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Determination of VOCs by USEPA Method 8260 with Extended Dynamic Range using Fast, Sensitive Capillary GC/MS

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Brahm Prakash, William Lipps, Di Wang, Shilpi Chopra,
Nicole Lock and Laura Chambers
Shimadzu Scientific Instruments, Columbia, MD, USA

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Introduction

The USEPA has developed and published multiple methods for the analysis of organic environmental pollutants, including Volatile Organic Compounds (VOCs), while standardizing on single-quadrupole gas chromatography-mass spectrometry (GC/MS). Over the years, GC/MS instrumentation has evolved with changes in MS detector design, resulting in improvements in sensitivity and reliability which help increase productivity of environmental laboratories, but there haven't been many significant advancements in the overall methodology since the mid-1980s.

USEPA Method 8260 is by far the most comprehensive method in terms of the number of VOCs included in the compound list, with as many as 100 or more RCRA compounds slated for testing. The method is used to determine VOCs in a variety of solid waste matrices, is applicable to nearly all types of samples, and is one of the most common VOC methods used by commercial testing laboratories today. The chemist is confronted with meeting regulatory compliance requirements for all compounds on a routine basis, which can be a challenging task.

This poster describes the effects of recent instrument improvements and method modifications on sensitivity for USEPA Method 8260. An extended calibration range minimizes the number of dilutions and re-analyses that are required for high-concentration compounds, while still reaching the required low detection limits. Analytical operating conditions including BFB tune parameters, calibration details, and a complete MDL and Precision and Accuracy study for almost 100 target compounds over an extended calibration range are described.

Figure 1: Shimadzu GCMS-QP2010 SE

Experimental

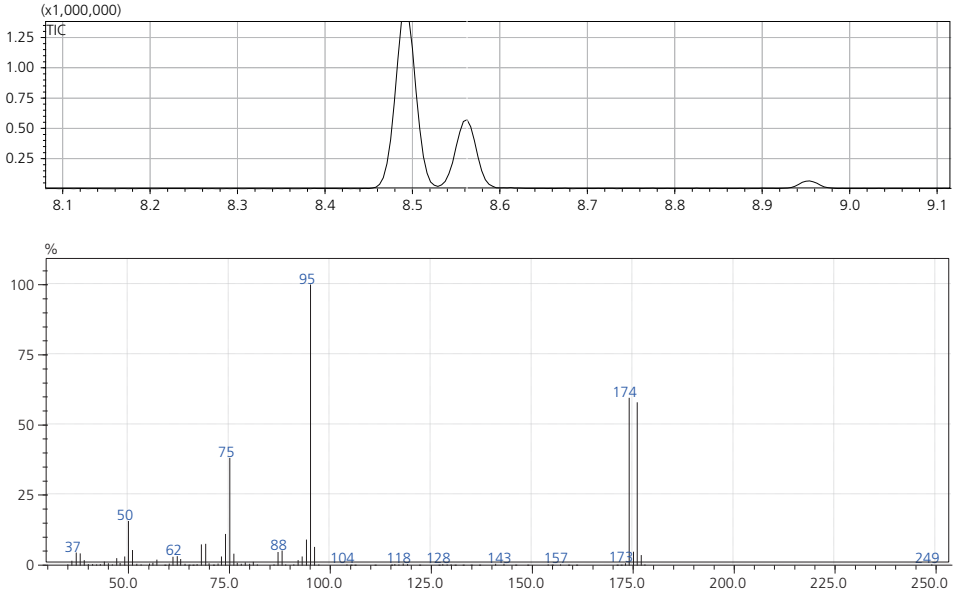
This study was conducted using the Shimadzu GCMS-QP2010 SE shown in Figure 1, configured with a Restek capillary column designed specifically for analysis of VOCs by US EPA Methods mentioned above. The GC was operated in the unique Constant Linear Velocity mode to provide optimum chromatographic resolution, 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.

The EST Evolution P&T and Centurion Water/Soil Autosampler were used for the extraction, concentration, and sample introduction steps.

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 listed in Shimadzu Application Note No. SSI-GCMS-1503. The BFB spectra were evaluated using the US EPA Method 8260C criteria. A representative example of a BFB chromatogram and spectrum are shown in Figure 2.



