

Gas Chromatography/
Mass Spectrometry**Authors**

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Method 8260C by Purge and Trap Gas Chromatography Mass Spectrometry using the Clarus SQ 8

Introduction

U.S. EPA Method 8260C – Volatile Organic Compounds (VOCs) by Gas Chromatography Mass Spectrometry (GC/MS) is one of the most common environmental applications for GC/MS. This method outlines the analysis of volatile organic compounds in a variety of solid waste matrices including various air sampling trapping media, ground and surface water, soils, and sediments among others. The method requires not

only demonstration of laboratory sample preparation and handling competence but instrument performance as well. The study presented here demonstrates the PerkinElmer® Clarus® SQ 8 GC/MS with purge and trap sample introduction both meets and exceeds the performance criteria set out in method 8260C and describes the analytical results and instrumental methodology.

Experimental

The PerkinElmer Clarus SQ 8C GC/MS operating in electron ionization mode with an Atomx purge and trap sample introduction system (Teledyne Tekmar, Mason, OH) was used to perform these experiments. The purge and trap conditions are presented in Table 1 and represent standard conditions for the analysis of method of VOCs by EPA Method 8260C.

Table 1. Purge and Trap Instrument Conditions.

Purge and Trap System:	Tekmar – Atomx
Trap	Tekmar #9 trap
Sample Size	5 mL
Purge Parameters:	
Valve Oven Temp	140 °C
Transfer Line Temp	140 °C
Sample Mount Temp	90 °C
Water Heater Temp	90 °C
Sample Vial Temp	20 °C
Sample Equilibrate Time	0.00 min
Standby Flow	10 mL/min
Purge Ready Temp	40 °C
Condensate Ready Temp	45 °C
Presweep Time	0.25 min
Prime Sample Fill Volume	3.0 mL
Sweep Sample Time	0.25 min
Sweep Sample Flow	100 mL/min
Spurge Vessel Heater	On
Purge Time	11.00 min
Purge Flow	40 mL/min
Purge Temp	40 °C
Condensate Purge Temp	20 °C
Dry Purge Time	2.00 min
Dry Purge Flow	100 mL/min
Dry Purge Temp	20 °C
Desorb Parameters:	
Water Needle Rinse Volume	7.0 mL
Sweep Needle Time	0.50 min
Desorb Preheat Temp	200 °C
GC Start Signal	Start of Desorb
Desorb Time	2.00 min
Drain Flow	300 mL/min
Desorb Temp	200 °C
Bake Parameters:	
Number of Water Bake Rinses	2
Water Bake Rinse Volume	7.0 mL
Bake Rinse Sweep Time	0.25 min
Bake Rinse Sweep Flow	100 mL/min
Bake Rinse Drain Time	0.40 min
Bake Time	6.00 min
Bake Flow	250 mL/min
Bake Temp	270 °C
Condensate Bake Temp	200 °C

The Clarus SQ 8C GC/MS conditions are presented in Table 2. The heated transfer line of the concentrator was connected directly to the injector port of the Clarus 680 GC. A 2 mm I.D. injector port liner was used inside the capillary injector. Split flow adjustments will increase or decrease the split ratio and the resulting sensitivity of the system and allow the analysts flexibility in optimizing their GC/MS system.

Table 2. Clarus SQ 8C GC/MS conditions.

Gas Chromatograph: PerkinElmer Clarus 680			
Analytical Column:	Elite 624 MS (30 m x 0.25 mm I.D. x 1.4 µm)		
Injector Temperature:	220 °C		
Carrier Gas:	Helium @ 1.0 mL/min		
Split Flow:	80 mL/min		
Oven Program:	Temperature	Hold Time	Rate
	40 °C	2 min	10 °C/min
	100 °C	0 min	30 °C/min
	200 °C	4 min	End
Mass Spectrometer: PerkinElmer Clarus SQ 8C			
GC Transfer Line Temperature:	220 °C		
Ion Source Temperature:	300 °C		
Function Type:	Full Scan		
Solvent Delay:	0 – 0.50 min		
Scan Range:	m/z 35 – 270		
Scan Time:	0.20 sec		
Interscan Delay:	0.10 sec		

