Application Note

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Novel Column Chemistry Raises the Bar on Sensitivity and Data Accuracy in the Analysis of Semivolatile Organic Compounds

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Abstract

As ionization sources continue to advance, lowering limits of detection and increasing confidence in analyte identification, column technologies can also be used in conjunction to push the practical limits of sensitivity and data accuracy. Increases in the detection of analyte response also result in unwanted increases in the detection of background noise. Gas chromatography/mass spectrometry (GC/MS) column technology that lowers interfering column bleed ions and elevated bleed baselines, maintains peak shape for active compounds, and can withstand aggressive thermal cycling can greatly enhance the performance and productivity of GC/MS methods. This application note examines how column attributes like bleed, inertness, and thermal stability can further benefit the sensitivity and accuracy of an MS. This study illustrates achievable data parameters, like sensitivity limits at trace levels, retention time consistencies, and data accuracy for active semivolatile organic compounds (SVOCs), when the Agilent 7010D triple quadrupole GC/MS (GC/TQ) system is used.

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Introduction

Governmental regulatory authorities have established method and performance criteria for GC/MS measurement of SVOCs that are identified as pollutants in environmental and industrial matrices. The United States Environmental Protection Agency (U.S. EPA) method 8270, for example, contains a list of over 200 compounds, some of which can be susceptible to unwanted chemical activity in the instrument flow path, resulting in data quality degradation. If the performance criteria of method 8270 are not met, system maintenance is often needed, such as liner replacement followed by column trimming or replacement, resulting in unplanned instrument downtime .

Monitoring of the DFTPP tuning standard, which contains 4,4'-DDT, pentachlorophenol, and benzidine, validates the suitability of the flow path and monitors when maintenance should be performed. The breakdown of 4,4'-DDT to 4,4'-DDE, and 4,4'-DDD, as well as the tailing factors of benzidine and pentachlorophenol, tests the flow path inertness, indicating the activity of susceptible acidic and basic analytes. GC columns contribute the largest surface area in the sample flow path and, therefore, are a critical factor in controlling interferences in the analytical path. Agilent Ultra Inert (UI) GC liners, along with an inert GC column phase, can improve the robustness of SVOCs analyses.[1]

Stationary phases used in GC/MS analysis of SVOCs are typically comprised of liquid polymers with a polysiloxane backbone. When heat is applied to the column during routine use, the terminal end of the stationary phase polymer can bend back and attack itself; this is called "backbiting." Ring structures, which are thermodynamically stable, are liberated from the stationary phase, increasing background noise and raising the baseline; this can be problematic for low signal-to-noise (S/N) analytes. Peak integration can become less repeatable, lowering quantitation accuracy. In addition, the increase in freed ring structures—which fragment in the ion source—and analytes can cause spectral interference in extracted mass spectra and decrease the qualitative score of a library spectral hit. The Agilent J&W HP-5Q and DB-5Q GC columns have an increased thermal stability at upper temperature limits, allowing for less spectral interference, lower levels of column bleed, and better data quality, especially for heavier analytes that may suffer from issues with lower S/N.[2]

The new Agilent high-efficiency ion source (HES) 2.0, as seen in Figures 1 and 2, is equipped with a novel dipolar RF lens that redirects carrier gas and low mass ions by > 95%. The deflected ions land on adjacent lenses and are pumped out before entering the mass analyzer, providing reduced noise and extended instrument robustness while maintaining sensitivity. A ramped RF amplitude versus mass is implemented to avoid spectrum tilt. The reduction of noise allows for a further increase of sensitivity to attogram-level detection limits. Built-in intelligence features such as SWARM autotune and early maintenance feedback further enhance instrument performance and diagnostic capabilities. The DB-5Q GC column and the HES 2.0 work in concert to increase the robustness of difficult analyses such as that of SVOCs.[3,4]

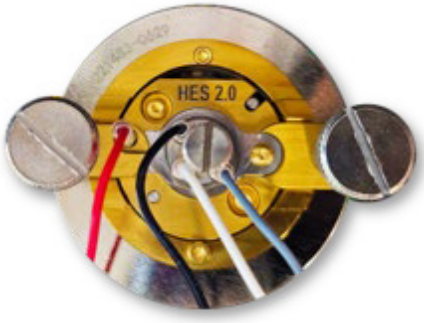


Figure 1. Front view of the Agilent HES 2.0.

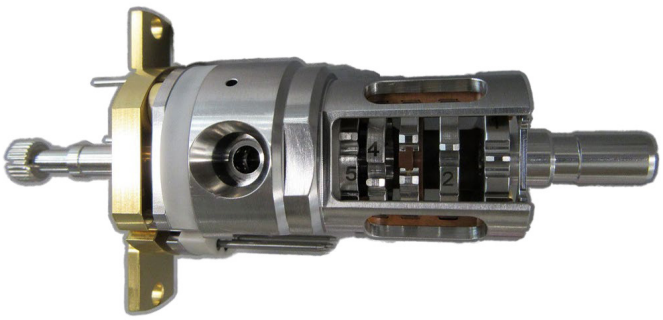


Figure 2. Side view of the Agilent HES 2.0.

Experimental

The Agilent 8000 Series semivolatiles standard (part number SVM-8270-1)—a representative mixture of semivolatile acids, bases, and neutrals—was prepared in dichloromethane (DCM) for calibration standards to be analyzed at 10 to 1,000 pg on column. A semivolatile internal standard mix (part number CRM48902) was procured from Sigma-Aldrich (Saint Louis, MO, U.S.).

The tuning standard, containing a mixture of benzidine, pentachlorophenol, 4,4'-diphenyltrichloroethane (4,4'-DDT), and decafluorodiphenyltrichloroethane (DFTPP) at 25 µg/mL, was used to obtain MS calibration and tuning settings.

A composite mixture of soils extracted with DCM prepared for method 8270 analysis, which is a representative matrix residue that is typically encountered in the lab, was procured from Pace Analytical (Mt. Juliet, TN, U.S.).