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

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. 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.

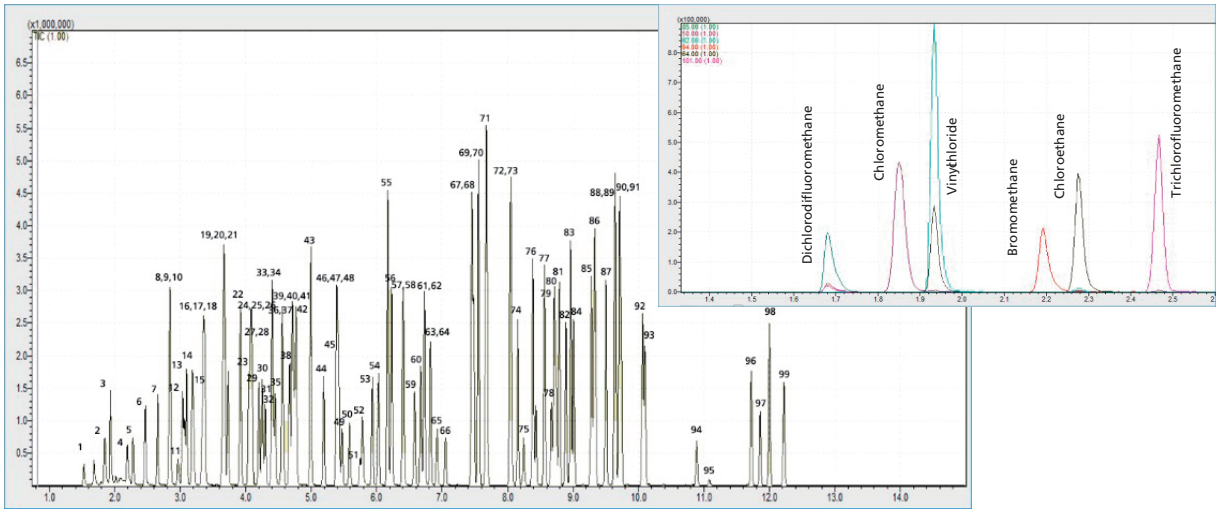


Figure 3: Total Ion Chromatogram from a mid-point Calibration Standard and EICP of the Six Light Gases.
Peak numbers correspond to compound names shown in Tables 3, 4, and 5.

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. Complete statistical results for the initial calibration curve are shown in Table 1.

Method Detection Limit Study

A Method Detection Limit (MDL) study[3] was conducted by analyzing 8 replicate aliquots of 0.5 µg/L standards. The MDL study are shown in table 2.

Determination of VOCs by USEPA Method 8260 with Extended Dynamic Range using Fast, Sensitive Capillary GC/MS