Calibration and performance standards were prepared from commercially available stock standards and diluted in Class-A volumetric flasks. Calibration standards were made from a combination of four multi-component standard mixes including a 76 component 8260 calibration mix, a 6 component 502.2 calibration gas mix, a 3 component VOA surrogate spike mix, and an 8260 internal standard mix. Stock standards were diluted to an intermediate concentration from which initial calibration standards were prepared. The calibration levels used in this study are presented in Table 3. Standards used for the Method Detection Limit (MDL) and precision experiments were prepared at appropriate concentration levels from intermediate standards. The internal standard mix was added to all samples such that a resulting concentration of 20 µg/L was achieved per 5 mL of sample. The tuning standard, 4-bromofluorobenzene, was prepared at 50 µg/L. Standards, stock standards, and associated QC/QA samples were stored in a manner consistent with the guidelines set out in the method.

Table 3. Calibration points employed in this study.

Calibration Level	Concentration ($\mu\text{g/L}$)
1	0.5
2	1.0
3	2.0
4	5.0
5	10
6	25
7	50
8	100
9	200

Results and Discussion

The GC conditions were optimized to provide adequate separation while keeping the analytical runtime as short as possible. Figure 1 demonstrates a mid-level (25 $\mu\text{g/L}$) total ion chromatogram (TIC) from this analysis. All of the expected analyte separation is achieved while allowing for a maximum of throughput per unit laboratory time. The injection-to-injection time is further enhanced by the performance of the Clarus 680 GC oven. The oven incorporates a dual walled design with a unique air flow path to allow the fastest cooling times of any commercially available GC oven on the market. Air flow through the Clarus 680 GC is unidirectional eliminating the mixing of heated exhaust and cool ambient air allowing for the fastest transport of heat out of the GC oven. This high speed cooling allows the user to dramatically decrease the idle time of the instrument

between analytical runs and in this study the injection-to-injection time, measured to be under 30 minutes, was limited by the purge and trap system.

Table 4 presents the analytical results of these experiments including the Retention Time (RT), Average Relative Response Factors (Avg RRF) and Percent Relative Standard Deviation (% RSD) of the initial calibration, the Method Detection Limits (MDL), and the method precision as Percent Recovery (% Rec) and accuracy as % RSD. All of the analytes presented meet or exceed the minimum method requirements and boast excellent detection limits, precision and accuracy. Method Detection Limits were determined by analyzing seven replicate samples at a concentration of 0.5 $\mu\text{g/L}$ and 1.0 $\mu\text{g/L}$. Precision and accuracy were measured by analyzing four replicates at a concentration of 25 $\mu\text{g/L}$.

The majority of compounds in this report are calibrated over the entire concentration range as presented in Table 3. Compounds whose calibration range varied from the bulk of analytes are highlighted in Table 5. Alternate calibration ranges are expected for this method especially for compounds referred to as "bad actors". In all cases, however, EPA method criteria are met. Overall improved results including MDL and precision and accuracy were obtained by operating the ion source at an elevated temperature than would regularly be used. Figure 2 shows a time selection of the seven TICs from the MDL study and illustrates the excellent repeatability of the system at a low concentration level. The inset presents the seven extracted ion chromatograms of naphthalene (EIC) at $m/z = 128$. The % RSD of the seven naphthalene EICs was measured to be 3.8%, which includes the sample handling performed by the purge and trap.