An Agilent 8890 GC coupled with an Agilent 5977B GC/MSD and Inert Extractor source, as well as an 8890 GC coupled with a 7010D triple quadrupole GC/MS (GC/TQ) system, upgraded with the HES 2.0, were used for the analysis.

Table 1. GC parameters for the Agilent 8890 GC.

Parameter	Value
Agilent 8890 GC	
Inlet	300 °C, Pulsed splitless mode
Injection Volume	0.5 mL
Inlet Liner	Agilent UI inlet liner, split, low pressure drop (p/n 5190-2295)
Injection Pulse Pressure	30 psi until 0.6 min
Purge Flow to Split Vent	50 mL/min at 0.6 min
Septum Purge Flow	3 mL/min
Oven	40 °C (0.5 min), ramp 10 °C/min to 100 °C, ramp 25 °C/min to 260 °C, ramp 5 °C/min to 280 °C, 15 °C/min to 320 °C (5 min), 10 °C/min to 330 °C (10 min), 10 °C/min to 340 °C (10 min)
Column	
Carrier Gas	Helium, 1.3 mL/min, constant flow
Column	– Agilent J&W DB-5Q, 30 m × 0.25 mm, 0.25 µm (p/n 122-5532Q) – Agilent J&W DB-5ms UI, 30 m × 0.25 mm, 0.25 µm (p/n 122-5532UI) – 5ms-Type column X, 30 m × 0.25 mm, 0.25 µm – 5ms-Type column Y, 30 m × 0.25 mm, 0.25 µm
Inlet Connection	Split/splitless inlet
Outlet Connection	MSD

Table 2. MS parameters for the Agilent 5977B GC/MSD.

Parameter	Value
Agilent 5977B GC/MSD	
Source	Agilent Inert Extractor source
Mode	Scan (35 to 500 amu)
Solvent Delay	2.5 min
Source Temperature	300 °C
Quadrupole Temperature	175 °C
Gain	1.0

Table 3. MS parameters for the Agilent 7010D GC/TQ.

Parameter	Value
Agilent 7010D GC/TQ	
Source	Agilent HES
Mode	Dynamic multiple reaction monitoring (dMRM)/scan
Solvent Delay	2.5 min
Source Temperature	300 °C
Quadrupole Temperature	175 °C
Gain	1.0

Table 4. Quantitative/qualitative transitions (dMRM based) for Agilent 7010D GC/TQ acquisition parameters.

	SVM-8270-1		Quantitative				Qualitative			
Peak	RT	Compound	Precursor Ion	Product Ion	Dwell	CE	Precursor Ion	Product Ion	Dwell	CE
1	3.043	NDMA	74	44	56.07	6	74	42	56.07	14
2	6.411	Phenol	94	66.1	14.17	15	94	65.1	14.17	20
3	6.670	Chlorophenol-2	128	64	9.22	15	128	63	9.22	30
4	6.940	1, 3-Dichlorobenzene	146	111	8.33	15	146	75	8.33	30
4.5	6.960	1, 4-Dichlorobenzene-d_4	150	115	9.31	15	150	78	9.31	3
5	7.074	1, 4-Dichlorobenzene	146	111	13.21	15	146	75	13.21	30
6	7.313	1, 2-Dichlorobenzene	146	111	9.63	15	146	75	9.63	30
7	7.700	Nitrosodi-n-propylamine N-	113.1	71	7.14	10	101	70	7.14	0
8	7.450	Methylphenol-2 (Cresol o-)	108	107	7.96	15	107	77	7.96	15
9	7.500	bis(2-Chloro-1-methylethyl)ether	121	77	7.68	5	121	49	7.68	30
10	7.700	Methylphenol-4 (Cresol p-)	108	107.1	8.36	15	107	77.1	8.36	15
11	7.800	Hexachloroethane	200.9	165.9	7.19	15	118.9	83.9	7.19	35
12	7.900	Nitrobenzene	123	77	8.28	10	77	51	8.28	15
13	8.250	Isophorone	138	82	10.46	5	82	54	10.46	5
14	8.370	Nitrophenol, 2-	138.9	81	11	15	109	81	11	10
15	8.450	Dimethylphenol 2,4- (2, 4-xylenol)	122.1	107	12.24	10	107.1	77.1	12.24	15
16	8.600	bis(2-Chloroethoxy)methane	95	65	10.37	5	93	63	10.37	5
17	8.700	Dichlorophenol, 2,4-	163.9	63	9.65	30	162	63	9.65	30
18	8.800	Trichlorobenzene, 1,2,4-	179.9	145	10.32	15	179.9	109	10.32	30
18.5	8.805	Naphthalene-d_8	136.1	108.1	9.59	20	136.1	84.1	9.59	25
19	8.900	Naphthalene	128.1	102.1	12.38	20	128.1	78.1	12.38	20
20	8.980	Chloroaniline,4-	127	92	13.18	15	127	65	13.18	20
21	9.070	Hexachlorobutadiene	226.9	191.9	28.71	15	224.8	189.9	28.71	1
22	9.570	Phenol 4-chloro-3-methyl-	142	107	34.24	15	107	77	34.24	15
23	9.750	Methylnaphthalene, 2-	142.1	141.1	22.34	15	141.1	115.1	22.34	15
24	9.940	Hexachlorocyclopentadiene	237	143	17.85	20	237	119	17.85	20
25	10.060	Trichlorophenol, 2,4,5-	197.9	97	16.66	25	195.9	97	16.66	25
26	10.100	Trichlorophenol, 2,4 6-	198	97	17.45	30	196	97	17.45	30
27	10.300	Chloronaphthalene, 2-	162	127.1	21.04	20	162	77	21.04	35
28	10.400	Nitroaniline, 2-	138	92	25.89	15	138	65	25.89	25
29	10.600	Dimethyl phthalate	163	92	23.89	30	163	77	23.89	20
30	10.670	Dinitrotoluene, 2,6-	165	90.1	20.02	15	165	63	20.02	25
31	10.740	Acenaphthylene	152.1	102.1	14.15	30	151.1	77	14.15	25
32	10.840	Nitroaniline, 3-	138	92	11.18	15	138	80	11.18	5
32.5	10.826	Acenaphthene-d_{10}	164.1	162.1	10.43	15	162.1	160.1	10.43	20
33	10.910	Acenaphthene	154.1	127	10.43	40	153.1	77	10.43	45
34	10.950	Phenol, 2,4-dinitro-	184	107	12.76	25	184	79	12.76	25
35	11.010	Nitrophenol, 4-	138.9	109	12.71	5	109	81	12.71	10
36	11.120	Dibenzofuran	168.1	139.1	13.47	25	139.1	63	13.47	35
37	11.080	Dinitrotoluene, 2,4-	165	119	12.55	5	165	63	12.55	45
38	11.340	Diethyl phthalate	149	93	12.42	15	149	65	12.42	20
39	11.460	Fluorene	166.1	165.1	10.14	15	165.1	163.1	10.14	35
40	11.470	Chlorophenyl phenyl ether, 4-	204	77	10.34	30	141.1	115.1	10.34	20

