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Application News

No. GCMS-1503

Gas Chromatograph Mass Spectrometer

Shimadzu Guide to US EPA Method 8260 for Analysis of Volatile Organic Compounds in Ground Water and Solid Waste

■ Introduction

Environmental contamination has been at the forefront of government policy and regulation since the US EPA was established in 1970. Over the years the US EPA has developed, published, and updated multiple methods for analysis of environmental pollutants, and single-quadrupole gas chromatography-mass spectrometry (GC/MS) has long been the technique of choice for determination of volatile organic contaminants (VOCs). As efforts to provide dependable analytical methods have progressed, the GC/MS instrumentation has evolved, with improvements in sensitivity, reliability, and user experience, but there haven't been many significant advancements in the overall methodology since the mid-1980s.

The VOC methods are all run using the purge-and-trap (P&T) sample introduction technique; headspace is not allowed for drinking water or wastewater compliance testing in the US. The required US EPA methods for VOCs are US EPA Methods 524.2, 524.3, and 524.4 (Drinking Water), Method 624 (Waste Water), and Method 8260 (Groundwater and Solid Waste). US EPA Method 8260 is by far the most comprehensive in terms of the number of VOCs included in the compound list, with as many as 100 or more RCRA VOCs included for testing. The method is used to determine VOCs in a variety of solid waste matrices, is applicable to nearly all types of samples, regardless of water content, and is one of the most common VOC methods used by commercial testing laboratories today.

This application note describes analytical operating conditions for analysis of US EPA Method 8260C[1], Revision 3, August 2006, and includes BFB tune parameters, calibration details, and a complete MDL and Precision and Accuracy study for almost 100 target compounds at multiple concentrations.

■ Experimental

This study was conducted using the Shimadzu GCMS-QP2010 SE shown in Figure 1, configured with a Restek capillary column designed specifically for analysis of VOCs by US EPA Methods mentioned above. The GC was operated in the unique Constant Linear Velocity mode to provide optimum chromatographic resolution, symmetric peak shape, and enhanced sensitivity for all compounds. A special, narrow ID inlet liner was used to minimize band broadening and retain ideal peak shape during transfer from the P&T, while still allowing high-split injections. Data were acquired in the full scan mode; quantitation and confirmation for most compounds were conducted using the quantitation and reference ion suggested in US EPA Method 8260C. Changes to quantitation and reference ions for a few selected compounds were made to improve overall sensitivity of the method.

Figure 1: Shimadzu GCMS-QP2010 SE

The EST Evolution P&T and Centurion Water/Soil Autosampler were used for the extraction, concentration, and sample introduction steps. The Evolution was configured with the optional sample heater to ensure that all samples were purged at precisely the same temperature for accuracy and precision of the data. The Centurion Water/Soil Autosampler was operated in the Water mode for this study; the Soil mode can also be used with similar results, albeit with slightly lower purge efficiency due to the needle sparging vs. frit sparging.

Each day before starting a sample sequence, the instrument was conditioned by cycling the P&T and VOCARB 3000 trap through two Bake cycles. Simultaneously, the oven, injection port, ion source, and MS interface temperatures were all raised to 220 °C for a minimum of one hour. The instrument bake-out procedure was run on all days, whether samples were analyzed or not. Complete instrument configuration and operating conditions are shown in Table 1.

Table 1: GC/MS and P&T Operating Conditions

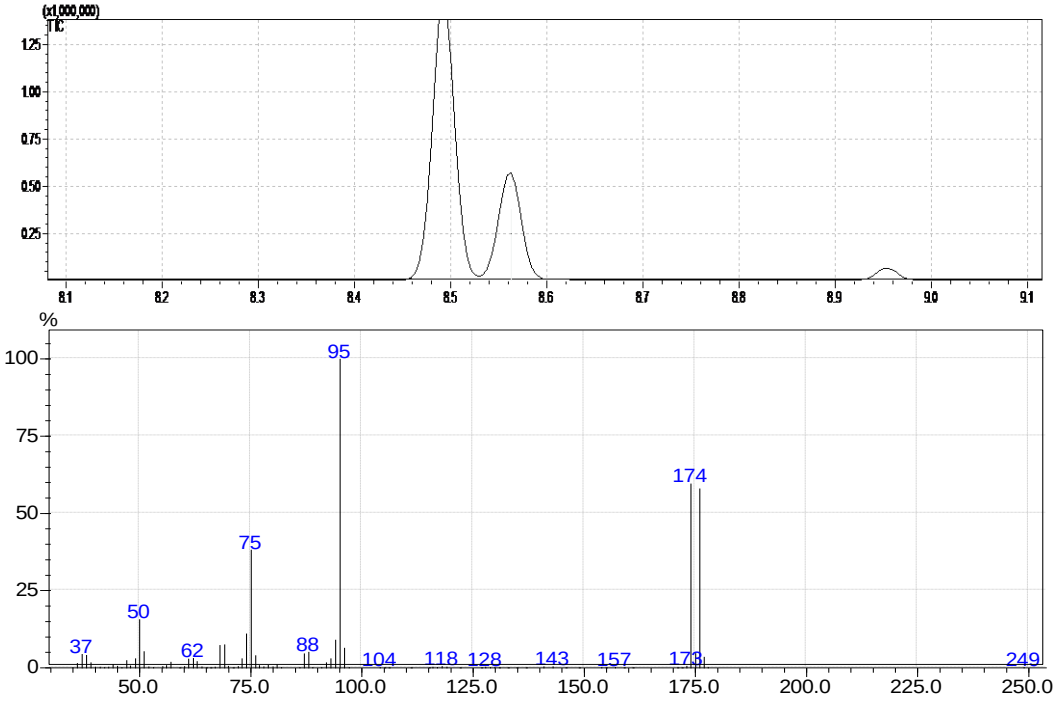
Gas Chromatograph	**GCMS-QP2010 SE**
Column	SH-RXI-624Sil MS, 30 m x 0.25 mm x 1.4 µm (Shimadzu PN 221-75962-30)
Oven Program	45 °C, hold 0.1 minute 15 °C/minute to 220 °C, hold 3.5 minutes
Injector	Split mode, split ratio 40:1 200 °C Low Volume Split Liner (Shimadzu PN 220-90784-10)
Primary Column Carrier Gas 8260 Column Carrier Gas	Helium Constant linear velocity mode, 36.2 cm/sec Total Flow 44.1 mL/min, Column Flow = 1.0 mL/min Purge Flow 3.0 mL/min
Interface Temperature	180 °C
Mass Spectrometer	**GCMS-QP2010 SE**
Ion Source Temperature	185 °C
MS Operating Mode	Full scan mode, m/z 35-270 Event time = 0.25 second/scan Solvent cut time = 0.7 minute Detector voltage set relative to tune + 0.1 kV Threshold = 100 NOTE: Scan rate was adjusted to provide a minimum of 10-12 spectra across all GC peaks for optimum quantitation
Purge-and-Trap Concentrator	**EST Encon Evolution with Centurion Autosampler**
Sample Volume	5 mL
Sample Temperature at Purge	40 °C
Trap	VOCARB 3000
Purge Flow Rate	Helium, 40 mL/minute for 11 minutes
Dry Purge	Helium, 40 mL/minute for 1 minute
Desorb	250 °C for 0.5 minute
Bake	260 °C for 8.0 minutes
Analysis Times	
GC Run Time	16 minutes
System Cycle Time	26 minutes

■ Results and Discussion

BFB Tune Results

At the beginning of the project the GCMS-QP2010 SE was tuned[2] to meet the US EPA Method 8260C requirements. Each day prior to running any samples, and at intervals of no longer than 12-hours during long sequences, an aliquot of the 4-bromofluorobenzene (BFB) was purged and analyzed using the method conditions shown in Table 1. The BFB spectra were evaluated using the US EPA Method 8260C criteria. Since BFB was one of the Surrogate Standards added to all samples, the BFB spectrum was available for evaluation for every run. A representative example of a BFB chromatogram and spectrum are shown in Figure 2.