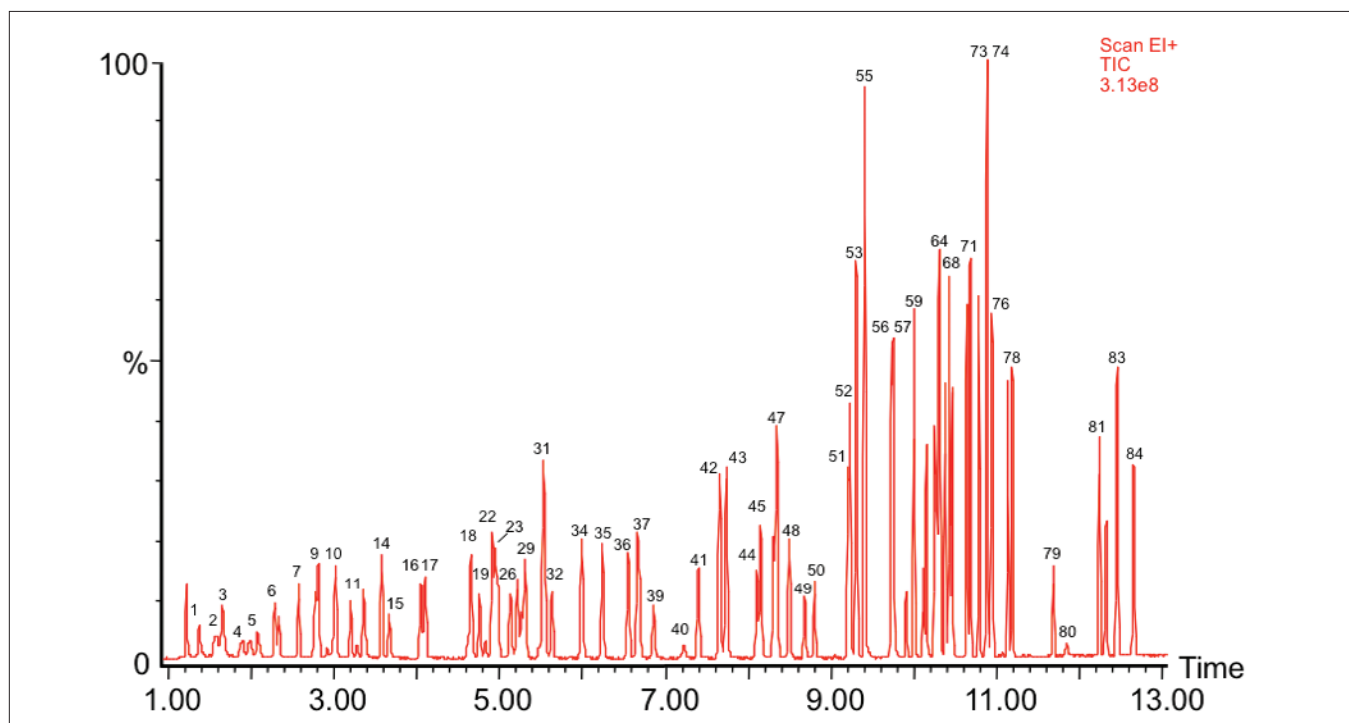


Figure 1. TIC of 8260C volatile organic standard mix at 25 µg/L. Numbering references compound as listed in Table 4.