Peak	SVM-8270-1		Quantitative				Qualitative			
	RT	Compound	Precursor Ion	Product Ion	Dwell	CE	Precursor Ion	Product Ion	Dwell	CE
41	11.480	Nitroaniline, 4-	138	108.1	10.1	5	108	80	10.1	15
42	11.510	DNOC (2-methyl-4 6-dinitrophenol)	198	167.9	13.44	5	198	121	13.44	10
43	11.630	Azobenzene	105	77.1	11.37	5	77	51	11.37	15
44	11.970	4-Bromophenyl phenyl ether	250	141	22.75	20	248	141	22.75	20
45	12.020	Hexachlorobenzene	283.8	213.9	28.52	30	248.9	214	28.52	15
46	12.220	Pentachlorophenol	265.9	167	30.92	25	165	130	30.92	25
47	12.430	Phenanthrene	178.1	152.1	22.36	25	176.1	150.1	22.36	25
47.5	12.360	Phenanthrene-d10	188.3	160.2	18.93	20	188.3	158.2	18.93	35
48	12.490	Anthracene	178.1	152.1	18.72	25	178.1	151.1	18.72	30
49	12.650	Carbazole	167	139	33.75	45	167	89	33.75	60
50	13.000	Di-n-butyl phthalate	149	121	74.98	15	149	65	74.98	25
51	13.690	Fluoranthene	202.1	152.1	26.52	30	201.1	200.1	26.52	15
52	13.980	Pyrene	202.1	151	21.27	45	201.1	200	21.27	15
53	14.900	Butyl benzyl phthalate	149	65	55.86	25	91	65	55.86	15
54	15.860	Benz[a]anthracene	228.1	226.1	23.12	30	226.1	224.1	23.12	35
54.5	15.842	Chrysene-d_{12}	240.2	236.2	16.17	3	236.1	232.1	16.17	40
55	15.930	Chrysene	226.1	224.1	23.59	40	113.1	112.1	23.59	10
56	16.000	bis(2-Ethylhexyl) phthalate	167	149	23.09	5	149	65	23.09	25
57	17.450	Di-n-octyl phthalate	149	93	27.51	20	149	65	27.51	25
58	18.050	Benzo[b]fluoranthene	252.1	250.1	18.69	35	126	113.1	18.69	10
59	18.150	Benzo[k]fluoranthene	252.1	250.1	18.56	30	126.1	113.1	18.56	10
60	18.700	Benzo[a]pyrene	252.1	250.1	21.83	35	125	124.1	21.83	10
60.5	18.754	Perylene-d_{12}	264.2	260.1	16.16	35	260.1	256.1	16.16	40
61	20.580	Indeno[1,2,3-cd]pyrene	276.1	274.1	30.66	40	137	136	30.66	15
62	20.660	Dibenz[a,h]anthracene	278.1	276.1	24.37	35	276.1	274.1	24.37	35
63	21.080	Benzo[g,h,i]perylene	276.1	274.1	45.33	45	138	137	45.33	1

Results and discussion

Reduced bleed stabilizes GC/MS baselines

According to EPA method 8270, the GC/MS system must meet the required performance criteria to confirm suitability before samples can be analyzed. The system suitability results, along with the chromatographic resolution criteria of closely eluting structural isomer pairs, have been described previously for an Agilent UI glass wool liner and UI 5ms-type column.[1] The chromatographic performance of the J&W DB-5Q GC column was tested for the suitability of method 8270 by GC/MS, and a representative chromatogram is demonstrated in Figure 3. When comparing the J&W DB-5Q to a conventional 5ms-type GC column, a significant decrease in column bleed stabilized the chromatographic baseline, which is ideal when analyzing low concentrations of compounds at high temperatures (Figure 4).

