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Improved Sensitivity and Dynamic Range Using the Clarus SQ 8 GC/MS System for EPA Method 8270D Semi-Volatile Organic Compound Analysis

Introduction

U.S. Environmental Protection Agency (EPA) Method 8270D – Semi-Volatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS) – is a common and wide ranging method employed in nearly all commercial environmental laboratories. The analysis focuses on the detection of trace level semi-volatile organic compounds in extracts from solid waste matrices, soils, air sampling media and water samples. The method lists over 200 compounds however a majority of laboratories target between 60 and 90 for most analyses. The study presented here demonstrates the PerkinElmer® Clarus® SQ 8 GC/MS, not only meets the method requirements but provides users flexibility to satisfy their individual productivity demands. An extended calibration range is presented as are the advantages of the Clarifi™ detector.

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Experimental

The PerkinElmer Clarus SQ 8T GC/MS system operating in electron ionization mode was used to perform these experiments. Experimental conditions are presented in Table 1 and represent standard conditions for EPA Method 8270D. Minimum inlet reactivity was achieved using a deactivated quartz liner (4-mm) without wool. As prescribed by the method, a pressure pulse injection scheme was employed and is described in Table 2. Data collection was achieved using the TurboMass™ v6 GC/MS software with environmental reporting. The TurboMass software comes with a built-in UltraTune™ (Standard – DFTPP/BFB) tuning procedure, which was used to establish the base detector setting.

Table 1. GC and MS experimental conditions.

Analytical Column:	Elite-5MS (30 m x 0.25 mm id x 0.25 μm)		
Injector Temperature:	300 °C		
Carrier Gas:	Helium @ 1.0 mL/min		
Oven Program:	**Temperature**	**Hold Time**	**Rate**
	37 °C	0.5 min	18 °C/min
	265 °C	0 min	6 °C/min
	287 °C	0 min	25°C/min
	320 °C	1.85 min	End
GC Transfer Line Temperature:	280 °C		
MS Ion Source Temperature:	280 °C		
MS Function Type:	Full Scan		
MS Solvent Delay:	0 – 2.30 min		
MS Scan Range:	m/z 35 – 500		
MS Scan Time:	0.10 sec		
MS Interscan Delay:	0.10 sec		

Table 2. Pressure plus flow settings.

Time (min)	Split Flow (mL/min)
-0.50	4
-0.25	0
0.75	1
1.00	50
5.00	20

Calibration and performance standards were prepared from commercially available stock standards and diluted in Class-A volumetric flasks. Calibration standards were made from a 76 component 8270 mega mix, a 15 component acids fortification mix and a 6 component semi-volatile internal standard mix. The acids were fortified with the fortification mix to double the concentration relative to the other components. 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. The internal standard mix was added to all samples such that a resulting concentration of 40 μg/mL was achieved. The tuning standard, Decafluorotriphenylphosphine (DFTPP), was prepared at 50 μg/mL. 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	"Acids" Concentration (μg/mL)	"Bases/Neutrals" Concentration (μg/mL)
1	2	1
2	4	2
3	8	4
4	12	6
5	20	10
6	30	15
7	40	20
8	80	40
9	160	80
10	200	100
11	300	150

Results and Discussion

An initial consideration when performing any method is to determine the operating range with respect to on-column concentration. The Clarus SQ 8 GC/MS allows the user to control the linear range by controlling the Clarifi detector voltage setting. The built-in UltraTune (Standard – DFTPP/BFB) tune procedure adjusts the mass spectrometer providing excellent spectral fidelity and sets the detector voltage such that low sensitivity work can be performed. This standard

setting can be used directly and is recommended for most applications. Additionally, the detector voltage can be increased for added sensitivity when needed, or, as is the case with this application note, the detector voltage can be tuned to provide both sensitivity and a wide dynamic range

Figure 1. EPA 8270D tune evaluation as performed by the built-in software. Passing result shown.
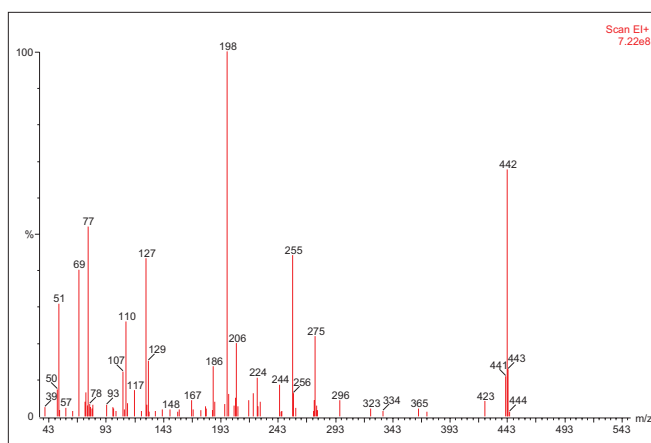

