2	—
Dibromochloromethane	*	*	*	*	*	*	16.1
1,2-Dibromoethane	*3.6*	112.0	*4.0*	106.3	*2.3*	106.4	—
Chlorobenzene	*2.2*	102.6	*4.4*	102.0	*2.5*	110.7	—
Ethylbenzene	*5.1*	102.0	*3.7*	101.4	*3.5*	115.2	—
1,1,1,2-Tetrachloroethane	*6.0*	108.6	*4.5*	106.3	*4.5*	110.1	—
m,p-Xylene	*5.1*	100.6	*4.3*	99.4	*3.4*	114.9	—
o-Xylene	*4.1*	97.1	*3.8*	98.9	*3.3*	111.5	—
Styrene	*4.9*	100.0	*4.3*	98.3	*3.1*	108.5	—
Bromoform	*	*	*	*	*	*	17.3
Isopropylbenzene	*4.2*	107.1	*4.1*	102.6	*3.6*	117.7	—
Bromobenzene	*5.8*	104.6	*4.7*	105.3	*3.2*	108.3	—
1,1,2,2-Tetrachloroethane	*3.1*	102.3	*2.8*	98.7	*2.8*	108.1	—
n-Propylbenzene	*2.9*	104.9	*5.4*	101.9	*4.0*	118.6	—
1,2,3-Trichloropropane	*6.8*	104.0	*6.9*	109.6	*3.1*	106.1	—
2-Chlorotoluene	*4.1*	105.7	*4.5*	106.9	*2.6*	110.9	—
1,3,5-Trimethylbenzene	*4.6*	100.6	*4.5*	101.9	*3.5*	116.5	—
4-Chlorotoluene	*3.3*	104.0	*3.2*	104.7	*3.7*	110.8	0.02
tert-butylbenzene	*4.5*	101.4	*6.0*	104.6	*3.5*	110.0	—
1,2,4-Trimethylbenzene	*6.3*	98.9	*4.7*	100.1	*3.9*	115.2	—
Pentachloroethane	*10.6*	103.4	*3.2*	103.3	*4.8*	111.1	—
sec-Butylbenzene	*2.4*	106.0	*5.5*	101.9	*4.7*	111.5	—
p-Isopropyltoluene	*1.5*	106.9	*4.5*	102.0	*3.9*	110.2	0.03
1,3-Dichlorobenzene	*4.8*	103.4	*4.8*	103.4	*3.2*	111.6	—
1,4-Dichlorobenzene	*3.6*	100.9	*4.4*	100.0	*3.0*	109.6	—
n-Butylbenzene	*9.4*	98.0	*7.0*	98.9	*5.9*	110.4	—
1,2-Dichlorobenzene	*3.9*	99.7	*4.2*	101.0	*4.8*	106.8	—
Hexachloroethane	*9.2*	116.6	*10.4*	112.1	*5.3*	118.6	—
1,2-Dibromo-3-chloropropane	*8.9*	102.0	*7.2*	105.7	*4.1*	117.8	—
1,2,4-Trichlorobenzene	*5.9*	93.4	*5.6*	105.6	*4.3*	111.6	—

Table 6 cont. Precision and accuracy of method compounds in tap water fortified at 0.5, 1.0, and 10 μg/L, full scan mode. The Relative Standard Deviation (RSD) must be less than 20% (Precision), and the average recovery must be between 80 and 120% of the expected concentration (Accuracy). Cells with an asterisk (*) indicate that the compound was found in the blank water at a concentration that interfered with the analysis.

Compound	Fortification Conc. 0.5 µg/L (n = 7)		Fortification Conc. 1.0 µg/L (n = 7)		Fortification Conc. 10 µg/L (n = 7)		Blank Tap Water
	Precision as %RSD	Accuracy as Average %Recovery	*Precision as %RSD*	Accuracy as Average %Recovery	*Precision as %RSD*	Accuracy as Average %Recovery	Conc. (ppb)
Hexachlorobutadiene	*6.6*	105.4	*4.6*	99.3	*4.8*	113.4	—
Naphthalene	*4.0*	98.3	*4.2*	105.0	*3.2*	109.0	—
1,2,3-Trichlorobenzene	*3.6*	97.7	*6.0*	106.3	*3.3*	110.7	—

Laboratory Reagent Blanks

The IDC requires an initial demonstration of low system background by analysis of a laboratory reagent blank (LRB) immediately following the highest calibration standard. The concentration of any method compound found in the LRB must not exceed one-half the MRL.