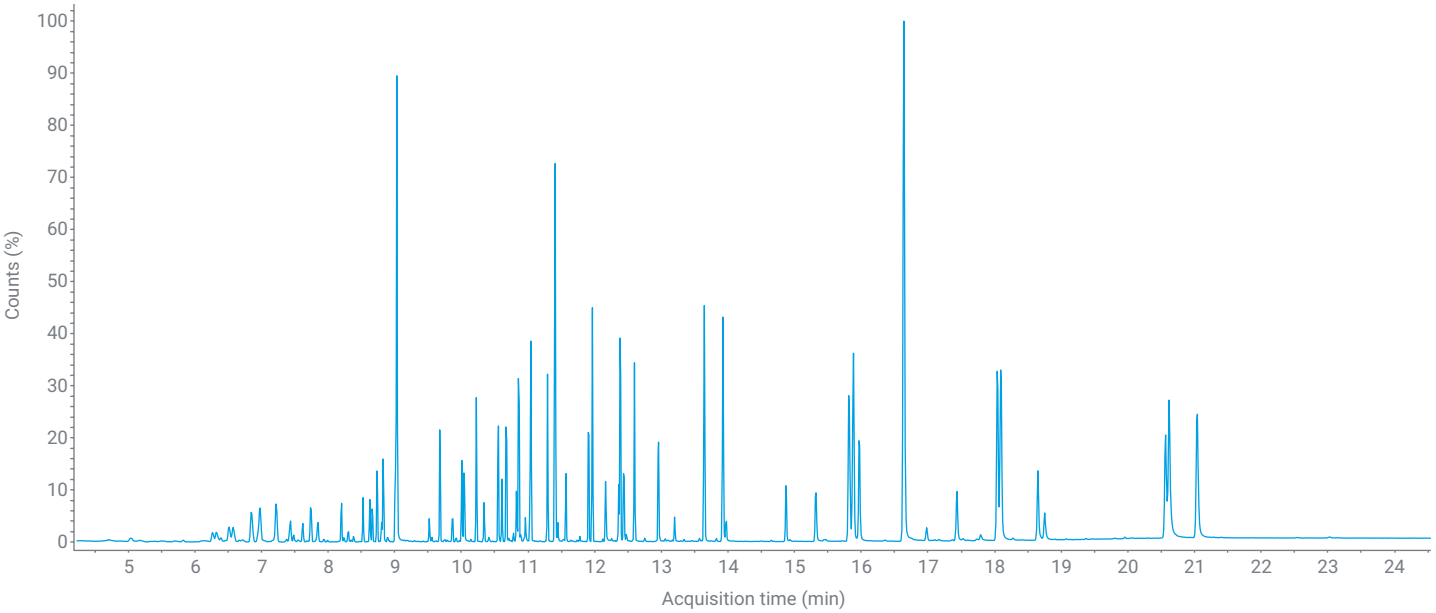


Figure 3. A representative chromatogram of 8,270 compounds analyzed on an Agilent J&W DB-5Q GC column and collected using an Agilent 5977B GC/MSD.

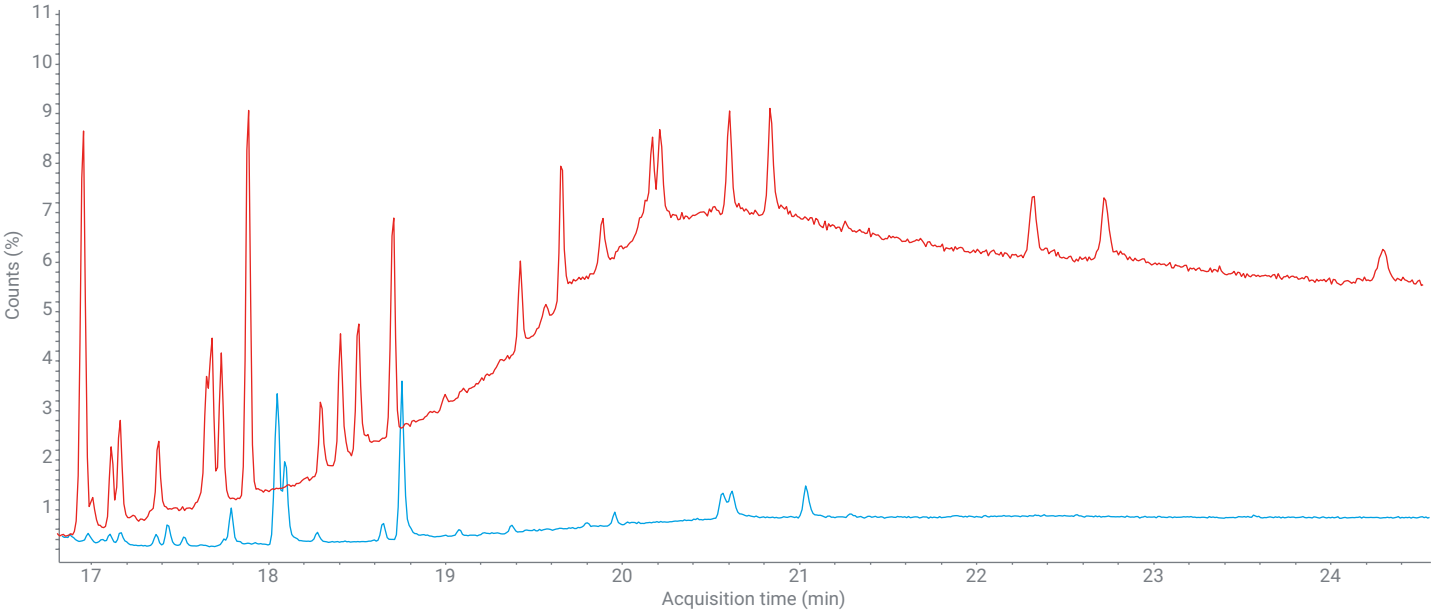


Figure 4. A standard of 50 pg on column of 8,270 compounds, analyzed on an Agilent J&W DB-5Q (blue) and the 5ms-type column Y (red), and collected on an Agilent 5977B GC/MSD.

Reduced column activity improves peak symmetry of problematic analytes

In EPA method 8270, column activity is observed as increased peak tailing, resulting in S/N loss. This is commonly observed with the more active compounds in the analyte panel. In Figure 5, the peak symmetry and S/N ratio for 2,4-dinitrophenol, a problematic analyte, was compared at 250 pg on column, analyzed on both a DB-5Q column and a conventional 5ms-type column. The column activity of the 5ms-type column X resulted in a loss of peak symmetry that significantly decreased analyte sensitivity. Also, the peak shape of another problematic compound, 2-methyl-4,6-dinitrophenol, was compared through analysis on two conventional 5ms-type columns (marked as X and Y) and the DB-5Q, as shown in Figure 6. The inertness of the DB-5Q allowed for better S/N, leading to better sensitivity for this difficult phenolic compound.

Lastly, Figure 7 demonstrates the comparison of pentachlorophenol on the DB-5Q and a conventional 5ms-type column. Again, when analyzed at the same concentration, the tailing factor of pentachlorophenol increased, leading to less S/N response. When working with difficult analytes, such as those in EPA method 8270, inert column chemistries, such as those observed on the DB-5Q, will optimize sensitivity.