Table 1: Statistical Results from the Initial Calibration

Peak #	Compound Name	9-Point Calibration		
		0.5 to 200 µg/L		
		R^2	Avg RF	RF %RSD
1	Dichlorodifluoromethane	1.000	0.16	11.0
2	Chloromethane	1.000	0.36	7.0
3	Vinyl Chloride	1.000	0.47	8.7
4	Bromomethane	1.000	0.16	15.1
5	Chloroethane	0.999	0.30	10.3
6	Trichlorofluoromethane	1.000	0.28	10.1
7	Diethylether	0.999	0.29	8.0
8	1,1,2-Trichlorofluoroethane	0.998	0.23	8.7
9	1,1-Dichloroethene	0.998	0.22	7.9
10	Acetone	0.999	0.17	20.6
11	Iodomethane	0.999	0.13	35.0
12	Carbon Disulfide	0.997	0.58	10.6
13	Acetonitrile	0.999	0.40	7.5
14	Methylene Chloride	0.996	0.19	11.9
15	Tert Butyl Alcohol	0.999	0.09	11.8
16	Acrylonitrile	0.999	0.20	11.1
17	MTBE	0.998	0.73	7.4
18	trans-1,2-Dichloroethene	0.998	0.23	10.6
19	Vinyl Acetate	0.999	0.90	8.7
20	Isopropylether	0.999	0.79	5.5
21	1,1-Dichloroethane	0.997	0.52	7.6
22	Ethyl Tert Butyl Ether	1.000	0.93	6.1
23	2-Butanone	0.998	1.05	61.9
24	Ethyl Acetate	0.998	0.06	19.7
25	cis-1,2-Dichloroethene	0.997	0.25	8.0
26	Propionitrile	0.998	9.00	9.9
27	2,2-Dichloropropane	0.997	0.25	10.0
28	Methyl Acrylate	0.999	0.44	6.7
29	Methacrylonitrile	0.999	0.24	8.8
30	Bromochloromethane	0.998	0.14	16.7
31	THF	0.998	0.17	9.4
32	Chloroform	0.998	0.27	8.3
33	Pentafluorobenzene (IS)	ISTD	ISTD	ISTD
34	Dibromofluoromethane (SURR)	NA	0.44	2.0
35	1,1,1-Trichloroethane	0.999	0.25	5.0
36	1,1-Dichloropropene	0.994	0.26	11.0
37	Carbon Tetrachloride	0.997	0.22	7.4
38	Methyl Acetate	0.998	0.59	8.2
39	Benzene	0.999	0.81	8.2
40	1,2-Dichloroethane	1.000	0.17	8.3
41	Isobutyl Alcohol	0.998	0.58	7.8
42	Tert Amyl Methyl Ether	0.997	0.88	8.3
43	1,4-Difluorobenzene (IS)	ISTD	ISTD	ISTD
44	Trichloroethene	0.995	0.12	11.4
45	Methyl Methacrylate	0.995	0.14	13.3
46	1,2-Dichloropropane	0.996	0.15	9.5
47	Propyl Acetate	0.998	0.28	7.8
48	1,4-Dioxane	0.999	0.00	10.4
