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Performance Enhancement of Volatile Organic Compounds in Water by EPA Method 8260 with Extended Dynamic Range using Fast, Sensitive Capillary Gas Chromatography/ Mass Spectromery

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Method Comparison

M8260B/C	M8260D!
.32 to 0.75 mm i.d., 1.5-um film thickness	• 0.18 to 0.25 mm i.d., 1.4-um film thickness,30m columns
0m or 70m Columns	
ryogenic interface; no Split Injection jet	• Split injection
eparator to MS	
or 25-mL purge volume	• 5-mL purge volume
rap: Tenax™–Silica Gel –Charcoal(No.3)	• Trap: Supelco – VOCARB 3000
ingle concentrator	• Single concentrator
internal standards	• 4 internal standards
luorobenzene	• Pentafluorobenzene
hlorobenzene-d5	• 1,4-difluorobenzene
,4-Dichlorobenzene-d4	• chlorobenzene-d_5
	• 1,4-dichlorobenzene-d_4

Method Comparison (Cont.)

M8260B/C

3 Surrogates
- 1,2-dichloroethane-d_4
- 4-bromofluorobenzene
- Toluene-d8

Preservation: HCl +ascorbic acid, pH < 2
BFB 12-hour tune criteria
Ambient purge
No dry purge
Water management not mentioned

M8260D!

- 3 Surrogates
  - Dibromofluorobenzene
  - Toluene-d8
  - 4-bromofluorobenzene
- BFB 12-hour tune criteria
- Heated purge (40oC)
- Dry purge used

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GCMS-QP2010 SE

s instrument provides the ability to calibrate over the ranges typically used for EPA
hods 8260, 624 and 524

Enhanced performance
Simple operation
Ecology mode

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EST Analytical Purge and Trap: Auto-Sampler for Volatiles Analysis

Purge and Trap Conditions for Method Studies
P&T Concentrator: ES&T

Purge temperature	40 ^{0}C
Purge volume	440 mL (11 minutes @ 40 mL/min)
Trap	Supelco VOCARB-3000
Moisture Reduction Trap Temperature	39 ^{0}C
Dry purge volume	40mL/minute for 1 minute
Desorb temperature	250 ^{0}C
Desorb time	0.5 minute
Bake temperature	260 ^{0}C @ 40 mL/min of Helium
Moisture Reduction Trap Bake Temp.	230 ^{0}C

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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
Liner	Low Volume Split Liner (Shimadzu PN 220-90784-10)
Primary 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

GC/MS Conditions for Method Studies
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-Cycle Time

Sample volume	5 mL
Sample temperature at Purge	40 ^{0}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 ^{0}C for 0.5 minutes
Bake	260 ^{0}C for 8.0 minutes

Analysis Times

- GC Run Time - 16 minutes
- System Cycle Time - 26 minutes

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Comparison of BFB Relative Abundance Criteria for US EPA VOC Methods

Relative Abundance Criteria					
Mass (m/z)	Method 524.2	Method 524.3	Method 624	Method 8260C	CLP-SOW
50	15 to 40% of 95	NA	15 to 40% of 95	15 to 40% of 95	15 to 40% of 95
75	30 to 80% of 95	NA	30 to 60% of 95	30 to 60% of 95	30 to 80% of 95
95	Base Peak, 100%	Base Peak, 100%	Base Peak, 100%	Base Peak, 100%	Base Peak, 100
96	5 to 9% of 95	5 to 9% of 95	5 to 9% of 95	5 to 9% of 95	5 to 9% of 95
173	<2% of 174	<2% of 174	<2% of 174	<2% of 174	<2% of 174
174	>50% of 95	>50% of 95	>50% of 95	>50% of 95	50 to 120% of 95
175	5 to 9% of 174	5 to 9% of 174	5 to 9% of 174	5 to 9% of 174	4 to 9% of 174
176	>95 to <101% of 174	>95 to < 105% of 174	>95 to <101% of 174	>95 to <101% of 174	95 to 101% of 174
177	5 to 9% of 176	5 to 10% of 176	5 to 9% of 176	5 to 9% of 176	5 to 9% of 176

Abstract of Method Detection Limit (MDL) Study Results Full

Scan at 0.5 ug/L and 1.0 ug/L concentration levels

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

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Precision and Accuracy Results Full Scan Reagent Water