Figure 2. Mass spectrum of DFTPP as analyzed by the tune evaluation shown in Figure 1.

suitable for the analysis at hand. In this study the Clarifi detector voltage was optimized such that both the low level samples were measurable while the high level samples were not saturating the detector. Specifically, the detector was lowered 260V to the operational 1400V. The added sensitivity of the Clarifi detector enhances a wider range of analyses so that even at low voltage settings the low concentration standards and samples are easily detected.
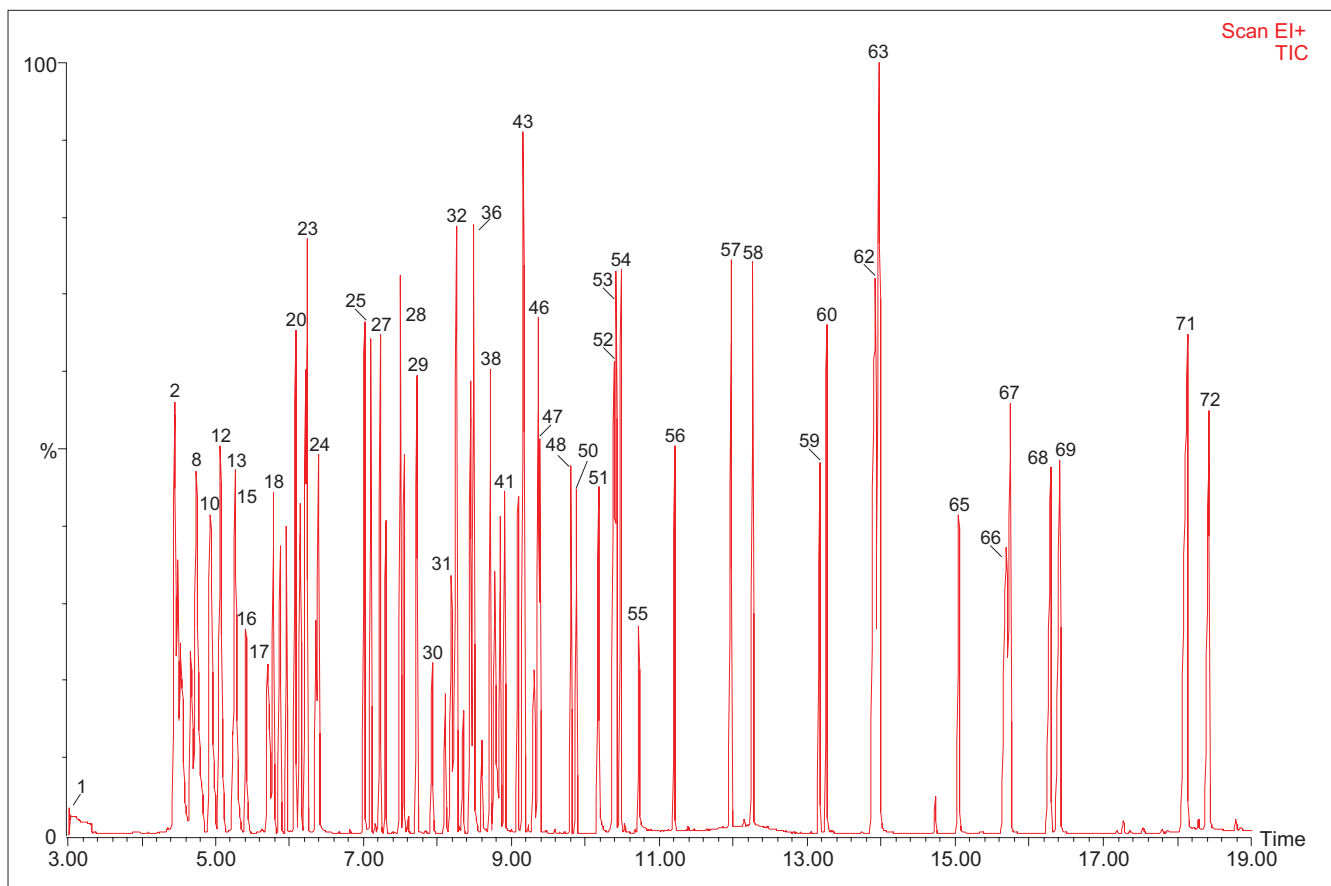