Table 2 lists the BFB results as compared to the method criteria from four selected analyses of BFB during one of the extended sequences. The BFB spectra met all method criteria for all samples evaluated throughout the project. The tune remained stable throughout the project, approximately 6 weeks, and the GCMS-QP2010 SE instrument did not require re-tuning at any time during the analysis period.



Mass (m/z)	Relative Abundance Criteria	Result	Status
50	15 to 40% of 95	15.8	Pass
75	30 to 60% of 95	40.1	Pass
95	Base Peak, 100%	100	Pass
96	5 to 9% of 95	6.8	Pass
173	< 2% of 174	0.45	Pass
174	> 50% of 95	80.8	Pass
175	5 to 9% of 174	6.7	Pass
176	> 95% but < 101% of 174	100.6	Pass
177	5 to 9% of 176	5.9	Pass

Figure 2: Typical Results from BFB Tune Evaluation Using US EPA Method 8260C Criteria

Table 2: Evaluation of BFB Spectra from 4 Different Runs across a Long Sequence, Compared to US EPA Method 8260C Criteria

m/z	Spectrum Check Criteria	Result		Result		Result		Result	
		BFB	Status	BFB	Status	BFB	Status	BFB	Status
50	15 to 40% of mass 95	15.2	Pass	15.2	Pass	15.5	Pass	16.1	Pass
75	30 to 60% of mass 95	38.1	Pass	37.4	Pass	35.9	Pass	34.1	Pass
95	Base Peak, 100% Relative Abundance	100	Pass	100	Pass	100	Pass	100	Pass
96	5 to 9% of mass 95	6.8	Pass	6.9	Pass	6.7	Pass	6.6	Pass
173	< 2% of mass 174	0.48	Pass	0.40	Pass	0.54	Pass	0.47	Pass
174	> 50% of mass 95	79.9	Pass	81.9	Pass	81.5	Pass	70.7	Pass
175	5 to 9% of mass 174	7.1	Pass	7.1	Pass	6.9	Pass	6.7	Pass
176	> 95% but < 101% of mass174	98.8	Pass	99.8	Pass	95.6	Pass	98.9	Pass
177	5 to 9% of mass 176	6.4	Pass	6.5	Pass	6.3	Pass	6.0	Pass

Initial Calibration and Continuing Calibration Verification

A series of nine initial calibration standards across the range of 0.5 to 200 µg/L (parts-per-billion, ppb) was prepared. The four internal standards (IS) were held constant at 50 µg/L, and the three surrogate standards (SURR) were held constant at 50 µg/L in all samples analyzed. A total ion chromatogram (TIC) from a mid-point standard is shown in Figure 3, along with an expanded view of the chromatography of the early-eluting gases.

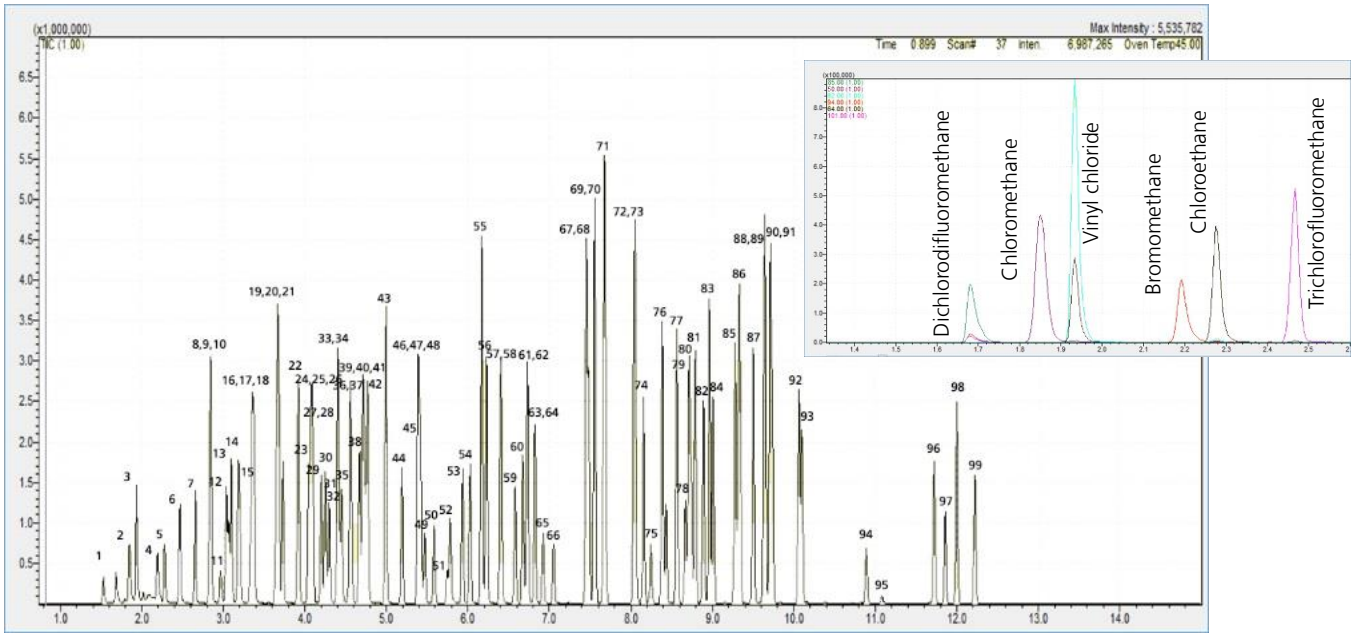


Figure 3: Total Ion Chromatogram from a mid-point Calibration Standard and EICP of the Six Light Gases. Peak numbers correspond to compound names shown in Tables 3, 4, and 5.

The calibration curve was evaluated two ways: using correlation coefficient (R^2) from a linear regression, and using the percent relative standard deviation (% RSD) of the calculated response factors (RF) for each data point in the curve. The calibration curve was evaluated across three different concentration ranges (0.5 to 50 µg/L, 0.5 to 100 µg/L, and 0.5 to 200 µg/L) to accommodate any type of VOC project, and passed the US EPA Method 8260C criteria (RF % RSD < 20%) for all except two compounds over the three concentration ranges.