Abstract of Precision & Accuracy at 10ug/L and 50 ug/L

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	
Dichlorodifluoromethane	7.8	78%	8.4	53.1	106%	
Chloromethane	9.2	92%	8.3	58.1	116%	
Vinyl Chloride	9.3	93%	8.5	59.9	120%	
Bromomethane	10.6	106%	9.2	66.9	134%	
Chloroethane	9.3	93%	4.1	56.9	114%	
Trichlorofluoromethane	8.8	88%	10.6	59.9	120%	
Diethylether	9.5	95%	1.5	55.1	110%	
1,1,2-Trichlorofluoroethane	9.7	97%	6.0	55.4	111%	
1,1-Dichloroethene	9.9	99%	4.6	54.7	109%	
Acetone	8.3	83%	9.1	59.6	119%	
Iodomethane	8.7	87%	10.4	54.4	109%	
Carbon Disulfide	10.8	108%	16.2	55.7	111%	
Acetonitrile	10.6	106%	24.2	56.9	114%	
Methylene Chloride	9.8	98%	4.9	56.3	113%	
Acrylonitrile	9.3	93%	2.8	58.9	118%	
MTBE	9.8	98%	8.0	55.3	111%	
trans-1,2-Dichloroethene	10.1	101%	4.3	55.8	112%	
Vinyl Acetate	9.7	97%	5.1	52.4	105%	
Isopropylether	9.9	99%	3.3	51.6	103%	
1,1-Dichloroethane	10.0	100%	7.7	50.8	102%	
Ethyl Tert Butyl Ether	9.6	96%	2.7	53.2	106%	
2-Butanone	9.7	97%	5.5	52.8	106%	
Ethyl Acetate	9.8	98%	4.1	52.8	106%	
cis-1,2-Dichloroethene	10.2	102%	4.5	51.0	102%	
Propionitrile	9.6	96%	3.3	52.2	104%	
2,2-Dichloropropane	11.8	118%	2.6	48.9	98%	
Methyl Acrylate	9.6	96%	3.9	52.3	105%	
Methacrylonitrile	9.5	95%	4.7	54.3	109%	
Bromochloromethane	10.2	102%	7.0	54.0	108%	
THF	9.4	94%	5.6	53.5	107%	
Chloroform	9.7	97%	3.3	54.3	109%	
Pentafluorobenzene (IS)	NA	NA	NA	NA	NA	
Dibromofluoromethane (SURR)	44.2	88%	2.0	48.6	97%	