For this study two LRBs were analyzed: one immediately following a mid-point (20 ppb) calibration standard, and one following the highest (40 ppb) calibration standard. Several compounds were found at trace levels in the second LRB, but they were all well below the acceptance criteria of one-half the MRL. (Blank contamination levels were all below the minimum reporting level, and were estimated by extrapolation.) Data for both LRBs are shown in Table 7.

Continuing Calibration Check (CCC) Samples

The method requires analysis of a CCC at or below the MRL at the beginning of each analysis batch to verify instrument sensitivity prior to analysis of samples. A CCC must also be run after every tenth field sample and at the end of the analysis batch, alternating between the remaining calibration levels. Calculated concentration of compounds fortified at the MRL must be within ±50% of their true value. All other concentrations, including the surrogates, must fall within ±30% of their true values.

During the precision and accuracy portion of this study, the 0.5-ppb standard was analyzed as a CCC sample before and after the sequence, and the 20-ppb standard was analyzed at the mid-point of the sequence. All compounds met the acceptance criteria in all three CCC analyses. Results are shown in Table 7.

Table 7. Results of Laboratory Reagent Blanks (LRBs) and Continuing Calibration Check (CCC) samples acquired during the Precision and Accuracy study. Acceptance criteria for the CCC at 0.5 ppb and 20 ppb are ±50% and ±30%, respectively

Compound	LRB after a 20 ppb standard (ppb)	LRB after a 40 ppb standard (ppb)	CCC at start of P&A sequence, 0.5 ppb		CCC at mid-point in P&A sequence, 20 ppb		CCC at end of P&A sequence, 0.5 ppb	
			Calculated Conc. (ppb)	*%Deviation (±50%)*	Calculated Conc. (ppb)	*%Deviation (±30%)*	Calculated Conc. (ppb)	*%Deviation (±50%)*
1,4-Difluorobenzene (IS)	10	10	10	—	10	—	10	—
Chlorobenzene-*d5* (IS)	10	10	10	—	10	—	10	—
1,4-Dichlorobenzene-*d4* (IS)	10	10	10	—	10	—	10	—
Methyl-*t*-butyl ether-*d3* (SS)	10.8	9.8	9.9	*-1*	10.2	*2*	10.7	*7*
4-Bromofluorobenzene (SS)	9.5	9.9	8.9	*-11*	9.8	*-2*	9.8	*-2*
1,2-Dichlorobenzene-*d4* (SS)	9.9	10.1	10.1	*1*	9.4	*-6*	9.3	*-7*
Dichlorodifluoromethane	—	—	0.51	*2*	20.6	*3.0*	0.34	*-32*
Chlorodifluoromethane	—	—	0.52	*4*	23.4	*17.2*	0.55	*10*
Chloromethane	—	—	0.46	*-8*	21.6	*8.0*	0.43	*-14*
Vinyl chloride	—	—	0.38	*-24*	20.6	*3.0*	0.45	*-10*
1,3-Butadiene	—	0.02	0.46	*-8*	22.3	*11.5*	0.52	*4*
Bromomethane	—	—	0.48	*-4*	23.0	*14.8*	0.43	*-14*
Trichloromonofluoromethane	—	—	0.59	*18*	16.6	*-17.2*	0.51	*2*
Ethyl ether	—	—	0.61	*22*	22.0	*10.1*	0.47	*-6*
1,1-Dichloroethene	—	—	0.49	*-2*	18.9	*-5.7*	0.42	*-16*
Methyl iodide	—	0.17	0.58	*16*	22.4	*11.9*	0.40	*-20*
Carbon disulfide	—	—	0.39	*-22*	19.5	*-2.3*	0.60	*20*
Allyl chloride	—	—	0.54	*8*	22.9	*14.5*	0.54	*8*
Methyl acetate	—	—	0.52	*4*	23.8	*19.1*	0.39	*-22*
Methylene chloride	—	—	0.33	*-34*	19.3	*-3.8*	0.37	*-26*
t-Butanol	—	—	0.55	*10*	22.3	*11.4*	0.35	*-30*
Methyl-*t*-butyl ether (MTBE)	—	—	0.54	*8*	22.3	*11.4*	0.52	*4*
trans-1,2-Dichloroethene	—	—	0.42	*-16*	21.0	*5.2*	0.35	*-30*
Diisopropylether (DIPE)	—	—	0.51	*2*	22.1	*10.5*	0.47	*-6*
1,1-Dichloroethane	—	—	0.45	*-10*	21.5	*7.3*	0.45	*-10*
t-Butylethylether (ETBE)	—	—	0.54	*8*	21.9	*9.3*	0.52	*4*
cis-1,2-Dichloroethene		0.01	0.36	*-28*	21.8	*9.0*	0.44	*-12*
Tetrahydrofuran	—	—	0.38	*-24*	23.3	*16.4*	0.38	*-24*
Bromochloromethane	—	—	0.36	*-28*	20.4	*1.9*	0.42	*-16*
Chloroform	—	—	0.40	*-20*	22.0	*9.8*	0.44	*-12*
1,1,1-Trichloroethane	—	—	0.40	*-20*	20.3	*1.5*	0.41	*-18*
1-Chlorobutane	—	—	0.41	*-18*	19.8	*-0.9*	0.41	*-18*
Carbon tetrachloride	—	—	0.46	*-8*	20.2	*1.2*	0.43	*-14*
1,1-Dichloropropene	—	—	0.43	*-14*	19.5	*-2.5*	0.31	*-38*
Benzene	—	—	0.48	*-4*	21.2	*5.7*	0.48	*-4*
t-Amyl methyl ether (TAME)	—	—	0.53	*6*	22.3	*11.3*	0.48	*-4*