Continuing calibration verifications (CCV) standards were analyzed periodically throughout the project, as specified in US EPA Method 8260C. The CCV concentrations varied throughout the project to monitor the entire calibration range, and were calculated based on one of the calibration curves. Recoveries were typical for most US EPA VOC methods (80 to 120%). Complete statistical results for the initial calibration curve and three representative CCVs analyzed during the project are shown in Table 3.

Table 3: Statistical Results from the Initial Calibration and Three Representative CCVs

Peak #	Compound Name	7-Point Calibration			8-Point Calibration			9-Point Calibration			CCV #1	CCV #2	CCV #3
		0.5 to 50 µg/L			0.5 to 100 µg/L			0.5 to 200 µg/L			Calculated Concentration		
		R^2	Avg RF	RF %RSD	R^2	Avg RF	RF %RSD	R^2	Avg RF	RF %RSD	5 µg/L	10 µg/L	20 µg/L
1	Dichlorodifluoromethane	1.000	0.16	11.5	1.000	0.19	11.5	1.000	0.16	11.0	5.4	9.9	19.5
2	Chloromethane	1.000	0.36	6.9	1.000	0.40	7.1	1.000	0.36	7.0	5.9	11.0	19.7
3	Vinyl Chloride	1.000	0.49	8.0	1.000	0.53	8.6	1.000	0.47	8.7	5.7	10.7	19.9
4	Bromomethane	0.999	0.22	39.0	1.000	0.31	40.2	1.000	0.16	15.1	6.6	12.6	19.6
5	Chloroethane	1.000	0.30	11.1	1.000	0.35	11.0	0.999	0.30	10.3	5.5	10.4	18.5
6	Trichlorofluoromethane	1.000	0.29	9.6	1.000	0.35	10.2	1.000	0.28	10.1	5.6	10.5	19.5
7	Diethylether	1.000	0.29	8.7	1.000	0.30	8.3	0.999	0.29	8.0	5.5	11.1	19.1
8	1,1,2-Trichlorofluoroethane	1.000	0.23	9.1	1.000	0.27	9.3	0.998	0.23	8.7	5.3	10.3	18.8
9	1,1-Dichloroethene	1.000	0.21	8.1	1.000	0.24	7.7	0.998	0.22	7.9	5.3	10.3	18.6
10	Acetone	1.000	0.25	59.2	1.000	0.24	60.0	0.999	0.17	20.8	6.3	11.3	14.2
11	Iodomethane	0.995	0.12	30.2	0.999	0.10	33.7	0.999	0.13	35.0	3.9	9.4	21.0
12	Carbon Disulfide	1.000	0.61	20.0	0.999	0.86	18.9	0.997	0.58	10.8	5.3	9.9	17.2
13	Acetonitrile	1.000	0.20	11.7	1.000	0.40	9.8	0.999	0.40	7.5	5.6	11.2	18.1
14	Methylene Chloride	1.000	0.23	33.7	1.000	0.38	33.4	0.996	0.19	11.9	5.1	9.3	16.3
15	Tert Butyl Alcohol	0.999	0.09	12.7	1.000	0.11	12.6	0.999	0.09	11.8	28.8	51.3	98.0
16	Acrylonitrile	1.000	0.20	11.7	1.000	0.23	11.8	0.999	0.20	11.1	5.8	10.8	19.6
17	MTBE	1.000	0.72	6.8	1.000	0.79	6.3	0.998	0.73	7.4	5.6	10.8	18.9
18	trans-1,2-Dichloroethene	1.000	0.23	11.8	1.000	0.28	11.2	0.998	0.23	10.6	5.4	10.3	18.6
19	Vinyl Acetate	0.999	0.91	8.5	0.999	1.00	9.3	0.999	0.90	8.7	4.7	8.3	17.6
20	Isopropylether	1.000	0.78	5.5	0.999	0.84	5.1	0.999	0.79	5.5	5.6	10.9	19.3
21	1,1-Dichloroethane	1.000	0.50	5.5	1.000	0.53	5.1	0.997	0.52	7.6	5.5	10.4	18.9
22	Ethyl Tert Butyl Ether	1.000	0.93	6.7	1.000	1.01	6.3	1.000	0.93	6.1	5.7	11.3	19.7
23	2-Butanone	1.000	1.16	61.1	1.000	2.57	62.4	0.998	1.05	61.9	6.2	10.8	12.8
24	Ethyl Acetate	0.999	0.06	21.8	1.000	0.09	21.1	0.998	0.06	19.7	5.3	10.6	17.3
25	cis-1,2-Dichloroethene	1.000	0.24	7.8	1.000	0.26	7.3	0.997	0.25	8.0	5.5	10.5	19.1
26	Propionitrile	0.999	0.09	7.1	1.000	0.09	7.1	0.998	9.00	9.9	5.4	10.3	19.5
27	2,2-Dichloropropane	1.000	0.25	10.5	1.000	0.29	10.0	0.997	0.25	10.0	4.6	9.0	15.5
28	Methyl Acrylate	1.000	0.44	7.0	1.000	0.46	6.8	0.999	0.44	6.7	5.8	11.0	19.4
29	Methacrylonitrile	1.000	0.24	9.7	1.000	0.27	9.3	0.999	0.24	8.8	5.7	10.9	19.3
30	Bromochloromethane	0.999	0.14	18.3	1.000	0.18	17.8	0.998	0.14	16.7	5.8	10.7	18.4
31	THF	1.000	0.21	37.1	1.000	0.35	36.6	0.998	0.17	9.4	6.2	11.1	16.3
32	Chloroform	1.000	0.27	8.9	1.000	0.31	8.7	0.998	0.27	8.3	5.5	10.6	18.6
33	Pentafluorobenzene (IS)	ISTD	ISTD	ISTD	ISTD	ISTD	ISTD	ISTD	ISTD	ISTD	50.0	50.0	50.0
34	Dibromofluoromethane (SURR)	NA	0.44	1.4	NA	0.44	1.5	NA	0.44	2.0	50.7	50.4	51.0
35	1,1,1-Trichloroethane	1.000	0.25	5.6	1.000	0.25	6.6	0.999	0.25	5.0	5.5	10.4	18.3
36	1,1-Dichloropropene	0.910	0.22	7.8	0.999	0.26	7.4	0.994	0.26	11.0	5.3	10.1	18.2
37	Carbon Tetrachloride	1.000	0.21	4.0	1.000	0.22	3.8	0.997	0.22	7.4	5.2	10.2	19.1
38	Methyl Acetate	1.000	0.59	8.8	1.000	0.67	8.6	0.998	0.59	8.2	5.7	10.9	19.1
39	Benzene	1.000	0.80	8.8	0.999	0.93	8.2	0.999	0.81	8.2	5.5	10.5	18.5
40	1,2-Dichloroethane	1.000	0.17	8.4	1.000	0.18	8.7	1.000	0.17	8.3	5.6	10.9	18.9
41	Isobutyl Alcohol	1.000	0.58	9.0	1.000	0.57	8.4	0.998	0.58	7.8	3.9	11.0	19.3
42	Tert Amyl Methyl Ether	1.000	0.66	6.0	0.999	0.70	5.7	0.997	0.68	8.3	5.5	10.8	19.0
43	1,4-Diflourobenzene (IS)	ISTD	ISTD	ISTD	ISTD	ISTD	ISTD	ISTD	ISTD	ISTD	50.0	50.0	50.0
44	Trichloroethene	1.000	0.12	9.1	0.998	0.14	8.5	0.995	0.12	11.4	5.3	11.0	18.4
45	Methyl Methacrylate	0.999	0.14	13.1	0.999	0.16	12.1	0.995	0.14	13.3	5.2	10.1	17.8
46	1,2-Dichloropropane	1.000	0.14	6.2	0.999	0.15	6.0	0.996	0.15	9.5	5.3	10.6	18.2
47	Propyl Acetate	1.000	0.28	8.2	1.000	0.29	7.6	0.998	0.28	7.8	5.5	10.8	19.2
48	1,4-Dioxane	0.999	0.00	26.6	0.999	0.00	24.2	0.999	0.00	10.4	5.9	22.7	41.7
49	Dibromomethane	1.000	0.07	10.3	1.000	0.08	9.9	0.998	0.07	9.4	5.6	10.6	18.2
50	Bromodichloromethane	1.000	0.10	9.5	1.000	0.08	8.8	0.999	0.10	8.5	5.5	11.1	19.2
51	2-Nitropropane	0.997	0.04	9.2	0.999	-	9.6	0.999	0.04	11.4	4.8	9.3	17.9
52	2-Chloroethylvinylether	1.000	0.19	4.9	1.000	0.19	5.4	0.997	0.19	6.0	5.7	11.1	18.3
53	cis-1,3-Dichloropropane	1.000	0.16	8.2	0.999	0.17	7.6	0.998	0.16	8.4	5.3	10.5	18.3
54	4-Methyl-2-pentanone	1.000	0.24	7.3	1.000	0.25	7.0	0.999	0.24	6.8	5.6	11.1	19.3
55	Toluene-d8 (SURR)	NA	0.96	1.3	NA	0.94	1.2	NA	0.96	1.4	50.3	50.7	50.3
56	Toluene	1.000	0.30	12.2	1.000	0.35	11.9	0.998	0.30	11.3	5.2	10.1	17.7
57	trans-1,3-Dichloropropene	1.000	0.14	4.9	0.999	0.14	5.2	0.996	0.14	9.7	5.1	10.4	18.1
58	Ethyl Methacrylate	0.999	0.21	11.5	0.999	0.25	10.7	0.995	0.21	12.7	5.0	10.2	17.8
59	1,1,2-Trichloroethane	1.000	0.11	8.3	1.000	0.11	8.3	0.999	0.11	7.8	5.6	11.0	19.0
60	Tetrachloroethane	0.998	0.11	7.3	0.988	0.12	13.9	0.993	0.12	21.4	7.3	15.0	23.2
61	1,3-Dichloropropane	0.999	0.16	6.2	0.999	0.17	5.9	0.995	0.17	10.1	5.4	10.5	18.1
62	2-Hexanone	0.999	0.19	8.2	1.000	0.21	7.6	0.998	0.19	8.4	5.6	10.7	18.9
63	Isopropyl Acetate	0.999	0.06	8.1	1.000	0.06	7.6	0.998	0.06	7.8	5.4	10.7	18.9
64	Butyl Acetate	0.999	0.17	10.2	1.000	0.19	10.0	0.999	0.17	9.4	5.5	10.8	18.9