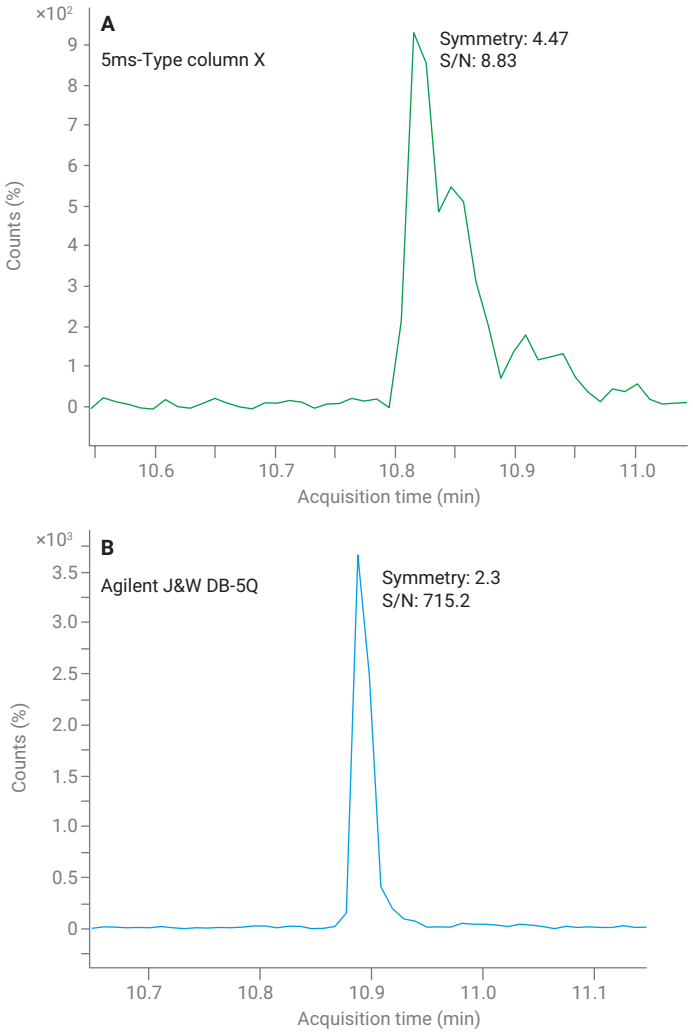


Figure 5. Integrated peak 250 pg on column 2,4-dinitrophenol, analyzed on the 5ms-type column X and an Agilent J&W DB-5Q GC column.

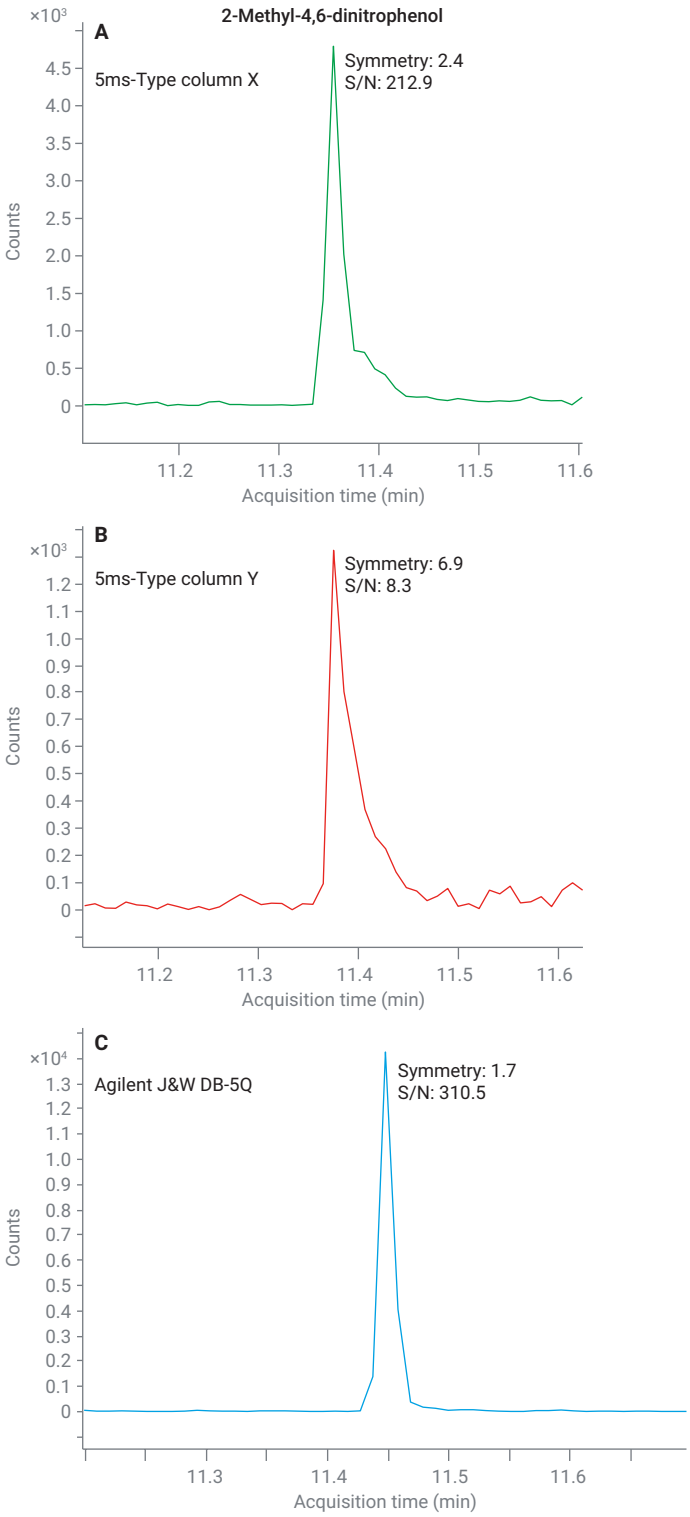


Figure 6. Integrated peak 250 pg on-column 2-methyl-4,6-dinitrophenol, analyzed on the 5ms-type columns X and Y, and an Agilent J&W DB-5Q GC column.