Table 7 cont. Results of Laboratory Reagent Blanks (LRBs) and Continuing Calibration Check (CCC) samples acquired during the Precision and Accuracy study. Acceptance criteria for the CCC at 0.5 ppb and 20 ppb are ±50% and ±30%, respectively

Compound	LRB after a 20 ppb standard (ppb)	LRB after a 40 ppb standard (ppb)	CCC at start of P&A sequence, 0.5 ppb		CCC at mid-point in P&A sequence, 20 ppb		CCC at end of P&A sequence, 0.5 ppb	
			Calculated Conc. (ppb)	*%Deviation (±50%)*	Calculated Conc. (ppb)	*%Deviation (±30%)*	Calculated Conc. (ppb)	*%Deviation (±50%)*
1,2-Dichloroethane	—	0.01	0.50	*0*	22.0	*9.8*	0.49	*-2*
Trichloroethylene	—	—	0.45	*-10*	19.0	*-4.8*	0.41	*-18*
t-Amyl ethyl ether (TAEE)	—	0.03	0.50	*0*	22.3	*11.3*	0.52	*4*
1,2-Dichloropropane	—	—	0.47	*-6*	21.5	*7.3*	0.54	*8*
Dibromomethane	—	—	0.45	*-10*	22.2	*10.8*	0.51	*2*
Bromodichloromethane	—	—	0.51	*2*	23.1	*15.5*	0.56	*12*
cis-1,3-Dichloropropene	—	0.02	0.50	*0*	23.6	*18.1*	0.55	*10*
Toluene	—	—	0.46	*-8*	20.1	*0.6*	0.44	*-12*
trans-1,3-Dichloropropene	—	0.03	0.48	*-4*	22.8	*14.0*	0.55	*10*
Ethyl methacrylate	—	—	0.59	*18*	22.0	*9.9*	0.59	*18*
1,1,2-Trichloroethane	—	—	0.57	*14*	21.6	*7.9*	0.50	*0*
Tetrachloroethylene	—	—	0.36	*-28*	18.6	*-7.0*	0.39	*-22*
1,3-Dichloropropane	—	—	0.51	*2*	21.0	*5.1*	0.54	*8*
Dibromochloromethane	—	0.05	0.52	*4*	24.3	*21.4*	0.57	*14*
1,2-Dibromoethane	—	—	0.47	*-6*	21.8	*9.1*	0.47	*-6*
Chlorobenzene	—	0.03	0.39	*-22*	21.1	*5.5*	0.47	*-6*
Ethylbenzene	—	—	0.46	*-8*	20.7	*3.7*	0.47	*-6*
1,1,1,2-Tetrachloroethane	—	—	0.47	*-6*	22.4	*11.8*	0.51	*2*
m,p-Xylene	—	0.02	0.42	*-16*	20.9	*4.5*	0.45	*-10*
o-Xylene	—	—	0.43	*-14*	21.2	*5.7*	0.47	*-6*
Styrene	—	0.02	0.52	*4*	21.2	*6.1*	0.46	*-8*
Bromoform	—	—	0.52	*4*	22.9	*14.7*	0.59	*18*
Isopropylbenzene	—	—	0.43	*-14*	19.9	*-0.4*	0.48	*-4*
Bromobenzene	—	0.05	0.42	*-16*	21.2	*5.7*	0.47	*-6*
1,1,2,2-Tetrachloroethane	—	—	0.50	*0*	21.7	*8.5*	0.51	*2*
n-Propylbenzene	—	0.02	0.39	*-22*	20.2	*1.2*	0.44	*-12*
1,2,3-Trichloropropane	—	—	0.37	*-26*	21.7	*8.4*	0.37	*-26*
2-Chlorotoluene	—	0.05	0.43	*-14*	21.2	*5.9*	0.54	*8*
1,3,5-Trimethylbenzene	—	—	0.41	*-18*	20.9	*4.6*	0.46	*-8*
4-Chlorotoluene	—	0.02	0.44	*-12*	21.0	*4.9*	0.49	*-2*
tert-Butylbenzene	—	—	0.33	*-34*	20.2	*1.2*	0.44	*-12*
1,2,4-Trimethylbenzene	—	0.02	0.44	*-12*	21.2	*6.0*	0.50	*0*
Pentachloroethane	—	—	0.47	*-6*	23.7	*18.4*	0.55	*10*
sec-Butylbenzene	—	—	0.39	*-22*	19.5	*-2.4*	0.48	*-4*
p-Isopropyltoluene	—	0.01	0.41	*-18*	20.2	*0.7*	0.46	*-8*
1,3-Dichlorobenzene	—	0.03	0.46	*-8*	21.4	*7.0*	0.45	*-10*