Table 3: continued

Peak #	Compound Name	7-Point Calibration			8-Point Calibration			9-Point Calibration			CCV #1	CCV #2	CCV #3
		0.5 to 50 µg/L			0.5 to 100 µg/L			0.5 to 200 µg/L			Calculated Concentration		
		R^2	Avg RF	RF %RSD	R^2	Avg RF	RF %RSD	R^2	Avg RF	RF %RSD	5 µg/L	10 µg/L	20 µg/L
65	Dibromochloromethane	0.999	0.08	4.9	0.999	0.09	5.0	0.998	0.09	8.1	5.1	10.7	19.0
66	1,2-Dibromoethane	1.000	0.12	7.4	1.000	0.12	7.1	0.999	0.12	6.8	5.7	11.4	19.1
67	Chlorobenzene-d5 (IS)	ISTD	ISTD	ISTD	ISTD	ISTD	ISTD	ISTD	ISTD	ISTD	50.0	50.0	50.0
68	Chlorobenzene	1.000	0.47	8.3	1.000	0.52	7.7	0.999	0.47	7.3	5.3	10.5	18.9
69	1,1,1,2-Tetrachloroethane	0.999	0.12	17.9	0.998	0.15	16.6	0.996	0.11	13.6	5.1	10.3	18.6
70	Ethylbenzene	1.000	0.60	8.2	0.999	0.66	7.7	1.000	0.59	7.8	5.4	10.6	18.8
71	Xylene (m&p)	1.000	0.48	8.1	0.999	0.52	7.6	0.993	0.46	10.8	10.9	21.5	38.3
72	Xylene (o)	1.000	0.47	8.2	0.999	0.50	7.7	0.999	0.47	7.3	5.4	10.6	18.6
73	Styrene	1.000	0.52	5.9	0.999	0.55	5.6	1.000	0.52	5.2	5.3	10.8	19.1
74	n-Amyl Acetate	1.000	0.29	8.7	1.000	0.30	8.3	0.999	0.29	7.8	5.6	11.1	19.1
75	Bromoform	0.999	0.08	11.4	0.999	0.09	10.6	0.999	0.08	10.6	4.9	9.8	18.3
76	Isopropylbenzene	1.000	2.01	9.2	0.999	2.25	8.6	0.998	1.97	9.6	5.7	10.8	18.8
77	BFB(SURR)	NA	1.02	1.3	NA	1.03	1.4	NA	1.02	1.5	51.2	51.1	49.9
78	1,1,2,2-Tetrachloroethane	0.999	0.44	12.1	1.000	0.52	12.2	0.999	0.44	11.5	5.2	9.9	18.0
79	Bromobenzene	0.999	0.41	9.5	0.999	0.46	9.1	0.997	0.41	9.2	5.4	10.4	17.5
80	1.2.3-Trichloropropane	1.000	0.63	7.1	0.998	0.63	7.0	0.995	0.65	11.7	5.4	10.4	17.6
81	n-Propylbenzene	0.999	1.77	8.7	0.999	1.95	8.5	1.000	1.74	8.8	5.6	10.9	18.7
82	2-Chlorotoluene	0.999	0.39	7.9	0.998	-	7.3	0.994	0.40	12.2	5.3	10.2	17.4
83	1,3,5-Trimethylbenzene	1.000	1.64	8.4	0.999	1.81	7.8	1.000	1.62	7.7	5.6	10.8	18.5
84	4-Chlorotoluene	0.999	0.40	9.5	0.997	0.46	8.9	0.994	0.42	12.9	5.2	10.1	17.6
85	tert-Butylbenzene	1.000	1.36	19.3	0.998	1.81	18.0	0.998	1.36	16.9	5.3	10.2	17.8
86	1,2,4-Trimethylbenzene	1.000	1.64	7.9	0.999	1.81	7.4	1.000	1.62	7.3	5.6	10.8	18.5
87	sec-Butylbenzene	1.000	0.37	11.5	0.998	0.40	9.6	0.998	0.36	9.6	5.3	10.3	17.6
88	1,3-Dichlorobenzene	1.000	0.72	8.4	0.998	0.79	7.7	0.995	0.74	10.2	5.3	10.5	17.9
89	Isopropyltoluene	1.000	1.47	6.3	0.997	1.66	8.1	0.999	1.52	8.2	5.3	10.2	17.9
90	1,4-Dichlorobenzene-d4 (IS)	ISTD	ISTD	ISTD	ISTD	ISTD	ISTD	ISTD	ISTD	ISTD	50.0	50.0	50.0
91	1,4-Dichlorobenzene	1.000	0.76	11.8	0.999	0.88	11.3	0.997	0.76	10.9	5.4	10.5	17.5
92	n-Butylbenzene	1.000	1.07	9.2	0.999	1.22	8.9	0.998	1.07	8.7	5.5	10.6	18.2
93	1,2-Dichlorobenzene	1.000	0.68	10.9	0.999	0.80	10.3	0.998	0.68	10.0	5.4	10.6	18.0
94	1,2-Dibromo-3-chloropropane	0.999	0.15	8.9	1.000	0.15	8.8	0.999	0.14	8.3	5.2	10.8	18.8
95	Nitrobenzene	0.998	0.01	10.3	0.999	0.01	10.0	0.992	0.01	21.8	4.6	9.7	15.5
96	1,2,4-Trichlorobenzene	1.000	0.35	8.0	0.998	0.40	7.6	0.996	0.37	10.7	5.4	10.4	17.3
97	Hexachlorobutadiene	0.999	0.14	7.5	1.000	0.14	7.5	0.999	0.14	7.1	5.7	10.7	18.1
98	Naphthalene	0.999	1.48	13.4	0.999	1.81	12.4	0.999	1.49	11.7	5.3	10.5	17.6
99	1,2,3-Trichlorobenzene	0.999	0.34	12.9	0.999	0.42	11.9	0.997	0.35	12.4	5.2	10.1	17.1