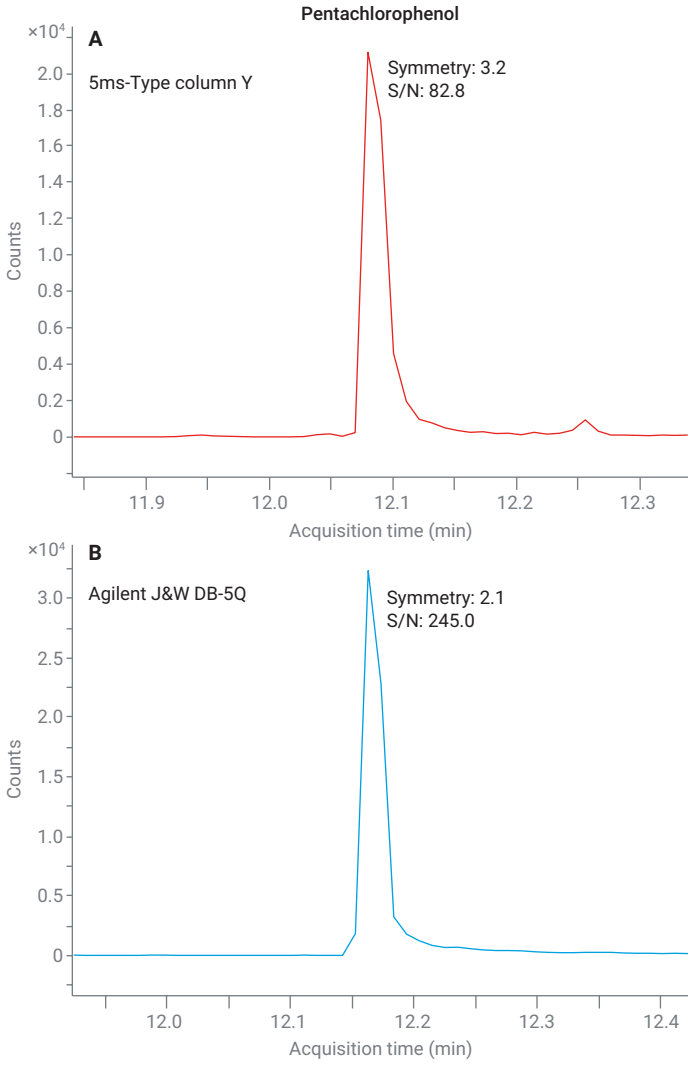
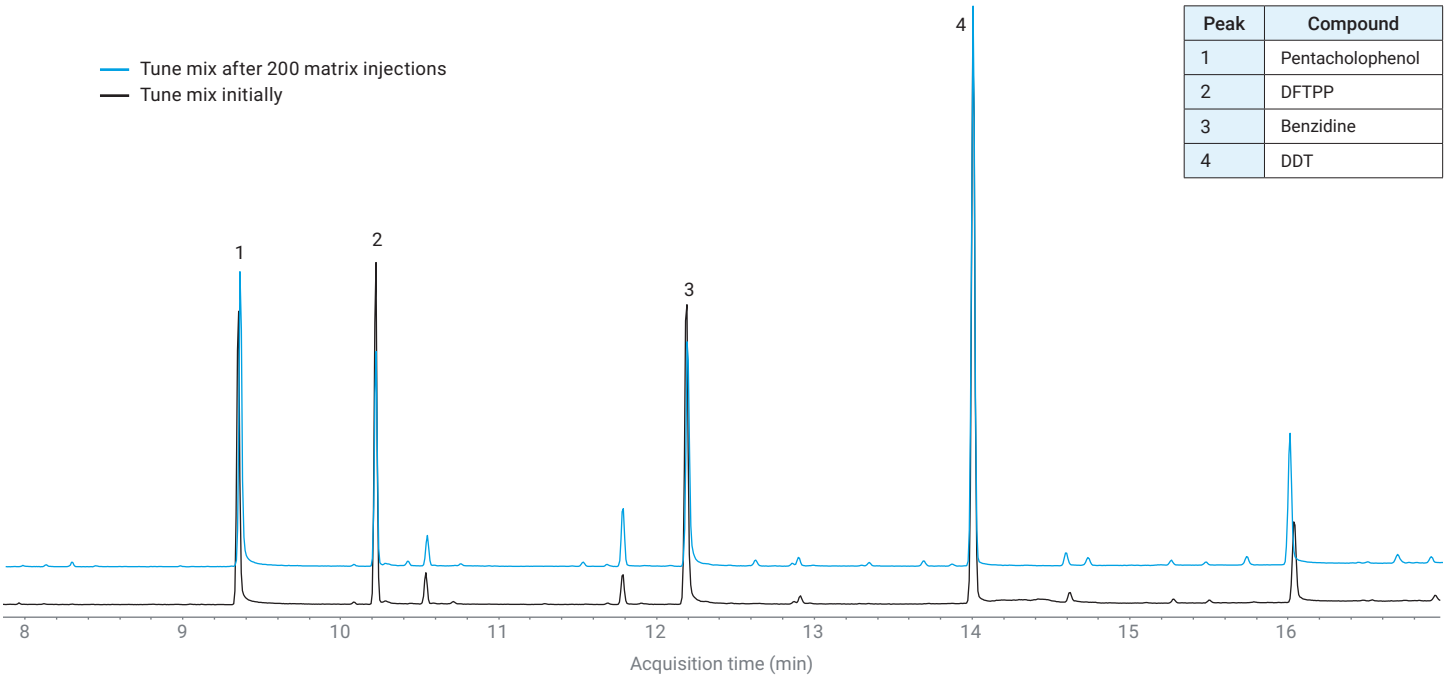


Figure 7. Integrated peak 250 pg on-column pentachlorophenol, analyzed the 5ms-type column Y and an Agilent J&W DB-5Q GC column.