Table 7 cont. Results of Laboratory Reagent Blanks (LRBs) and Continuing Calibration Check (CCC) samples acquired during the Precision and Accuracy study. Acceptance criteria for the CCC at 0.5 ppb and 20 ppb are ±50% and ±30%, respectively

Compound	LRB after a 20 ppb standard (ppb)	LRB after a 40 ppb standard (ppb)	CCC at start of P&A sequence, 0.5 ppb		CCC at mid-point in P&A sequence, 20 ppb		CCC at end of P&A sequence, 0.5 ppb	
			Calculated Conc. (ppb)	*%Deviation (±50%)*	Calculated Conc. (ppb)	*%Deviation (±30%)*	Calculated Conc. (ppb)	*%Deviation (±50%)*
1,4-Dichlorobenzene	—	0.03	0.47	*-6*	20.0	*0.2*	0.42	*-16*
n-Butylbenzene	—	0.02	0.40	*-20*	19.3	*-3.7*	0.41	*-18*
1,2-Dichlorobenzene	—	0.03	0.42	*-16*	20.3	*1.4*	0.42	*-16*
Hexachloroethane	—	—	0.64	*28*	23.0	*15.0*	0.59	*18*
1,2-Dibromo-3-chloropropane	—	—	0.46	*-8*	24.3	*21.5*	0.39	*-22*
1,2,4-Trichlorobenzene	—	0.05	0.48	*-4*	20.4	*2.1*	0.42	*-16*
Hexachlorobutadiene	—	0.07	0.39	*-22*	18.7	*-6.8*	0.45	*-10*
Naphthalene	—	0.08	0.50	*0*	21.1	*5.7*	0.45	*-10*
1,2,3-Trichlorobenzene	0.03	0.09	0.48	*-4*	20.6	*2.9*	0.54	*8*

SIM Mode

A total of six compounds were chosen for analysis by MS SIM mode. The compounds were chosen based on their status as emerging contaminants (chlorodifluoromethane and 1,3-butadiene), low response during full scan mode, and availability of unique quantitation ions which can be baseline-resolved in the chromatogram.

This project included a full method validation study for these six compounds using MS SIM mode. A calibration curve from 4.0 to 1,000 ppt was evaluated using the same criteria as described above. All six compounds met the acceptance criteria at all levels. The results of the SIM mode calibration are shown in Table 8.

The MRL was evaluated at 4.0 ppt. Three compounds (chlorodifluoromethane, 1,3-butadiene, and trichloroethylene) failed the upper PIR, illustrating what can happen when validating a method at extremely low levels if the native compounds are present in the laboratory reagent water at concentrations at or near the fortification levels. The MRL confirmation data calculated DLs and LCMRLs, plus results from analysis of blank reagent water are shown in Table 9.

Finally, a precision and accuracy study was performed by fortifying blank reagent water with the six compounds at 4, 10, and 100 ppt and analyzing multiple aliquots using the MS SIM mode. The precision and accuracy criteria are the same as those used for the full scan study, and all compounds met the criteria at all fortification levels. Precision and accuracy results are shown in Table 10.

Table 8. Calibration acceptance data for U.S. EPA Method 524.3, SIM mode. Concentration of compounds at 4.0 ppt must be within ±50% of their true value. Concentration of compounds at all other concentrations must be within ±30% of their true value. For this project, all compounds passed the acceptance criteria at all calibration levels.