Method Detection Limit Study

A Method Detection Limit (MDL) study[3] was conducted by analyzing 8 replicate aliquots each of the 0.5 and 1.0 µg/L standards. The MDLs were calculated using the procedure outlined in the Federal Register, and all MDLs easily met the criteria. The MDL study results at both concentrations are shown in table 4.

Table 4: Method Detection Limit (MDL) Study Results

Peak #	Compound Name	0.5 µg/L n = 8		1.0 µg/L n = 8	
		% RSD	MDL	% RSD	MDL
1	Dichlorodifluoromethane	5.4	0.10	9.1	0.35
2	Chloromethane	7.1	0.15	6.2	0.29
3	Vinyl Chloride	5.2	0.10	7.2	0.34
4	Bromomethane	12.3	0.35	5.0	0.27
5	Chloroethane	5.9	0.11	12.9	0.50
6	Trichlorofluoromethane	5.6	0.11	8.6	0.39
7	Diethylether	4.6	0.09	4.1	0.17
8	1,1,2-Trichlorofluoroethane	4.6	0.08	6.4	0.26
9	1,1-Dichloroethene	6.0	0.11	7.6	0.32
10	Acetone	16.9	0.61	5.9	0.29
11	Iodomethane	18.7	0.28	11.5	0.34
12	Carbon Disulfide	13.4	0.31	2.6	0.10
13	Acetonitrile	12.0	0.29	6.1	0.26
14	Methylene Chloride	3.1	0.09	4.7	0.22
15	Tert Butyl Alcohol	14.0	1.41	7.3	1.43
16	Acrylonitrile	8.1	0.17	7.1	0.32
17	MTBE	3.7	0.06	5.2	0.19
18	trans-1,2-Dichloroethene	8.6	0.16	4.4	0.19
19	Vinyl Acetate	12.4	0.21	11.4	0.43
20	Isopropylether	3.8	0.07	6.3	0.26
21	1,1-Dichloroethane	5.9	0.10	4.6	0.17
22	Ethyl Tert Butyl Ether	3.5	0.06	4.3	0.18
23	2-Butanone	17.4	0.67	2.9	0.14
24	Ethyl Acetate	23.0	0.46	12.6	0.56
25	cis-1,2-Dichloroethene	8.2	0.16	6.4	0.27
26	Propionitrile	7.9	0.16	26.2	1.09
27	2,2-Dichloropropane	8.2	0.12	5.1	0.14
28	Methyl Acrylate	5.4	0.10	5.9	0.25
29	Methacrylonitrile	4.2	0.08	4.3	0.17
30	Bromochloromethane	6.0	0.13	5.6	0.24
31	THF	5.8	0.16	5.0	0.23
32	Chloroform	6.4	0.12	5.1	0.21
33	Pentafluorobenzene (IS)	NA	NA	NA	NA
34	Dibromofluoromethane (SURR)	1.7	2.55	1.6	2.29
35	1,1,1-Trichloroethane	4.3	0.08	5.1	0.21
36	1,1-Dichloropropene	8.8	0.16	5.5	0.20
37	Carbon Tetrachloride	8.2	0.12	8.5	0.29
38	Methyl Acetate	4.8	0.09	4.2	0.16
39	Benzene	4.3	0.08	4.4	0.17
40	1,2-Dichloroethane	3.1	0.06	5.3	0.25
41	Isobutyl Alcohol	3.4	0.06	5.0	0.20
42	Tert Amyl Methyl Ether	5.9	0.10	4.3	0.16
43	1,4-Diflourobenzene (IS)	NA	NA	NA	NA
44	Trichloroethene	6.2	0.12	8.7	0.37
45	Methyl Methacrylate	9.8	0.19	7.0	0.29
46	1,2-Dichloropropane	10.4	0.18	4.1	0.16
47	Propyl Acetate	3.4	0.06	4.2	0.18
48	1,4-Dioxane	21.3	0.80	36.6	2.70
49	Dibromomethane	5.9	0.12	6.9	0.30
50	Bromodichloromethane	5.9	0.11	7.1	0.31
51	2-Nitropropane	14.3	0.25	22.0	0.74
52	2-Chloroethylvinylether	9.9	0.17	6.7	0.24
53	cis-1,3-Dichloropropane	3.6	0.06	4.9	0.18