49	Dibromomethane	0.998	0.07	9.4
50	Bromodichloromethane	0.999	0.10	8.5
51	2-Nitropropane	0.999	0.04	11.4
52	2-Chloroethylvinylether	0.997	0.19	6.0
53	cis-1,3-Dichloropropane	0.998	0.16	8.4
54	4-Methyl-2-pentanone	0.999	0.24	6.8
55	Toluene-d8 (SURR)	NA	0.98	1.4
56	Toluene	0.998	0.30	11.3
57	trans-1,3-Dichloropropene	0.996	0.14	9.7
58	Ethyl Methacrylate	0.995	0.21	12.7
59	1,1,2-Trichloroethane	0.999	0.11	7.8
60	Tetrachloroethane	0.993	0.12	21.4
61	1,3-Dichloropropane	0.995	0.17	10.1
62	2-Hexanone	0.998	0.19	8.4
63	Isopropyl Acetate	0.998	0.06	7.8
64	Butyl Acetate	0.999	0.17	9.4
65	Dibromochloromethane	0.998	0.09	8.1
66	1,2-Dibromoethane	0.999	0.12	6.8
67	Chlorobenzene-d5 (IS)	ISTD	ISTD	ISTD
68	Chlorobenzene	0.999	0.47	7.3
69	1,1,1,2-Tetrachloroethane	0.996	0.11	13.6
70	Ethylbenzene	1.000	0.59	7.8
71	Xylene (m&p)	0.993	0.46	10.8
72	Xylene (o)	0.999	0.47	7.3
73	Styrene	1.000	0.52	5.2
74	n-Amyl Acetate	0.999	0.29	7.8
75	Bromoform	0.999	0.08	10.6
76	Isopropylbenzene	0.998	1.97	9.6
77	BFB(SURR)	NA	1.02	1.5
78	1,1,2,2-Tetrachloroethane	0.999	0.44	11.5
79	Bromobenzene	0.997	0.41	9.2
80	1,2,3-Trichloropropane	0.995	0.65	11.7
81	n-Propylbenzene	1.000	1.74	8.8
82	2-Chlorotoluene	0.994	0.40	12.2
83	1,3,5-Trimethylbenzene	1.000	1.62	7.7
84	4-Chlorotoluene	0.994	0.42	12.9
85	tert-Butylbenzene	0.998	1.36	16.9
86	1,2,4-Trimethylbenzene	1.000	1.62	7.3
87	sec-Butylbenzene	0.998	0.36	9.6
88	1,3-Dichlorobenzene	0.995	0.74	10.2
89	Isopropyltoluene	0.999	1.52	8.2
90	1,4-Dichlorobenzene-d4 (IS)	ISTD	ISTD	ISTD
91	1,4-Dichlorobenzene	0.997	0.76	10.9
92	n-Butylbenzene	0.998	1.07	8.7
93	1,2-Dichlorobenzene	0.998	0.68	10.0
94	1,2-Dibromo-3-chloropropane	0.999	0.14	8.3
95	Nitrobenzene	0.992	0.01	21.8
96	1,2,4-Trichlorobenzene	0.996	0.37	10.7
97	Hexachlorobutadiene	0.999	0.14	7.1
98	Naphthalene	0.999	1.49	11.7
99	1,2,3-Trichlorobenzene	0.997	0.35	12.4