Compound	4.0 ppt		10 ppt		100 ppt		1,000 ppt (1.0 ppb)	
	Conc. (ppt)	*%Dev.*	Conc. (ppt)	*%Dev.*	Conc. (ppt)	*%Dev.*	Conc. (ppt)	*%Dev.*
Chlorodifluoromethane	4.5	*12.8*	10.6	*5.5*	93.8	*-6.2*	984	*-1.6*
1,3-Butadiene	3.6	*-9.5*	11.1	*11.0*	95.8	*-4.2*	1012	*1.2*
Trichloroethylene	3.9	*-2.8*	10.7	*7.2*	100	*0.4*	999	*-0.1*
Tetrachloroethylene	4.5	*13.3*	9.7	*-2.9*	103	*2.9*	1044	*4.4*
1,2-Dibromoethane	5.0	*24.5*	8.2	*-18.1*	99.4	*-0.6*	1002	*0.2*
1,2-Dibromo-3-chloropropane	3.4	*-16.0*	11.8	*18.0*	102	*1.6*	1017	*1.7*

Table 9. Minimum Reporting Level (MRL) confirmation, Detection Limits (DL), and Lowest Concentration Minimum Reporting Level (LCMRL), SIM mode. The failed Upper Prediction Interval Results (PIR) illustrate what can happen when validating a method for extremely low levels if the native compounds are present in the Laboratory Reagent Blank (LRB). (See U.S. EPA Method 524.3, Section 9.2.4, for details.) The DLs were determined following Section 9.2.6 of the method. The LCMRL data were determined using the U.S. EPA calculator; data shown here were reported for the second laboratory validation study.

Compound	MRL Confirmation Data for MRL at 4.0 ppt								DL, n=7 (ppt)	LCMRL (ppt)
	Conc. In LRB (ppt)	Mean Calculated Conc, n=7 (ppt)	Standard Deviation (ppt)	Half Range of Prediction Interval (ppt)	Lower PIR (%Recy)	*PASS/FAIL*	Upper PIR (%Recy)	*PASS/FAIL*		
Chlorodifluoromethane	4.0	8.2	1.1	4.4	95.6	*PASS*	233.7	*FAIL*	5.9	11.0
1,3-Butadiene	5.2	11.0	1.5	6.0	125.3	*PASS*	312.8	*FAIL*	16.0	32.0
Trichloroethylene	1.1	6.0	0.6	2.4	89.3	*PASS*	165.0	*FAIL*	4.0	10.0
Tetrachloroethylene	0.9	4.3	0.4	1.5	69.3	*PASS*	117.2	*PASS*	5.8	9.0
1,2-Dibromoethane	0.0	4.1	0.4	1.5	62.9	*PASS*	111.5	*PASS*	2.9	4.8
1,2-Dibromo-3-chloropropane	0.0	4.3	0.4	1.6	68.2	*PASS*	118.2	*PASS*	5.4	18.0

Table 10. Precision and accuracy of method compounds in DI water fortified at 4, 10, and 100 μg/L (ppt), SIM mode. The Relative Standard Deviation (RSD) must be less than 20% (Precision), and the average recovery must be between 80 and 120% of the expected concentration (Accuracy). The %Recoveries shown here have not been adjusted for the concentration of compounds found in the blank water, as this correction is expressly prohibited by the method.

Compound	Fortification Conc. 4 ng/L (n = 4)		Fortification Conc. 10 ng/L (n = 4)		Fortification Conc. 100 ng/L (n = 4)		Blank DI Water
	Precision as %RSD	Accuracy as Average %Recovery	*Precision as %RSD*	Accuracy as Average %Recovery	*Precision as %RSD*	Accuracy as Average %Recovery	Conc. (ppb)
Chlorodifluoromethane	*13.5*	205.9	*7.4*	127.9	*3.8*	87.2	4.0
1,3-Butadiene	*13.7*	275.0	*16.1*	193.0	*6.7*	86.3	5.2
Trichloroethylene	*10.2*	149.8	*14.6*	112.9	*3.3*	101.5	1.1
Tetrachloroethylene	*9.0*	107.6	*5.1*	101.1	*1.3*	101.0	0.9
1,2-Dibromoethane	*9.6*	101.7	*2.3*	98.2	*2.1*	96.8	0.0
1,2-Dibromo-3-chloropropane	*9.3*	108.1	*21.7*	95.9	*11.2*	88.2	0.0

Analysis of Real-World Samples

Duplicate samples of drinking water were collected from three municipalities (Bryan, College Station, and Wellborn) and one bottled-water facility in Texas. All samples were collected in 40-mL VOA vials to which both of the acid preservatives had been added. The samples were analyzed using the analytical conditions described in Table 2 and quantified using the initial calibration curve shown in Table 3. Chromatograms from analysis of all four samples are shown in Figures 3 through 6, and a summary of concentrations found is shown in Table 11.