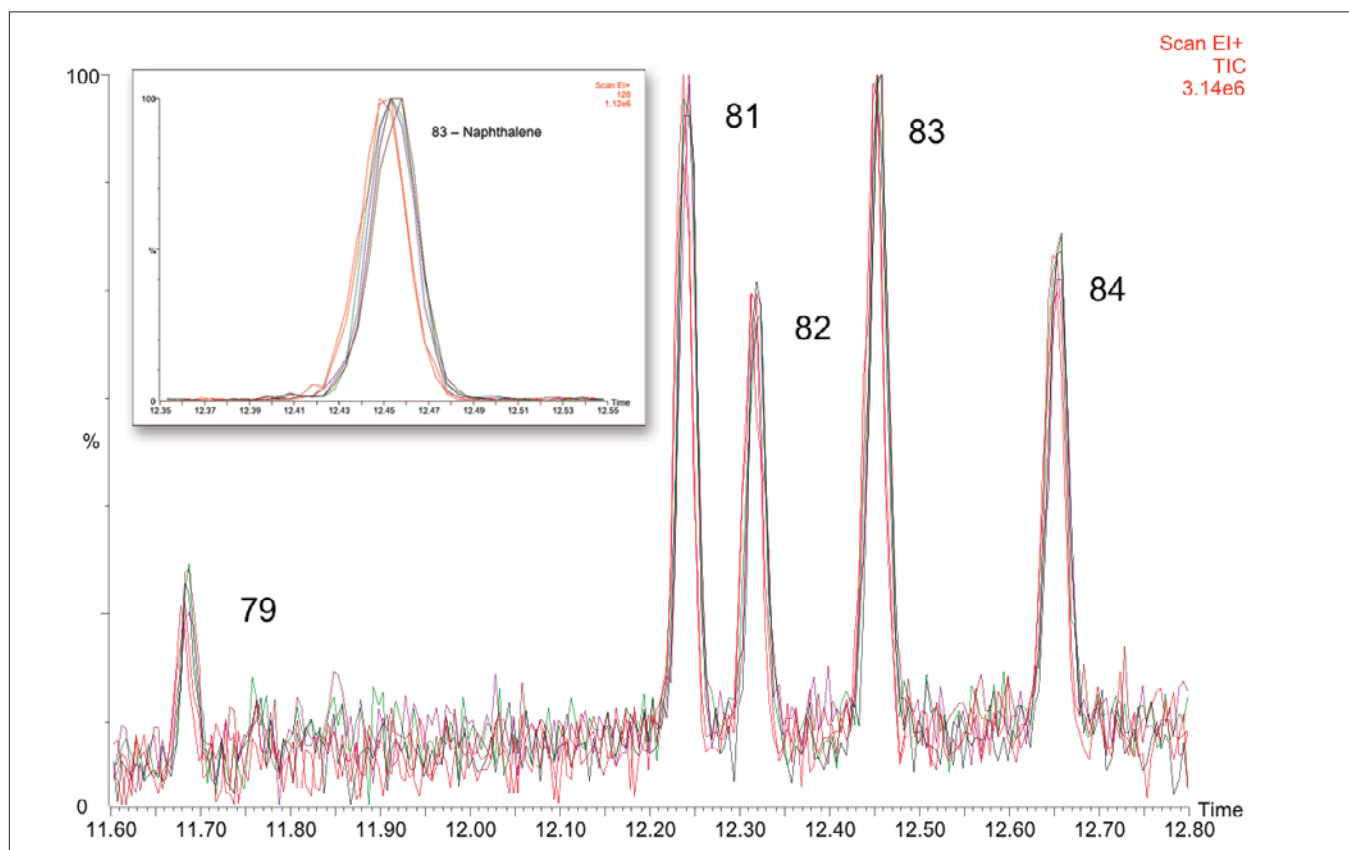


Figure 2. Zoom of the seven MDL samples. TICs overlaid to illustrate the excellent repeatability achieved at low levels. Inset shows the naphthalene EIC at $m/z = 128$; the % RSD was measured to be 3.8%.

Table 4. Summarized initial calibration results of the analyzed VOCs from 0.5 – 200 µg/L for most compounds.

A hyphen (-) indicates value either not provided by the method or not generated in this work.

A plus sign (+) indicates calibration calculated using linear regression with R² presented in table.