Table 2: Method Detection Limit (MDL) Study Results

Peak #	Compound Name	0.5 µg/L n = 8	
		% RSD	MDL
1	Dichlorodifluoromethane	5.4	0.10
2	Chloromethane	7.1	0.15
3	Vinyl Chloride	5.2	0.10
4	Bromomethane	12.3	0.35
5	Chloroethane	5.9	0.11
6	Trichlorofluoromethane	5.6	0.11
7	Diethylether	4.6	0.09
8	1,1,2-Trichlorofluoroethane	4.6	0.08
9	1,1-Dichloroethene	6.0	0.11
10	Acetone	16.9	0.61
11	Iodomethane	18.7	0.28
12	Carbon Disulfide	13.4	0.31
13	Acetonitrile	12.0	0.29
14	Methylene Chloride	3.1	0.09
15	Tert Butyl Alcohol	14.0	1.41
16	Acrylonitrile	8.1	0.17
17	MTBE	3.7	0.06
18	trans-1,2-Dichloroethene	8.6	0.16
19	Vinyl Acetate	12.4	0.21
20	Isopropylether	3.8	0.07
21	1,1-Dichloroethane	5.9	0.10
22	Ethyl Tert Butyl Ether	3.5	0.06
23	2-Butanone	17.4	0.67
24	Ethyl Acetate	23.0	0.46
25	cis-1,2-Dichloroethene	8.2	0.16
26	Propionitrile	7.9	0.16
27	2,2-Dichloropropane	8.2	0.12
28	Methyl Acrylate	5.4	0.10
29	Methacrylonitrile	4.2	0.08
30	Bromochloromethane	6.0	0.13
31	THF	5.8	0.16
32	Chloroform	6.4	0.12
33	Pentafluorobenzene (IS)	NA	NA
34	Dibromofluoromethane (SURR)	1.7	2.55
35	1,1,1-Trichloroethane	4.3	0.08
36	1,1-Dichloropropene	8.8	0.16
37	Carbon Tetrachloride	8.2	0.12
38	Methyl Acetate	4.8	0.09
39	Benzene	4.3	0.08
40	1,2-Dichloroethane	3.1	0.06
41	Isobutyl Alcohol	3.4	0.06
42	Tert Amyl Methyl Ether	5.9	0.10
43	1,4-Difluorobenzene (IS)	NA	NA
44	Trichloroethene	6.2	0.12
45	Methyl Methacrylate	9.8	0.19
46	1,2-Dichloropropane	10.4	0.18
47	Propyl Acetate	3.4	0.06
48	1,4-Dioxane	21.3	0.80
49	Dibromomethane	5.9	0.12
50	Bromodichloromethane	5.9	0.11
51	2-Nitropropane	14.3	0.25
52	2-Chloroethylvinylether	9.9	0.17
53	cis-1,3-Dichloropropane	3.6	0.06
54	4-Methyl-2-pentanone	3.1	0.06
55	Toluene-d8 (SURR)	1.3	2.08
56	Toluene	2.8	0.06
57	trans-1,3-Dichloropropene	7.7	0.14
58	Ethyl Methacrylate	4.6	0.08
59	1,1,2-Trichloroethane	10.1	0.19
60	Tetrachloroethane	18.0	0.34
61	1,3-Dichloropropane	2.8	0.05
62	2-Hexanone	4.5	0.09
63	Isopropyl Acetate	5.0	0.09
64	Butyl Acetate	4.7	0.09
65	Dibromochloromethane	6.1	0.10
66	1,2-Dibromoethane	4.2	0.08
67	Chlorobenzene-d5 (IS)	NA	NA
68	Chlorobenzene	4.7	0.09
69	1,1,1,2-Tetrachloroethane	11.7	0.26
70	Ethylbenzene	3.0	0.06
71	Xylene (m&p)	4.3	0.17
72	Xylene (o)	3.7	0.07
73	Styrene	3.7	0.07
74	n-Amyl Acetate	7.1	0.13
75	Bromoform	14.7	0.26
76	Isopropylbenzene	4.4	0.08
77	BFB(SURR)	1.6	2.41
78	1,1,2,2-Tetrachloroethane	5.1	0.09
79	Bromobenzene	7.5	0.14
80	1,2,3-Trichloropropane	29.2	0.44
81	n-Propylbenzene	4.7	0.09
82	2-Chlorotoluene	8.5	0.15
83	1,3,5-Trimethylbenzene	4.3	0.08
84	4-Chlorotoluene	5.4	0.10
85	tert-Butylbenzene	6.1	0.11
86	1,2,4-Trimethylbenzene	6.5	0.12
87	sec-Butylbenzene	7.5	0.13
88	1,3-Dichlorobenzene	6.2	0.12
89	Isopropyltoluene	7.8	0.13
90	1,4-Dichlorobenzene-d4 (IS)	NA	NA
91	1,4-Dichlorobenzene	9.5	0.19
92	n-Butylbenzene	10.5	0.20
93	1,2-Dichlorobenzene	8.1	0.15
94	1,2-Dibromo-3-chloropropane	9.0	0.15
95	Nitrobenzene	27.6	0.47
96	1,2,4-Trichlorobenzene	15.5	0.31
97	Hexachlorobutadiene	16.5	0.34
98	Naphthalene	15.2	0.29
99	1,2,3-Trichlorobenzene	14.8	0.27