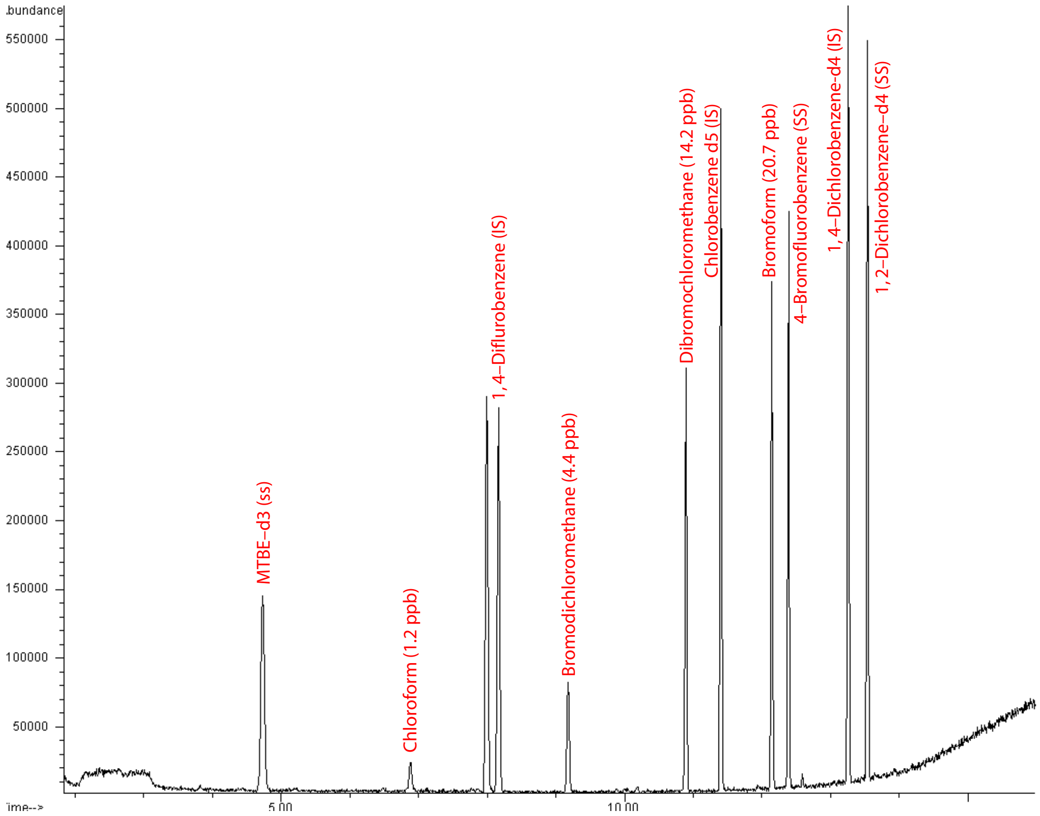

Figure 3. Chromatogram of Finished Drinking Water from Bryan, TX

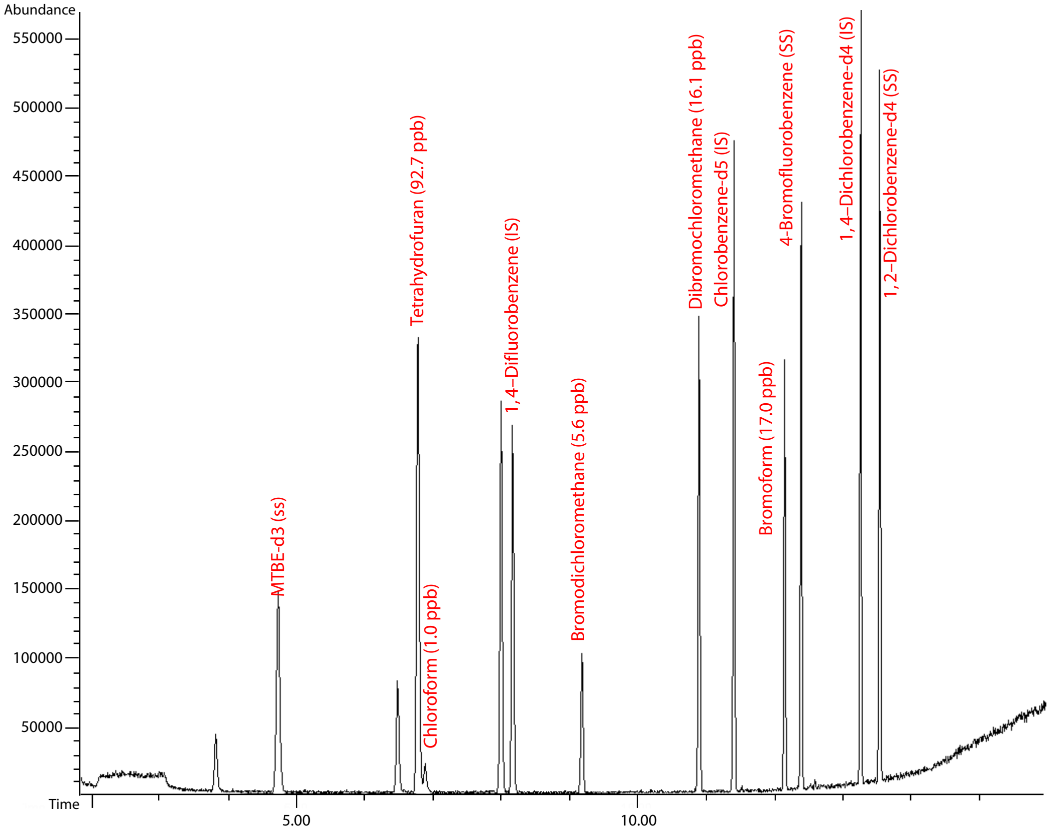

Figure 4. Chromatogram of Finished Drinking Water from College Station, TX

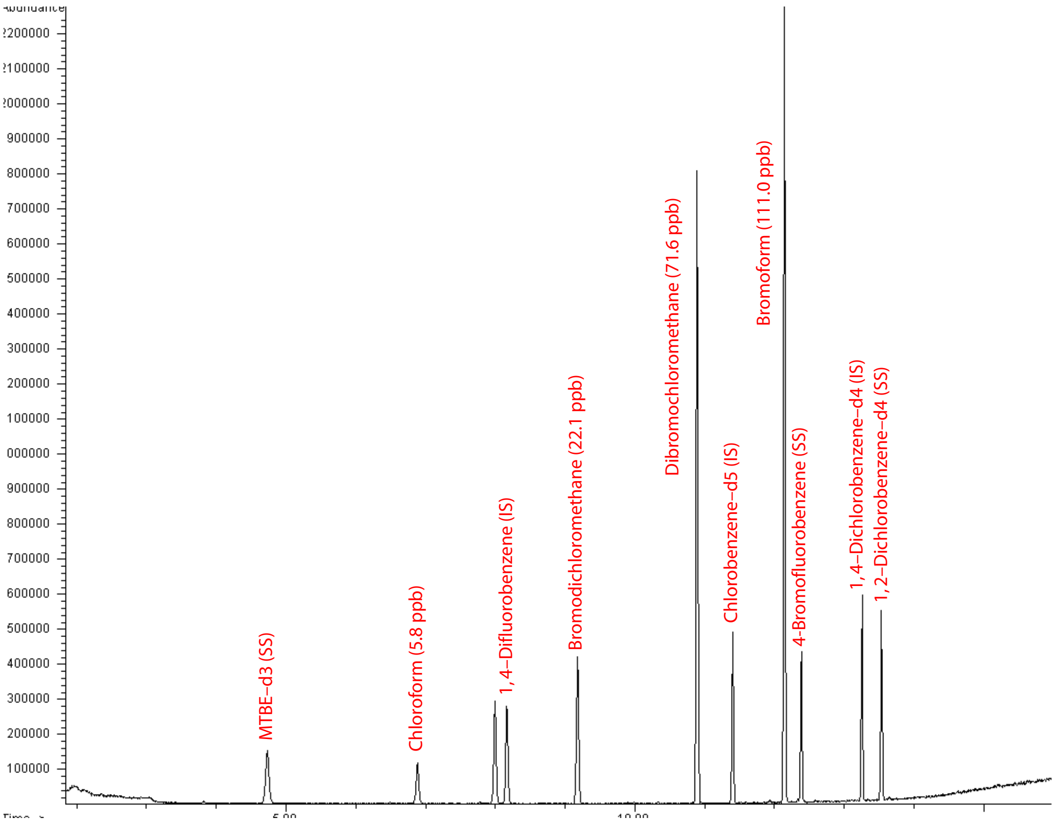

Figure 5. Chromatogram of Finished Drinking Water from Wellborn, TX

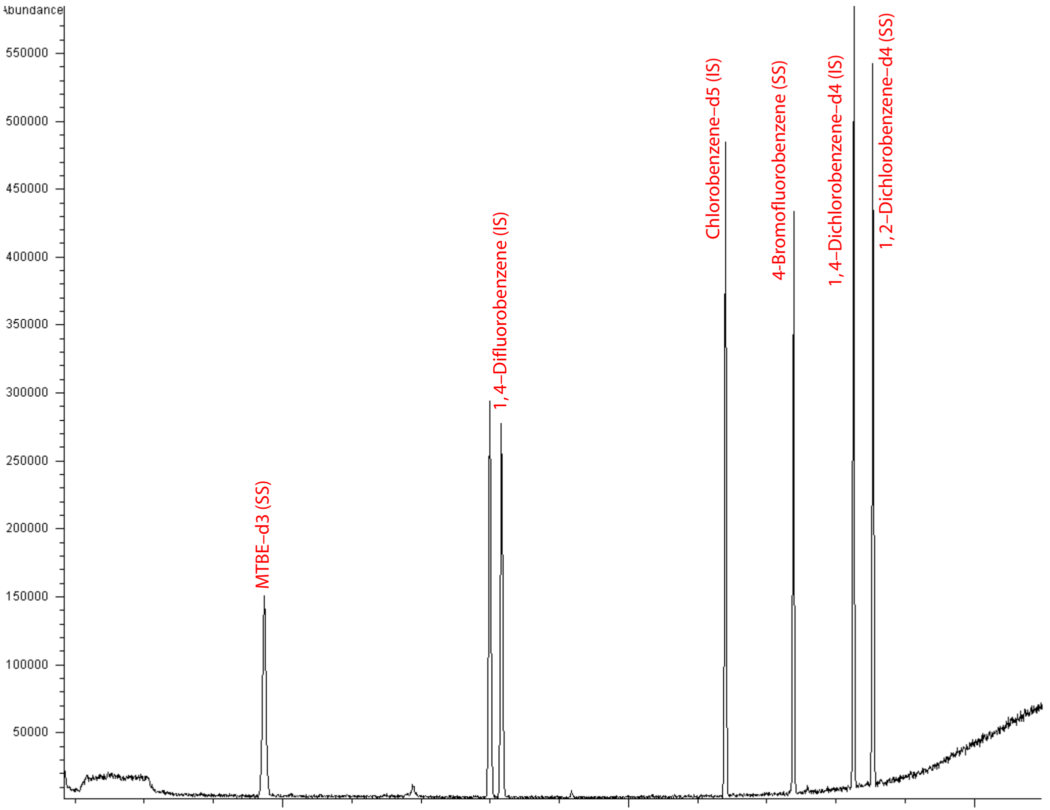

Figure 6. Chromatogram of Finished Drinking Water from a Bottle Water Facility in Central, TX

Table 11. Summary of analytical results from analysis of four different samples of finished drinking water, MS full scan mode. Only those compounds with concentrations above the Minimum Reporting Level (MRL) of 0.5 ppb listed