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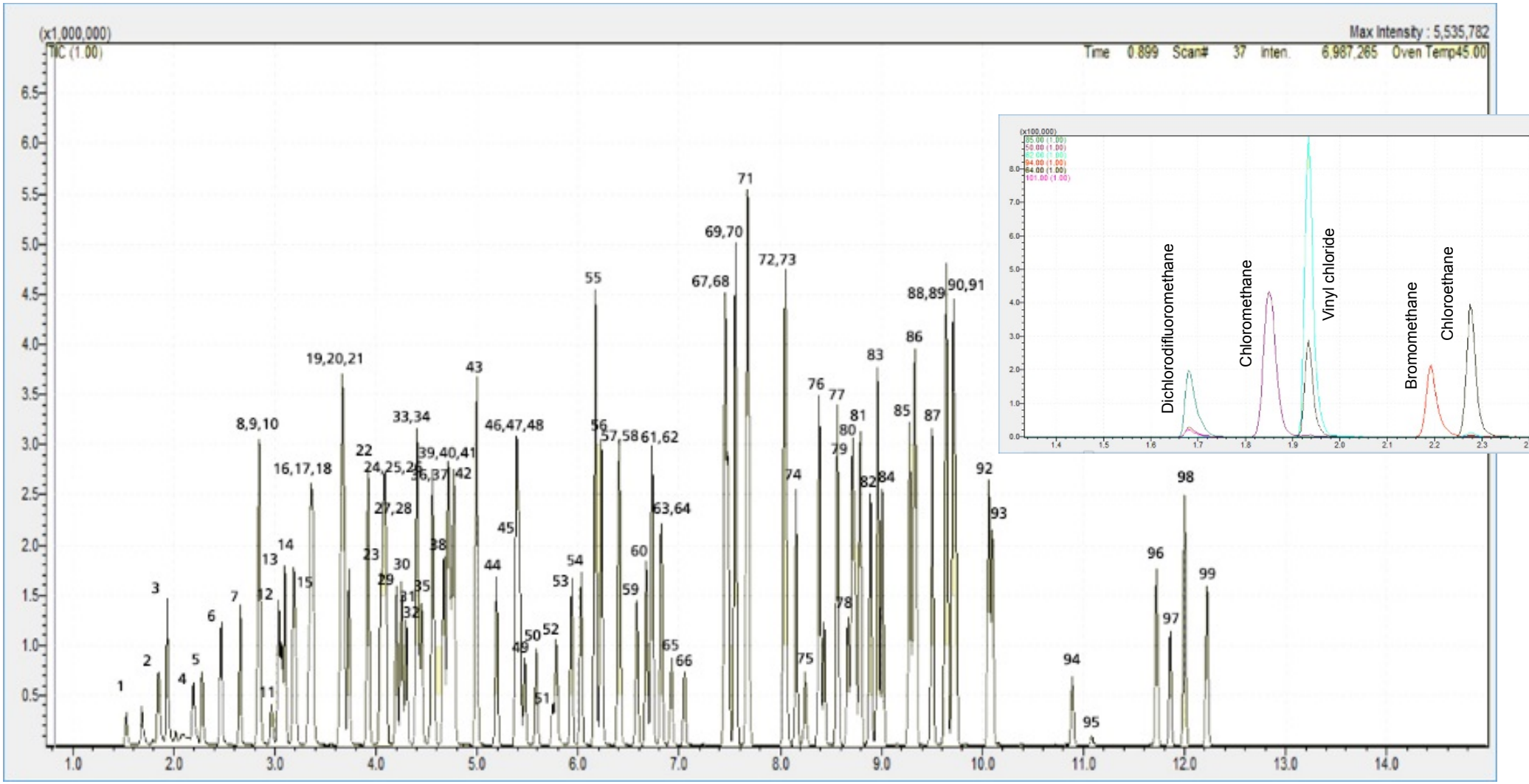
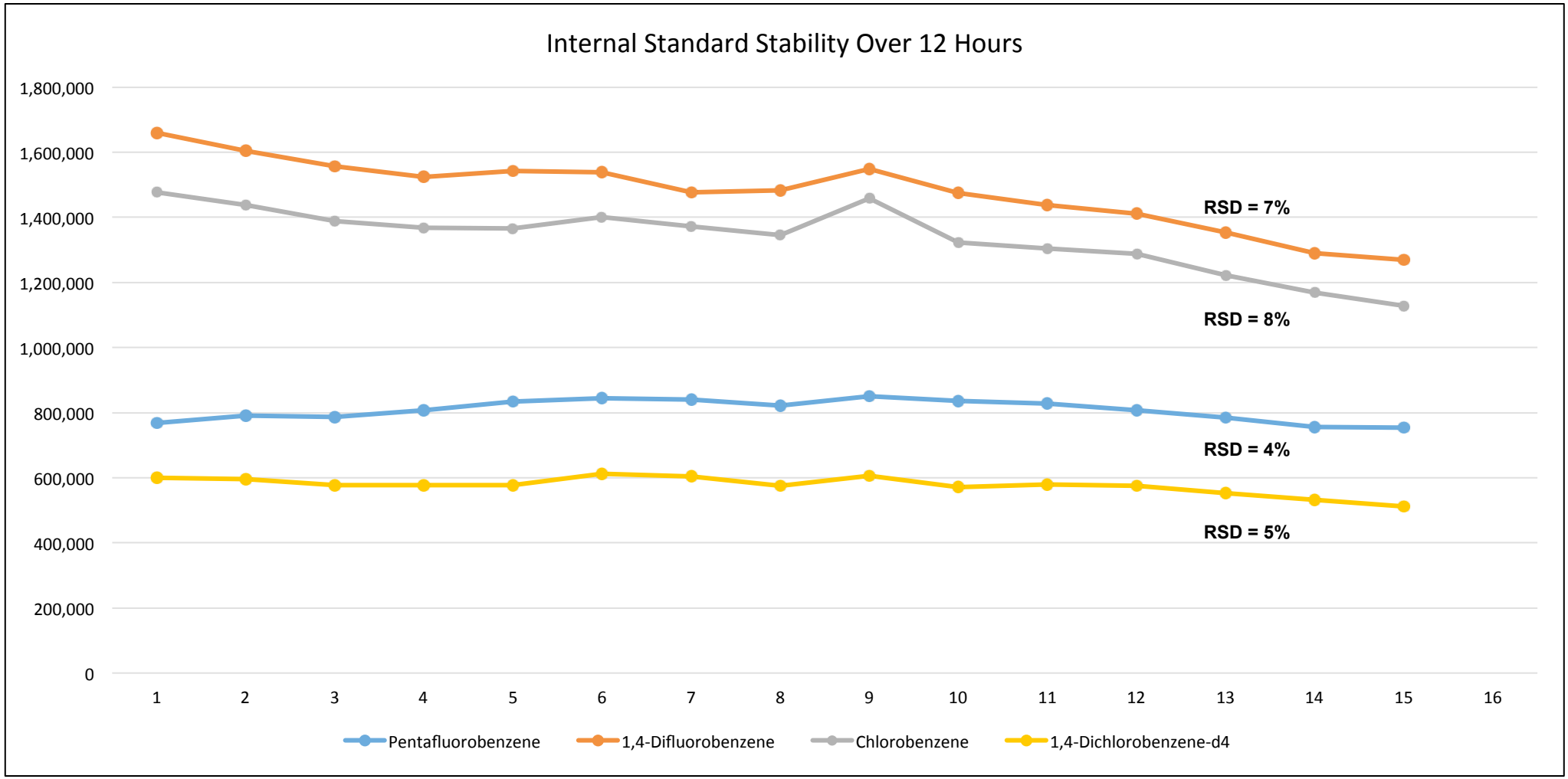
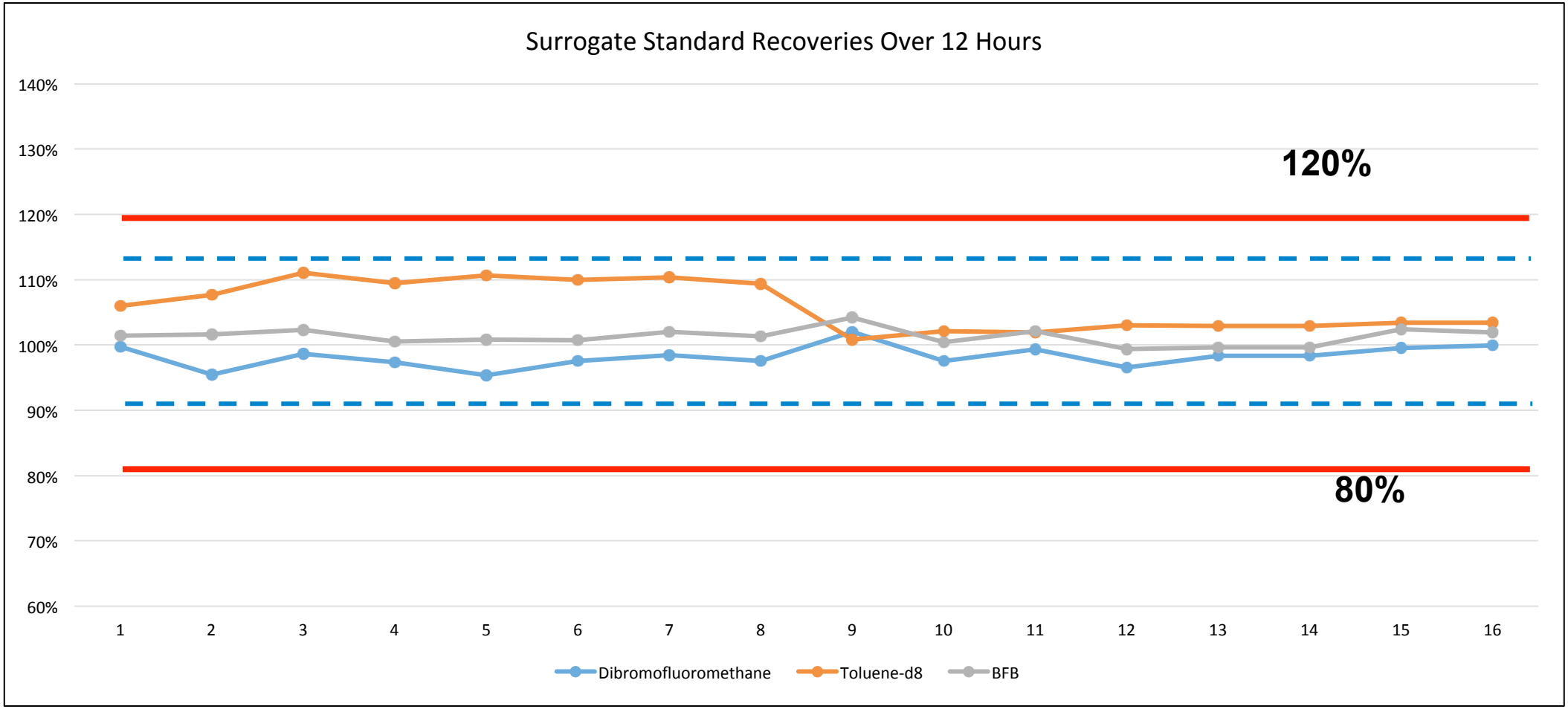
US EPA Method 8260 on GCMS-QP2010 SE



Internal Standard Stability Over 12 Hours



Surrogate Standard Recoveries Over 12 Hours



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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 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.

himadzu Guide to US EPA Method 8260 for Analysis of Volatile Organic Compounds in Ground Water and Solid Waste Shimadzu App Note No. GCMS-1503