Improved durability leads to consistent chromatography

To stress the robustness of the GC system in a real-world application, a heavy soil matrix was diluted in DCM and analyzed over multiple thermal cycles. DFTPP tuning standard was analyzed every five matrix injections, using %DDT breakdown as an indicator to replace the inlet liner. The inlet liner and septum were replaced every 20 matrix injections, as they failed the method criteria after %DDT breakdown. The peak shapes of pentachlorophenol and benzidine were used as indicators of increased column activity resulting from matrix accumulation and thermal degradation. Figure 8 demonstrates that after 200 matrix injections, the retention times and peak shapes for all test compounds were consistent with minimal data quality reduction. The DB-5Q column is durable to withstand routine, high-throughput cycling shape, even when working with difficult matrices such as soil extracts.



Peak	Compound
1	Pentacholophenol
2	DFTPP
3	Benzidine
4	DDT

Figure 8. DFTPP tune mix initially (black) and after 200 matrix injections (blue) on an Agilent J&W DB-5Q column.

Optimal sensitivity and acquisition flexibility

The improved sensitivity of the HES 2.0 ion source, with the triple off-axis detector configuration, allows for fast MRM speeds. Data can now be acquired in dMRM and scan modes simultaneously. This improvement allows for targeted and untargeted analyses at the same time. The dMRM is useful in setting up MRM methods, as once the retention time is inputted into Agilent MassHunter acquisition software, the dwell time is calculated automatically. While this streamlines the method setup process, if retention times shift from matrix accumulation or thermal instability, it can be helpful to collect scan data and dMRM in the same acquisition method. In Figures 9 and 10, a 10 pg on-column standard was analyzed using dMRM/scan collection mode. Figure 9 demonstrates the extracted scan chromatogram, which is zoomed-in on later-eluting compounds to display their S/N ratios. With the combination of the improved HES 2.0 ion source, along with the improved thermal stability of the DB-5Q column, it is possible to simultaneously acquire selective methods, such as dMRM and scan mode.

Selectivity matching eases column adoption

A standard EPA method 8270 analysis was conducted at 1,000 pg on-column, using the same instrumentation and method conditions, on a DB-5ms UI and a DB-5Q column. The similar selectivity allows for upgrading analytical methods without the need for more development, as seen in Figure 11. Also, with the same selectivity, there is no need to update retention times, which makes the DB-5Q compatible with existing retention time locking libraries.

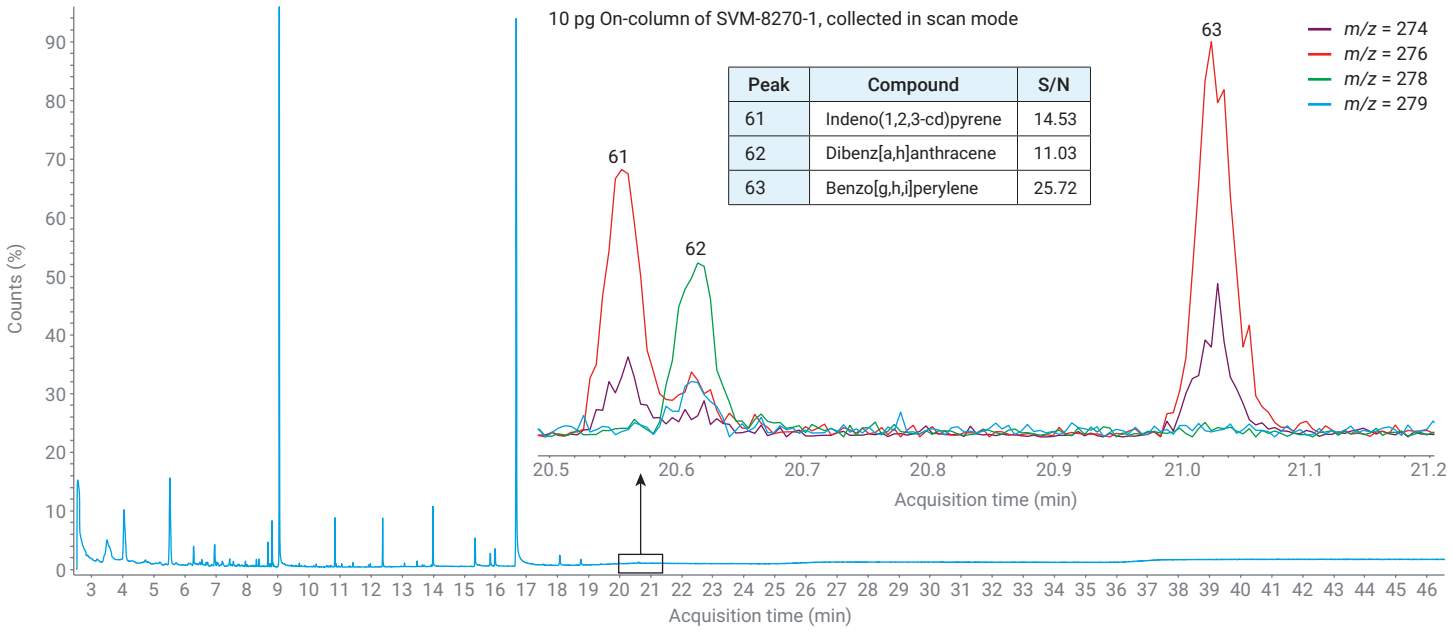


Figure 9. A standard of SVOCs analyzed at 10 pg on column, collected by dMRM/scan mode with the extracted scan data.