Compound	Bryan, TX	College Station, TX	Wellborn, TX	Bottled Water Facility
Surrogate Standard %Recovery				
MTBE-d3	102%	104%	104%	104%
4-Bromofluorobenzene	97%	98%	98%	99%
1, 2–Dichlorobenzene-d4	101%	102%	102%	104%
Target Compound Concentration Detected Above the MRL (ppb)				
Tetrahydrofuran	< MRL	92.7	< MRL	< MRL
Chloroform	1.2	1.0	5.8	< MRL
Bromodichloromethane	4.4	5.6	22.1	< MRL
Dibromochloromethane	14.2	16.1	71.6	< MRL
Bromoform	20.7	17.0	111.0	< MRL

Conclusions

The new method permits much greater latitude in setting instrument operating parameters within specified ranges, and includes significant changes to calibration acceptance criteria and minimum reporting limits. The instrument operating conditions used for this study have been shown to provide method validation and quality control data that consistently meet or exceed all of the new performance criteria specified in U.S. EPA Method 524.3.

Using modified purge parameters of 60 mL/minute for 6 minutes, heating the sample to 40 °C, and employing proven water-management techniques produced data that passed all initial and continuing QC criteria, and shortens the purge-and-trap cycle time for each sample by 5 minutes.

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P.O. Box 9010
College Station, TX 77842-9010
Tel: (979) 690-1711 • Fax: (979) 690-0440 • www.oico.com

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