Table 4: continued

Peak #	Compound Name	0.5 µg/L n = 8		1.0 µg/L n = 8	
		% RSD	MDL	% RSD	MDL
54	4-Methyl-2-pentanone	3.1	0.06	5.0	0.22
55	Toluene-d8 (SURR)	1.3	2.08	1.6	2.58
56	Toluene	2.8	0.06	5.6	0.26
57	trans-1,3-Dichloropropene	7.7	0.14	4.4	0.17
58	Ethyl Methacrylate	4.6	0.08	5.6	0.22
59	1,1,2-Trichloroethane	10.1	0.19	4.7	0.22
60	Tetrachloroethane	18.0	0.34	26.4	1.08
61	1,3-Dichloropropane	2.8	0.05	3.1	0.13
62	2-Hexanone	4.5	0.09	5.6	0.24
63	Isopropyl Acetate	5.0	0.09	10.9	0.43
64	Butyl Acetate	4.7	0.09	4.5	0.19
65	Dibromochloromethane	6.1	0.10	4.7	0.18
66	1,2-Dibromoethane	4.2	0.08	5.9	0.27
67	Chlorobenzene-d5 (IS)	NA	NA	NA	NA
68	Chlorobenzene	4.7	0.09	5.4	0.23
69	1,1,1,2-Tetrachloroethane	11.7	0.26	15.9	0.70
70	Ethylbenzene	3.0	0.06	6.8	0.31
71	Xylene (m&p)	4.3	0.17	5.7	0.53
72	Xylene (o)	3.7	0.07	6.3	0.29
73	Styrene	3.7	0.07	3.2	0.14
74	n-Amyl Acetate	7.1	0.13	4.9	0.21
75	Bromoform	14.7	0.26	5.6	0.22
76	Isopropylbenzene	4.4	0.08	3.6	0.14
77	BFB(SURR)	1.6	2.41	0.6	0.92
78	1,1,2,2-Tetrachloroethane	5.1	0.09	6.4	0.25
79	Bromobenzene	7.5	0.14	4.3	0.18
80	1.2.3-Trichloropropane	29.2	0.44	31.2	1.07
81	n-Propylbenzene	4.7	0.09	4.5	0.18
82	2-Chlorotoluene	8.5	0.15	4.5	0.16
83	1,3,5-Trimethylbenzene	4.3	0.08	3.6	0.14
84	4-Chlorotoluene	5.4	0.10	5.0	0.18
85	tert-Butylbenzene	6.1	0.11	5.3	0.19
86	1,2,4-Trimethylbenzene	6.5	0.12	3.1	0.12
87	sec-Butylbenzene	7.5	0.13	4.7	0.18
88	1,3-Dichlorobenzene	6.2	0.12	3.5	0.14
89	Isopropyltoluene	7.8	0.13	2.8	0.10
90	1,4-Dichlorobenzene-d4 (IS)	NA	NA	NA	NA
91	1,4-Dichlorobenzene	9.5	0.19	3.2	0.14
92	n-Butylbenzene	10.5	0.20	5.3	0.21
93	1,2-Dichlorobenzene	8.1	0.15	5.9	0.25
94	1,2-Dibromo-3-chloropropane	9.0	0.15	7.2	0.26
95	Nitrobenzene	27.6	0.47	26.6	0.79
96	1,2,4-Trichlorobenzene	15.5	0.31	1.9	0.07
97	Hexachlorobutadiene	16.5	0.34	5.6	0.25
98	Naphthalene	15.2	0.29	3.2	0.12
99	1,2,3-Trichlorobenzene	14.8	0.27	4.6	0.17

Precision and Accuracy Study

A Precision and Accuracy (P&A) study was conducted to gauge the expected performance of the method at different concentration levels. Eight replicate aliquots each of the 10 and 50 µg/L standards were analyzed using the operating conditions shown above. Table 5 lists the detailed results of the P&A study, reporting the average concentration reported for each compound (n = 8), the percent recovery, and the %RSD for all compounds at both concentration levels.

Table 5: Precision and Accuracy (P&A) Study Results

Peak #	Compound Name	Precision and Accuracy at 10 µg/L n = 8			Precision and Accuracy at 50 µg/L n = 8		
		Mean Concentration (µg/L)	Recovery	% RSD	Mean Concentration (µg/L)	Recovery	% RSD
1	Dichlorodifluoromethane	7.8	78%	8.4	53.1	106%	13.6
2	Chloromethane	9.2	92%	8.3	58.1	116%	8.2
3	Vinyl Chloride	9.3	93%	8.5	59.9	120%	6.4
4	Bromomethane	10.6	106%	9.2	66.9	134%	6.8
5	Chloroethane	9.3	93%	4.1	56.9	114%	15.5
6	Trichlorofluoromethane	8.8	88%	10.6	59.9	120%	6.3
7	Diethylether	9.5	95%	1.5	55.1	110%	14.1
8	1,1,2-Trichlorofluoroethane	9.7	97%	6.0	55.4	111%	8.4
9	1,1-Dichloroethene	9.9	99%	4.6	54.7	109%	11.7
10	Acetone	8.3	83%	9.1	59.6	119%	12.7
11	Iodomethane	8.7	87%	10.4	54.4	109%	13.7
12	Carbon Disulfide	10.8	108%	16.2	55.7	111%	19.8
13	Acetonitrile	10.6	106%	24.2	56.9	114%	12.1
14	Methylene Chloride	9.8	98%	4.9	56.3	113%	16.7
15	Tert Butyl Alcohol	43.8	88%	2.6	290.4	116%	14.2
16	Acrylonitrile	9.3	93%	2.8	58.9	118%	18.0
17	MTBE	9.8	98%	8.0	55.3	111%	15.9
18	trans-1,2-Dichloroethene	10.1	101%	4.3	55.8	112%	19.2
19	Vinyl Acetate	9.7	97%	5.1	52.4	105%	6.7
20	Isopropylether	9.9	99%	3.3	51.6	103%	7.6
21	1,1-Dichloroethane	10.0	100%	7.7	50.8	102%	6.8
22	Ethyl Tert Butyl Ether	9.6	96%	2.7	53.2	106%	7.9
23	2-Butanone	9.7	97%	5.5	52.8	106%	7.1
24	Ethyl Acetate	9.8	98%	4.1	52.8	106%	6.5
25	cis-1,2-Dichloroethene	10.2	102%	4.5	51.0	102%	6.9
26	Propionitrile	9.6	96%	3.3	52.2	104%	7.8
27	2,2-Dichloropropane	11.8	118%	2.6	48.9	98%	5.4
28	Methyl Acrylate	9.6	96%	3.9	52.3	105%	7.3
29	Methacrylonitrile	9.5	95%	4.7	54.3	109%	7.0
30	Bromochloromethane	10.2	102%	7.0	54.0	108%	7.6
31	THF	9.4	94%	5.6	53.5	107%	8.1
32	Chloroform	9.7	97%	3.3	54.3	109%	6.5
33	Pentafluorobenzene (IS)	NA	NA	NA	NA	NA	NA
34	Dibromofluoromethane (SURR)	44.2	88%	2.0	48.6	97%	3.3
35	1,1,1-Trichloroethane	9.5	95%	6.3	56.4	113%	5.6
36	1,1-Dichloropropene	10.2	102%	5.4	51.5	103%	7.1
37	Carbon Tetrachloride	9.4	94%	3.9	54.3	109%	5.6
38	Methyl Acetate	9.5	95%	1.2	54.3	109%	6.9
39	Benzene	10.3	103%	4.3	50.2	100%	7.2
40	1,2-Dichloroethane	10.1	101%	14.2	58.5	117%	5.3
41	Isobutyl Alcohol	8.8	88%	21.6	54.3	109%	6.9
42	Tert Amyl Methyl Ether	9.6	96%	4.9	51.5	103%	7.7
43	1,4-Diflourobenzene (IS)	NA	NA	NA	NA	NA	NA
44	Trichloroethene	10.8	108%	5.6	53.5	107%	4.8
45	Methyl Methacrylate	10.1	101%	1.5	52.4	105%	4.7
46	1,2-Dichloropropane	10.2	102%	2.9	52.0	104%	5.0
47	Propyl Acetate	10.1	101%	3.7	55.6	111%	4.9