Figure 3. TIC of 40 µg/mL calibration sample. Retention Times are listed in Table 4 (Page 4).
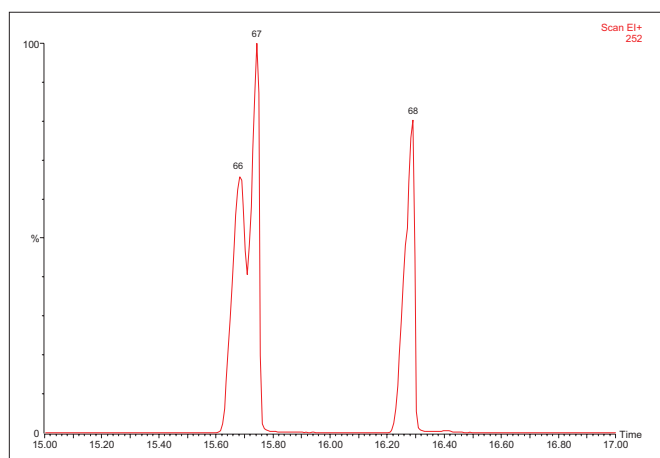
Figure 4. Zoom of EIC at m/z = 252 showing separation of benzo[b] fluoranthene (66) and benzo[k]fluoranthene (67). Benzo[a]pyrene (68) also shown.

In addition to providing a solid foundation from which to perform analyses the UltraTune (Standard – DFTPP/BFB) function also produces a satisfactory tune, which meets the tune evaluation requirements set out in Method 8270D. Figure 1 demonstrates the passing DFTPP tune evaluation sample while Figure 2 shows the mass spectrum utilized in the tune evaluation test.

The GC conditions were optimized to provide analytical separation and Figure 3 demonstrates a mid-level (40 µg/mL) total ion chromatogram (TIC) from this analysis. All of the expected analyte separation is achieved and a listing of retention times (RT) measured using the instrument parameters as described in Table 1 is presented. The Elite-5MS column provided excellent separation and Figure 4, for example, demonstrates the separation of the benzo[b]fluoranthene and benzo[k]fluoranthene.

Table 4. **Calibration data table with retention times listed in Figure 3 (Page 3).**

#	Name	RT (min)	Average RRF	8270D Criteria RRF	% RSD
1	Pyridine	3.09	0.2		8.98
2	Aniline	4.44	1.2		13.16
3	Phenol	4.45	1.7	0.8	9.52
4	N-Nitrosodimethylamine	4.45	0.1		10.3
5	Bis (2-chloroethyl) ether	4.49	2.1	0.7	12.66
6	1,3-Dichlorobenzene	4.66	1.1		15.56
7	1,4-Dichlorobenzene - D4 (ISTD)	4.73			8.83
8	1,4-Dichlorobenzene	4.75	1.0		9.73
9	1,2-Dichlorobenzene	4.91	1.3		11.27
10	Benzyl Alcohol	4.94	1.0		11.86
11	Bis (2-chloroisopropyl) ether	5.05	1.7		9.34
12	2-Methylphenol	5.07	0.6	0.7	10.66
13	3-Methylphenol	5.26	0.7		11.71
14	4-Methylphenol	5.26	0.9	0.6	8.59
15	Hexachloroethane	5.28	0.5	0.3	10.62
16	Nitrobenzene	5.41	0.4	0.2	9.91
17	Isophorone	5.70	0.7	0.4	11.31
18	2-Nitrophenol	5.78	0.2		11.86
19	Bis(2-chloroethoxy)methane	5.96	0.5	0.3	15.45
20	2,4-Dichlorophenol	6.08	0.3	0.2	16.69
21	1,2,4-Trichlorobenzene	6.14	0.4		14.19
22	Naphthalene - D8 (ISTD)	6.21			7.41
23	Naphthalene	6.24	1.1	0.7	9.63
24	Hexachlorobutadiene	6.39	0.2	0.01	10.38
25	4-chloro-3-methyl-phenol	7.01	0.3	0.2	16.86
26	2-Methylnaphthalene	7.09	0.6	0.4	14.73
27	1-Methylnaphthalene	7.22	0.6		13.96
28	Hexachlorocyclopentadiene	7.30	0.2	0.05	9.14
29	2-Chloronaphthalene	7.72	1.4	0.8	12.09