#	Compound	RT	8260C			8260C		Precision (% Rec)	Accuracy (% RSD)
			Avg RRF	Minimum RRF	% RSD	% RSD Criteria	MDL (µg/L)		
1	Dichlorodifluoromethane	1.38	0.44	0.1	14	20	0.14	90	2.9
2	Chloromethane ⁺	1.59	0.72	0.1	0.9992	0.990	0.15	96	4.9
3	Vinyl chloride	1.66	0.79	0.1	8.2	20	0.21	95	1.8
4	Bromomethane	2.00	0.26	0.1	18	20	0.18	105	4.1
5	Chloroethane	2.08	0.40	0.1	4.9	20	0.24	99	1.9
6	Trichlorofluoromethane	2.29	0.57	0.1	5.9	20	0.06	109	1.2
7	Diethyl ether	2.58	0.37	-	6.7	20	0.11	98	4.6
8	1,1,2-Trichloro-1,2,2-trifluor	2.78	0.38	0.1	13	20	0.15	99	1.1
9	1,1-Dichloroethene	2.82	0.44	0.1	15	20	0.30	102	1.8
10	Carbon disulfide	3.02	1.46	0.1	5.2	20	0.05	93	1.4
11	Allyl chloride ⁺	3.21	0.17	-	0.9940	0.990	0.05	76	2.7
12	Acetonitrile ⁺	3.29	0.20	-	0.9999	0.990	0.38	96	5.5
13	Methylene chloride	3.37	0.51	0.1	16	20	0.29	94	2.5
14	trans-1,2 Dichloroethene	3.59	0.46	0.1	9.3	20	0.34	105	1.3
15	Acrylonitrile	3.67	0.44	-	8.8	20	0.14	97	4.6
16	1,1,-Dichloroethane	4.06	0.98	0.2	9.2	20	0.16	107	2.3
17	Chloroprene	4.11	0.70	-	11	20	0.25	89	1.7
18	2,2,-Dichloropropane ⁺	4.63	0.15	-	0.9996	0.990	-	56	7.4
19	cis-1,2,-Dichloroethene	4.66	0.53	0.1	9.6	20	0.24	106	1.9
20	Methyl acrylate	4.76	0.92	-	4.2	20	0.14	100	5.3
21	Propionitrile	4.84	0.22	-	4.4	20	0.12	100	5.7
22	Tetrahydrofuran	4.92	0.53	-	13	20	0.15	86	4.7
23	Bromochloromethane	4.92	0.26	-	4.5	20	0.09	107	3.6
24	Methacrylonitrile	4.96	0.83	-	8.9	20	0.12	90	4.7
25	Chloroform	4.99	0.69	0.2	4.2	20	0.09	103	2.1
26	1,1,1-Trichloroethane	5.14	0.55	0.1	5.5	20	0.20	107	0.9
27	Pentafluorobenzene (ISTD)	5.22							
28	Carbon tetrachloride	5.27	0.38	0.1	12	20	0.13	108	1.2
29	1,1-Dichloropropene	5.32	0.43	-	5.9	20	0.25	89	1.6
30	Isobutyl alcohol	5.49	0.09	-	11.5	20	0.22	89	5.6
31	Benzene	5.53	1.33	0.5	6.9	20	0.22	90	1.6
32	1,2-dichloroethane-d4 (Surr)	5.55							
33	1,2-Dichloroethane	5.64	0.42	0.1	9.8	20	0.09	91	2.0
34	1,4-Difluorobenzene (ISTD)	6.00							
35	Trichloroethene	6.25	0.32	0.2	8.9	20	0.28	103	2.5
36	1,2-Dichloropropane	6.56	0.47	0.1	6	20	0.15	96	1.8
37	Methyl methacrylate	6.67	0.39	-	6.2	20	0.17	91	3.9
38	Dibromomethane	6.70	0.19	-	4.9	20	0.10	106	2.7
39	Bromodichloromethane	6.87	0.28	0.2	7.4	20	0.17	102	1.9
40	2-Nitropropane ⁺	7.23	0.06	-	0.9996	0.990	-	94	4.7
41	cis-1,3-Dichloropropene	7.41	0.47	0.2	8.7	20	0.08	90	1.6
42	Toluene-d8 (Surr)	7.66							