Table 3: Precision and Accuracy (P&A) Study Results

Peak #	Compound Name	Precision and Accuracy at 50 µg/L n = 8		
		Mean Concentration (µg/L)	Recovery	% RSD
1	Dichlorodifluoromethane	53.1	106%	13.6
2	Chloromethane	58.1	116%	8.2
3	Vinyl Chloride	59.9	120%	6.4
4	Bromomethane	66.9	134%	6.8
5	Chloroethane	56.9	114%	15.5
6	Trichlorofluoromethane	59.9	120%	6.3
7	Diethylether	55.1	110%	14.1
8	1,1,2-Trichlorofluoroethane	55.4	111%	8.4
9	1,1-Dichloroethene	54.7	109%	11.7
10	Acetone	59.6	119%	12.7
11	Iodomethane	54.4	109%	13.7
12	Carbon Disulfide	55.7	111%	19.8
13	Acetonitrile	56.9	114%	12.1
14	Methylene Chloride	56.3	113%	16.7
15	Tert Butyl Alcohol	290.4	116%	14.2
16	Acrylonitrile	58.9	118%	18.0
17	MTBE	55.3	111%	15.9
18	trans-1,2-Dichloroethene	55.8	112%	19.2
19	Vinyl Acetate	52.4	105%	6.7
20	Isopropylether	51.6	103%	7.6
21	1,1-Dichloroethane	50.8	102%	6.8
22	Ethyl Tert Butyl Ether	53.2	106%	7.9
23	2-Butanone	52.8	106%	7.1
24	Ethyl Acetate	52.8	106%	6.5
25	cis-1,2-Dichloroethene	51.0	102%	6.9
26	Propionitrile	52.2	104%	7.8
27	2,2-Dichloropropane	48.9	98%	5.4
28	Methyl Acrylate	52.3	105%	7.3
29	Methacrylonitrile	54.3	109%	7.0
30	Bromochloromethane	54.0	108%	7.6
31	THF	53.5	107%	8.1
32	Chloroform	54.3	109%	6.5
33	Pentafluorobenzene (IS)	NA	NA	NA
34	Dibromofluoromethane (SURR)	48.6	97%	3.3
35	1,1,1-Trichloroethane	56.4	113%	5.6
36	1,1-Dichloropropene	51.5	103%	7.1
37	Carbon Tetrachloride	54.3	109%	5.6
38	Methyl Acetate	54.3	109%	6.9
39	Benzene	50.2	100%	7.2
40	1,2-Dichloroethane	58.5	117%	5.3
41	Isobutyl Alcohol	54.3	109%	6.9
42	Tert Amyl Methyl Ether	51.5	103%	7.7
43	1,4-Difluorobenzene (IS)	NA	NA	NA
44	Trichloroethene	53.5	107%	4.8
45	Methyl Methacrylate	52.4	105%	4.7
46	1,2-Dichloropropane	52.0	104%	5.0
47	Propyl Acetate	55.6	111%	4.9
48	1,4-Dioxane	112.9	113%	10.4
49	Dibromomethane	57.4	115%	6.0
50	Bromodichloromethane	57.2	114%	4.9
51	2-Nitropropane	54.7	109%	6.5
52	2-Chloroethylvinylether	55.8	112%	6.7
53	cis-1,3-Dichloropropane	54.5	109%	3.9
54	4-Methyl-2-pentanone	57.4	115%	4.3
55	Toluene-d8 (SURR)	52.0	104%	1.8
56	Toluene	54.2	108%	4.7
57	trans-1,3-Dichloropropene	53.4	107%	4.2
58	Ethyl Methacrylate	52.3	105%	4.2
59	1,1,2-Trichloroethane	55.6	111%	4.4
60	Tetrachloroethane	57.4	115%	5.3
61	1,3-Dichloropropane	53.2	106%	4.1
62	2-Hexanone	56.1	112%	4.9
63	Isopropyl Acetate	55.1	110%	4.1
64	Butyl Acetate	55.7	111%	4.5
65	Dibromochloromethane	56.0	112%	4.6
66	1,2-Dibromoethane	55.5	111%	4.6
67	Chlorobenzene-d5 (IS)	NA	NA	NA
68	Chlorobenzene	53.7	107%	4.6
69	1,1,1,2-Tetrachloroethane	51.3	103%	4.4
70	Ethylbenzene	54.0	108%	4.5
71	Xylene (m&p)	111.5	111%	4.8
72	Xylene (o)	54.1	108%	4.5
73	Styrene	53.3	107%	4.6
74	n-Amyl Acetate	55.9	112%	4.7
75	Bromoform	57.6	115%	5.2
76	Isopropylbenzene	55.8	112%	5.0
77	BFB(SURR)	49.2	98%	1.3
78	1,1,2,2-Tetrachloroethane	54.4	109%	4.2
79	Bromobenzene	54.0	108%	4.6
80	1,2,3-Trichloropropane	52.2	104%	4.1
81	n-Propylbenzene	55.8	112%	5.3
82	2-Chlorotoluene	52.9	106%	4.4
83	1,3,5-Trimethylbenzene	54.8	110%	4.8
84	4-Chlorotoluene	52.1	104%	5.1
85	tert-Butylbenzene	53.2	106%	4.4
86	1,2,4-Trimethylbenzene	53.4	107%	4.9
87	sec-Butylbenzene	52.9	106%	5.3
88	1,3-Dichlorobenzene	50.9	102%	4.3
89	Isopropyltoluene	51.5	103%	5.5
90	1,4-Dichlorobenzene-d4 (IS)	NA	NA	NA
91	1,4-Dichlorobenzene	54.0	108%	4.4
92	n-Butylbenzene	55.8	112%	5.7
93	1,2-Dichlorobenzene	53.9	108%	4.0
94	1,2-Dibromo-3-chloropropane	56.5	113%	5.8
95	Nitrobenzene	48.0	96%	7.2
96	1,2,4-Trichlorobenzene	55.5	111%	4.4
97	Hexachlorobutadiene	60.4	121%	6.0
98	Naphthalene	51.0	102%	3.3
99	1,2,3-Trichlorobenzene	54.3	109%	3.9

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Precision and Accuracy Study

Table 3 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 50 µg/L concentration levels.