Table 4 continued

#	Name	RT (min)	Average RRF	8270D Criteria RRF	% RSD
30	2-Nitroaniline	7.93	0.4	0.01	9.54
31	Dimethyl phthalate	8.19	1.4	0.01	10.67
32	2,6-Dinitrotoluene	8.25	0.3	0.2	13.95
33	Acenaphthylene	8.25	2.0	0.9	8.27
34	Acenaphthene - D10 (ISTD)	8.45			7.56
35	Acenaphthene	8.49	1.5	0.9	9.85
36	3-Nitroaniline	8.49	0.2	0.01	14.4
37	2,4-Dinitrophenol	8.60	0.1	0.01	8.17
38	Dibenzofuran	8.71	1.7	0.8	11.83
39	4-Nitrophenol	8.79	0.1	0.01	10.14
40	2,3,4,6-Tetrachlorophenol	8.85	0.2		12.71
41	2,3,5,6-Tetrachlorophenol	8.91	0.2		10.17
42	Diethylphthalate	9.09	1.1	0.01	9.93
43	Fluorene	9.15	1.3	0.9	11.93
44	4-Chlorodiphenylether	9.17	0.5	0.4	13.53
45	4,6-Dinitro-2-methylphenol	9.29	0.1	0.01	16.04
46	4-Nitroaniline	9.31	0.1	0.01	12.33
47	N-Nitrosodiphenylamine	9.36	0.5	0.01	11.4
48	4-Bromophenyl phenyl ether	9.80	0.2	0.1	9.57
49	Azobenzene	9.81	0.1		10.13
50	Hexachlorobenzene	9.88	0.2	0.1	10.17
51	Pentachlorophenol	10.18	0.1	0.05	8.01
52	Phenathrene - D10 (ISTD)	10.38			3.48
53	Phenanthrene	10.42	1.1	0.7	13.5
54	Anthracene	10.48	1.1	0.7	15.16
55	Carbazole	10.72	0.4	0.01	8.39
56	Di-n-butyl phthalate	11.20	0.8	0.01	11.42
57	Fluoroanthene	11.97	1.0	0.6	8.52
58	Pyrene	12.26	1.2	0.6	9.62
59	Butyl benzyl phthalate	13.16	0.4	0.01	12.35
60	Bis (2-ethylhexyl) adipate	13.26	0.5		14.38
61	Benzo[a]anthracene	13.89	1.0	0.8	11.8
62	Chrysene - D12 (ISTD)	13.92			6.34
63	Chrysene	13.96	1.0	0.7	16.57
64	Bis (2-ethylhexyl) phthalate	13.98	0.6	0.01	17.47
65	Di-n-Octyl phthalate	15.04	1.0		11.13
66	Benzo[b]fluoranthene	15.68	1.2	0.7	12.55
67	Benzo[k]fluoranthene	15.74	0.9	0.7	13.52
68	Benzo[a]pyrene	16.29	1.0	0.7	9.46
69	Perylene - D12 (ISTD)	16.42			4.24
70	Indeno(1,2,3-c,d)pyrene	18.00	1.2	0.5	8.72
71	Dibenz[a,h]anthracene	18.12	1.0	0.4	9.25
72	Benzo[g,h,i] perylene	18.42	1.0	0.5	7.98

The results of the initial calibration curve for EPA Method 8270D are presented in Table 4 and include retention time, average relative response factor (Avg. RRF), method criteria, and percent relative standard deviation (% RSD). Satisfactory results are obtained for all for the compounds listed.

Conclusion

In this application note the Clarus SQ 8 GC/MS system is shown to provide wide concentration range applicability to U.S. EPA Method 8270D, allowing the analysts flexibility in performing experimentation to meet their needs. Satisfactory analytical results were demonstrated over a concentration range from 1.0 – 150 µg/mL for a majority of analyte compounds using the full scan approach providing library searchable spectra at all concentration levels. 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 that is currently unmatched.

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