Table 4 continued

#	Compound	RT	Avg RRF	8260C Minimum RRF	% RSD	8260C % RSD Criteria	MDL (µg/L)	Precision (% Rec)	Accuracy (% RSD)
43	Toluene	7.74	0.67	0.4	6.5	20	0.22	100	1.5
44	trans-1,3-Dichloropropene	8.11	0.39	0.1	17	20	0.11	93	2.5
45	Ethyl methacrylate	8.16	0.66	-	11	20	0.07	101	2.6
46	1,1,2-Trichloroethane	8.31	0.28	0.1	4.3	20	0.06	96	1.9
47	Tetrachloroethene	8.35	0.43	0.2	20	20	0.17	123	4.6
48	1,3-Dichloropropane	8.50	0.65	-	4.4	20	0.06	94	3.1
49	Chlorodibromomethane	8.69	0.28	0.1	12	20	0.10	108	3.7
50	Ethylene dibromide	8.81	0.40	0.1	3.6	20	0.07	111	2.8
51	Chlorobenzene-d5 (ISTD)	9.21							
52	Chlorobenzene	9.24	1.08	0.5	4.7	20	0.23	102	1.0
53	Ethylbenzene	9.31	1.34	0.1	2.2	20	0.20	104	1.4
54	1,1,1,2-Tetrachloroethane	9.31	0.27	-	7.8	20	0.19	105	1.9
55	p- & m-Xylene	9.41	1.09	0.1	4.4	20	0.23	101	1.6
56	o-Xylene	9.73	1.15	0.1	2.5	20	0.19	103	2.2
57	Styrene	9.76	1.09	0.3	3.8	20	0.18	106	1.8
58	Bromoform ⁺	9.91	0.22	0.1	0.9996	0.990	0.10	104	2.8
59	Isopropylbenzene	10.01	1.61	0.1	2.8	20	0.18	106	1.8
60	cis-1,4-Dichloro-2-butene ⁺	10.12	0.22	-	0.9986	0.990	0.09	68	2.2
61	Bromofluorobenzene (Surr)	10.15							
62	Bromobenzene	10.25	0.98	-	8.5	20	0.15	98	2.3
63	1,1,2,2-Tetrachloroethane	10.28	1.17	0.3	5.9	20	0.16	93	9.9
64	n-Propylbenzene	10.30	3.21	-	4.8	20	0.20	101	1.1
65	1,2,3-Trichloropropane	10.32	1.76	-	5.8	20	0.10	91	3.3
66	trans-1,4-Dichloro-2-butene ⁺	10.33	0.25	-	0.9991	0.990	0.05	71	2.2
67	2-Chlorotoluene	10.38	1.88	-	4.4	20	0.19	102	0.9
68	1,3,5-Trimethylbenzene	10.43	3.00	-	6.3	20	0.21	104	1.1
69	4-Chlorotoluene	10.47	1.99	-	7.6	20	0.15	100	3.2
70	tert-Butylbenzene	10.64	2.57	-	9.2	20	0.18	94	1.3
71	1,2,4-Trimethylbenzene	10.69	2.94	-	4.8	20	0.19	105	1.2
72	sec-Butylbenzene	10.79	3.48	-	5.1	20	0.20	107	1.7
73	4-Isopropyltoluene	10.88	2.98	-	4.5	20	0.22	97	1.0
74	1,3-Dichlorobenzene	10.89	1.64	0.6	9	20	0.22	98	0.7
75	1,4-Dichlorobenzene-d4 (ISTD)	10.93							
76	1,4-Dichlorobenzene	10.95	1.65	0.5	9.4	20	0.18	97	1.4
77	n-Butylbenzene	11.14	2.10	-	6.5	20	0.17	98	1.2
78	1,2-Dichlorobenzene	11.19	1.60	0.4	4.5	20	0.12	102	1.5
79	1,2-Dibromo-3-chloropropane	11.69	0.33	0.05	9.8	20	0.08	98	3.6
80	Nitrobenzene ⁺	11.84	0.06	-	0.9999	0.990	-	102	5.4
81	1,2,4-Trichlorobenzene	12.24	1.19	0.2	9.3	20	0.16	92	1.3
82	Hexachlorobutadiene	12.32	0.50	-	16	20	0.23	91	1.3
83	Naphthalene	12.46	3.60	-	7.3	20	0.06	102	2.4
84	1,2,3-Trichlorobenzene	12.65	1.13	0.2	7.2	20	0.09	94	1.6

Table 5. Alternate calibration range compounds.