Stability of Internal and Surrogate Standards

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.

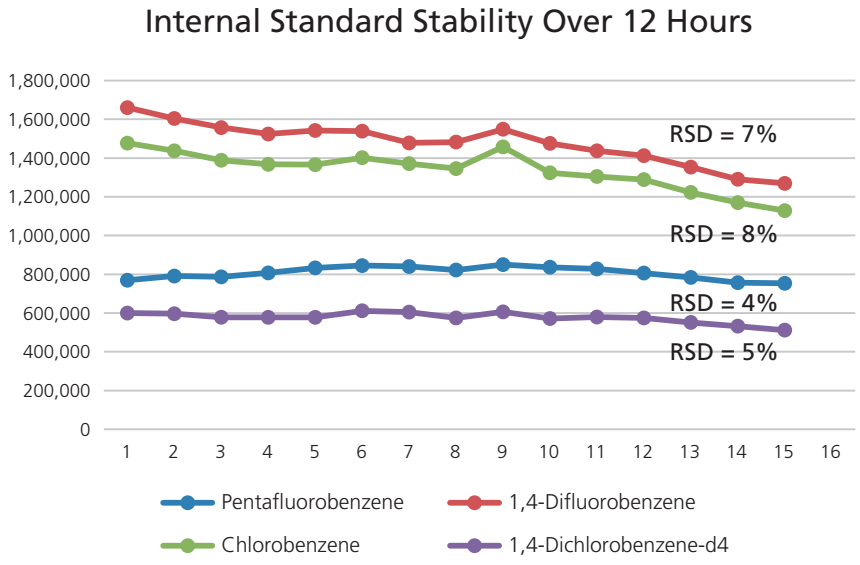

Figure 4: Internal Standard Response over a Representative 12-Hour Tune Period during This Study

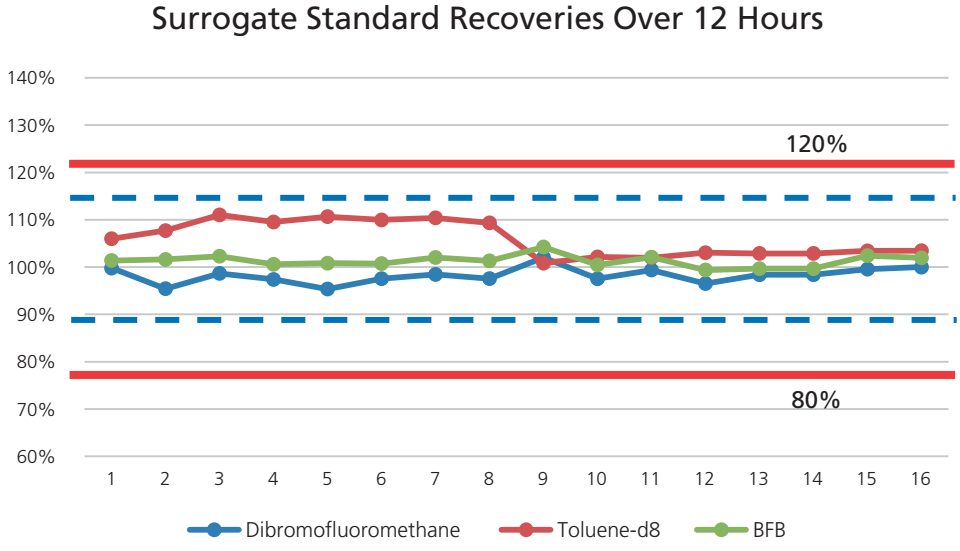

Figure 5: Surrogate Standard Recoveries over a Representative 12-hour Tune Period during This Study

Determination of VOCs by USEPA Method 8260 with Extended Dynamic Range using Fast, Sensitive Capillary GC/MS

Summary and Conclusions

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 0.5 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.

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