Table 5: continued

Peak #	Compound Name	Precision and Accuracy at 10 µg/L n = 8			Precision and Accuracy at 50 µg/L n = 8		
		Mean Concentration (µg/L)	Recovery	% RSD	Mean Concentration (µg/L)	Recovery	% RSD
48	1,4-Dioxane	15.3	76%	16.8	112.9	113%	10.4
49	Dibromomethane	10.3	103%	2.6	57.4	115%	6.0
50	Bromodichloromethane	10.3	103%	9.5	57.2	114%	4.9
51	2-Nitropropane	8.6	86%	8.5	54.7	109%	6.5
52	2-Chloroethylvinylether	8.7	87%	16.9	55.8	112%	6.7
53	cis-1,3-Dichloropropane	10.5	105%	2.3	54.5	109%	3.9
54	4-Methyl-2-pentanone	10.0	100%	4.4	57.4	115%	4.3
55	Toluene-d8 (SURR)	51.0	102%	3.8	52.0	104%	1.8
56	Toluene	10.5	105%	6.8	54.2	108%	4.7
57	trans-1,3-Dichloropropene	10.5	105%	2.0	53.4	107%	4.2
58	Ethyl Methacrylate	10.0	100%	3.2	52.3	105%	4.2
59	1,1,2-Trichloroethane	10.2	102%	7.6	55.6	111%	4.4
60	Tetrachloroethane	11.3	113%	13.9	57.4	115%	5.3
61	1,3-Dichloropropane	10.2	102%	2.3	53.2	106%	4.1
62	2-Hexanone	9.9	99%	4.2	56.1	112%	4.9
63	Isopropyl Acetate	9.8	98%	5.1	55.1	110%	4.1
64	Butyl Acetate	9.8	98%	3.7	55.7	111%	4.5
65	Dibromochloromethane	10.2	102%	6.1	56.0	112%	4.6
66	1,2-Dibromoethane	10.0	100%	3.0	55.5	111%	4.6
67	Chlorobenzene-d5 (IS)	NA	NA	NA	NA	NA	NA
68	Chlorobenzene	10.4	104%	4.1	53.7	107%	4.6
69	1,1,1,2-Tetrachloroethane	10.5	105%	9.3	51.3	103%	4.4
70	Ethylbenzene	10.7	107%	10.6	54.0	108%	4.5
71	Xylene (m&p)	21.5	107%	10.6	111.5	111%	4.8
72	Xylene (o)	10.5	105%	10.4	54.1	108%	4.5
73	Styrene	9.9	99%	5.2	53.3	107%	4.6
74	n-Amyl Acetate	9.9	99%	6.6	55.9	112%	4.7
75	Bromoform	9.9	99%	5.2	57.6	115%	5.2
76	Isopropylbenzene	9.7	97%	6.8	55.8	112%	5.0
77	BFB(SURR)	49.2	98%	2.0	49.2	98%	1.3
78	1,1,2,2-Tetrachloroethane	9.5	95%	5.0	54.4	109%	4.2
79	Bromobenzene	10.2	102%	3.1	54.0	108%	4.6
80	1.2.3-Trichloropropane	9.6	96%	6.3	52.2	104%	4.1
81	n-Propylbenzene	10.0	100%	5.9	55.8	112%	5.3
82	2-Chlorotoluene	10.3	103%	4.2	52.9	106%	4.4
83	1,3,5-Trimethylbenzene	9.7	97%	6.2	54.8	110%	4.8
84	4-Chlorotoluene	10.2	102%	3.6	52.1	104%	5.1
85	tert-Butylbenzene	10.0	100%	5.1	53.2	106%	4.4
86	1,2,4-Trimethylbenzene	9.6	96%	6.3	53.4	107%	4.9
87	sec-Butylbenzene	10.7	107%	4.4	52.9	106%	5.3
88	1,3-Dichlorobenzene	10.2	102%	4.7	50.9	102%	4.3
89	Isopropyltoluene	10.0	100%	5.1	51.5	103%	5.5
90	1,4-Dichlorobenzene-d4 (IS)	NA	NA	NA	NA	NA	NA
91	1,4-Dichlorobenzene	10.2	102%	4.2	54.0	108%	4.4
92	n-Butylbenzene	10.2	102%	5.5	55.8	112%	5.7
93	1,2-Dichlorobenzene	10.4	104%	2.9	53.9	108%	4.0
94	1,2-Dibromo-3-chloropropane	9.7	97%	3.2	56.5	113%	5.8
95	Nitrobenzene	10.0	100%	7.2	48.0	96%	7.2
96	1,2,4-Trichlorobenzene	10.3	103%	4.6	55.5	111%	4.4
97	Hexachlorobutadiene	11.0	110%	5.7	60.4	121%	6.0
98	Naphthalene	10.4	104%	3.2	51.0	102%	3.3
99	1,2,3-Trichlorobenzene	10.3	103%	4.7	54.3	109%	3.9

Internal standard response remained stable during the entire study at ≤ 8%, and Surrogate recoveries fell within the 80 to 120 % method criteria for all analyses. IS and SURR results from a representative 12-hour sequence are shown in Figures 4 and 5, respectively.