Calibration Concentration Range	Compound
0.5 – 100 µg/L	Tetrachloroethene
1.0 – 200 µg/L	Bromomethane Allyl chloride Acetonitrile Isobutyl alcohol
2.0 – 200 µg/L	2,2-Dichloropropane 2-Nitropropane Nitrobenzene
1.0 – 400 µg/L	p- & m-Xylene

Design advancements in the Clarus SQ 8 mass spectrometer allow such a wide operating range with the Clarifi™ detector providing much of the advantage. The detector's enhanced sensitivity enables full scan mass spectrometry methods to be performed resulting in library searchable spectra at the lowest possible concentration levels. With the added sensitivity of SIFI™ (selected ion full ion) or SIM (selected ion monitoring) data acquisition at even lower limits are possible for specific compounds.

The voltage setting on the Clarifi detector was important in developing the method for such a wide concentration range and deserves mention here. The UltraTune™ (Standard – DFTPP/BFB) function built into the TurboMass™ v6.0 software is designed to set the voltage such that the m/z = 69 peak of the tune gas FC43 is approximately 80% in the tune window. This setting is appropriate for general instrument analyses however users are encouraged to fine tune this setting to suit their specific analytical needs. In our case this was achieved by analyzing two samples, the high and low concentration level of our calibration, at voltage settings below that set during UltraTune. The optimum voltage setting produced measurable signal at the lowest level while not saturating the detector at the highest level. In our case the initial UltraTune setting was 1570V with test measurements performed at -50V and -100V of this value. The analysis was performed at 1520V. The stability of the Clarus SQ 8 system allows this setting to be used for extended periods of time and need only be reproduced periodically.

The UltraTune (Standard – DFTPP/BFB) function also produces a satisfactory tune which meets the Tune Evaluation requirements set out in the method. Figure 3 demonstrates the passing BFB Tune Evaluation Sample. Figure 4 shows the mass spectrum utilized in the Tune Evaluation Test and all of the necessary peak intensity comparisons are achieved.

Mass	Reference Mass	Relative Abundance	Criterion	Pass/Fail
50	95	16.3%	>= 15% and <= 40%	Pass
75	95	48.5%	>= 30% and <= 60%	Pass
95	BPI	100%	= 100%	Pass
96	95	7.4%	>= 5% and <= 9%	Pass
173	174	0.7%	< 2%	Pass
174	95	93.6%	> 50% and < 100%	Pass
175	174	7.7%	>= 5% and <= 9%	Pass
176	174	97.9%	>= 95% and < 101%	Pass
177	176	6.0%	>= 5% and <= 9%	Pass

Figure 3. TurboMass 6.0 EPA BFB tune evaluation results.

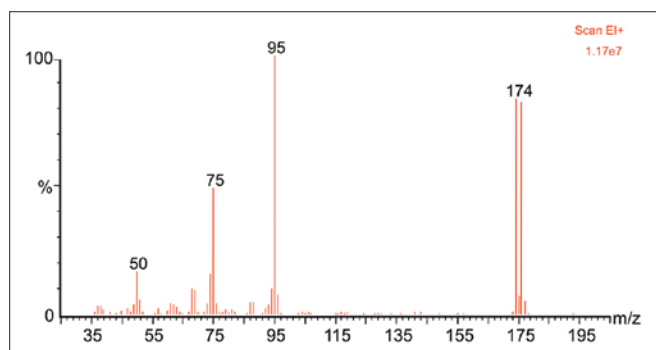


Figure 4. Mass spectrum of EPA BFB tune evaluation used for test in Figure 3.

Conclusion

The analysis of VOCs by purge and trap GC/MS following EPA Method 8260C is easily achievable over a wide concentration range using the Clarus SQ 8 GC/MS system. Satisfactory analytical results were achieved for a concentration range from 0.5 – 200 µg/L for a majority of analyte compounds using the full scan approach providing library searchable spectra at all concentration levels. Excellent detection limits are reported as are accuracy and precision measurements. A number of technological advances make the Clarus SQ 8 GC/MS the ideal systems for laboratories wishing to perform high throughput and sensitivity analyses with an ease of operation currently unmatched.