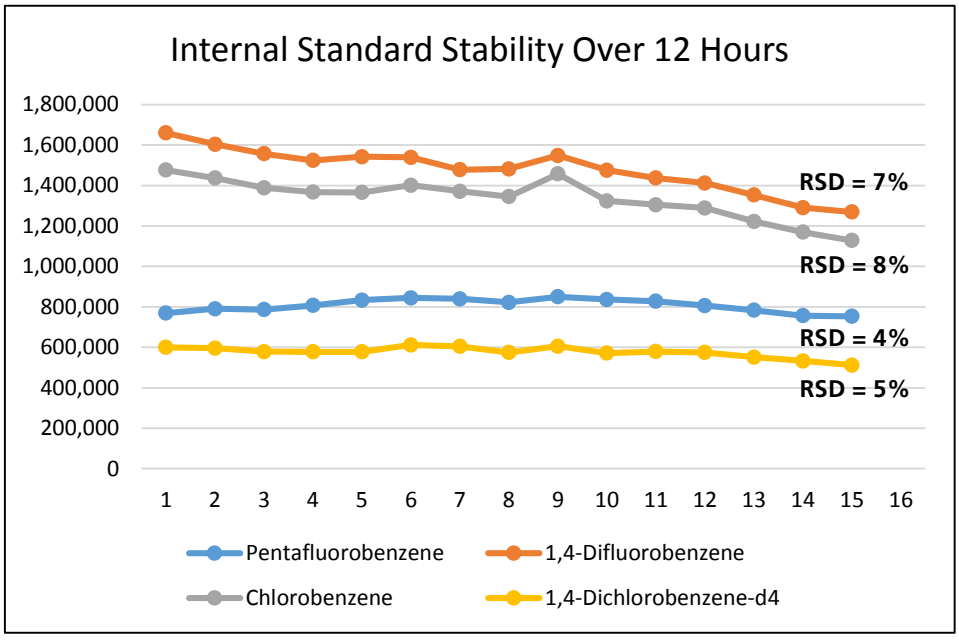


Figure 4: Internal Standard Response over a Representative 12-Hour Tune Period during This Study

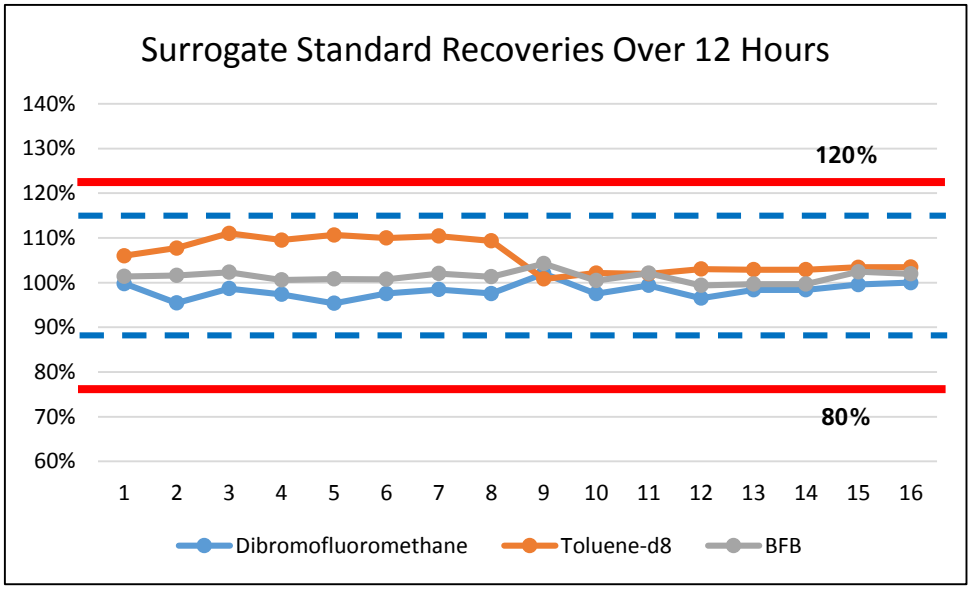


Figure 5: Surrogate Standard Recoveries over a Representative 12-hour Tune Period during This Study

■ Summary and Conclusion

The instrumentation and analytical conditions shown here have been demonstrated to provide outstanding results for US EPA Method 8260C, far exceeding all existing method criteria. The narrow-bore capillary column and Constant Linear Velocity mode provided outstanding chromatography for all compounds, including the early-eluting light gases, in less than 13 minutes. Calibration curves over narrow or wide ranges can be used to meet the project or contract needs. MDLs are easily well below 0.5 µg/L for all compounds when measured at either 0.5 or 1.0 µg/L, and a high level of precision and accuracy can be expected across any calibration rage, particularly at the lower concentrations.

■ References

1. US EPA Method 8260C, VOLATILE ORGANIC COMPOUNDS BY GAS CHROMATOGRAPHY/MASS SPECTROMETRY (GC/MS), Revision 3, August 2006.
2. Shimadzu Guide to BFB Tuning for Analysis of Volatile Organic Compounds, GCMS Application News No. GCMS-1405.
3. Definition and Procedure for the Determination of the Method Detection Limit. *Fed. Regist.* **1984**. 49 (209), Appendix B to Part 136.
4. Shimadzu Guide to US EPA Method 624 for Analysis of Volatile Organic Compounds in Wastewater, GCMS Application News No. GCMS-1406.

■ Ordering Information for Replacement Consumables

The consumables used in this application note are shown in the table below. To order any of these items please contact Customer Service at Shimadzu Scientific Instruments at 1-800-477-1227, or visit our web store at http://store.shimadzu.com.

Part Number	Item Name	Photo	Item Description
221-75962-30	Capillary Column		SH-RXI-624 SIL MS, 30 m x 0.25 mm x 1.40 µm
220-90784-10	Inlet Liner		Low-volume Liner, 1.0 mm ID, Straight, 5/Pkg (Restek)
220-94775-10	VOA Tuning Compound		1-Bromo-4-fluorobenzene (BFB), 5,000 µg/mL in P&T MeOH, 1 mL/ampule, CAS #: 460-00-4 (Restek)
220-94775-14	502.2 Calibration Mix #1, Gases (6 Components)		2,000 µg/mL each in P&T MeOH, 1 mL/ampule (Restek)
Restek PN 30633	8260 MegaMix Calibration Mix (76 components)		2,000 µg/mL each in P&T MeOH, 1 mL/ampule (Restek)
Restek PN 30465	California Oxygenates Mix (5 components)		2,000 µg/mL each in P&T MeOH, 1 mL/ampule (Restek) (TBA at 10,000 µg/mL)

Restek PN 32087	1,4-Dioxane		2,000 µg/mL each in P&T MeOH, 1 mL/ampule (Restek)
Restek PN 30006	VOA Calibration Mix #1 (ketones) (4 components)		5,000 µg/mL each in P&T MeOH, 1 mL/ampule (Restek)
Restek PN 30489	8260 Acetate Mix		2,000 µg/mL each in P&T MeOH, 1 mL/ampule (Restek)
Restek PN 30265	2-CLEVE		2,000 µg/mL each in P&T MeOH, 1 mL/ampule (Restek)
Restek PN 30073	8260 Surrogate Mix (3 components)		2,500 µg/mL each in P&T MeOH, 1 mL/ampule (Restek)
Restek PN 30074	8260 Internal Standard Mix (4 components)		2,500 µg/mL each in P&T MeOH, 1 mL/ampule (Restek)
220-94775-00	n-Alkane Mix		AART Standard for determination of Retention Index (RI) and Retention Times (RT)
220-94594-00	Electronic Flow Meter		ProFLOW 6000 Electronic Flow Meter (Restek)
220-94594-01	Electronic Leak Detector		Electronic Leak Detector With Hard-Sided Carrying Case and Universal Charger Set (Restek)

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