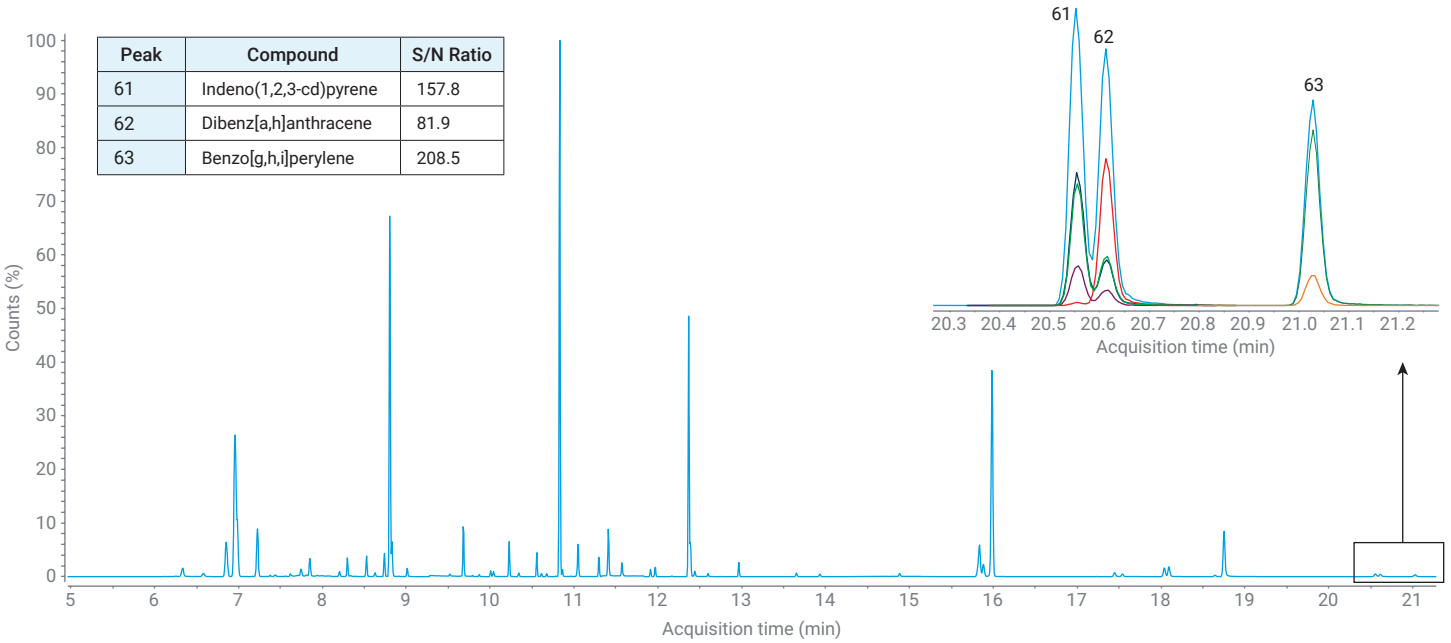


Figure 10. A standard of SVOCs analyzed at 10 pg on column, collected by dMRM/scan mode with the extracted MRMs.

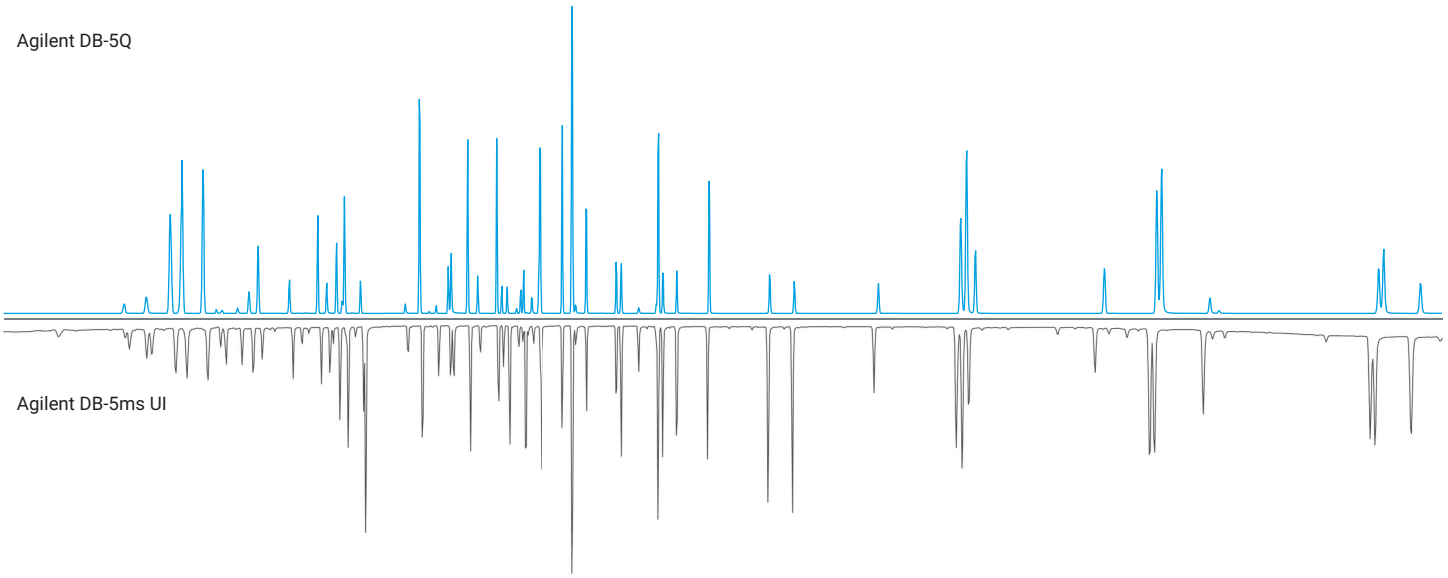


Figure 11. The Agilent J&W DB-5Q has similar selectivity to an Agilent J&W DB-5ms UI, as demonstrated in the analysis of 8,270 compounds.

Conclusion

This application note demonstrates that the Agilent J&W DB-5Q GC column can exceed the performance requirements of EPA method 8270. Agilent Ultra Inert chemistry across the sample flow path will maintain peak symmetry of problematic analytes, leading to improved limits of detection and accurate integration. Ultralow-bleed chemistry stabilizes baselines and reduces interfering bleed ions. High-temperature stability allows for the repeated temperature cycling needed for high throughput methods, even when analyzing heavy, complex soil matrices. The matching selectivity of the J&W DB-5Q compared to the Agilent J&W DB-5ms UI allows for seamless adoption, including compatibility with existing retention time locking libraries. The analytical performance of the DB-5Q coupled with the upgraded Agilent HES 2.0 allows for optimal sensitivity, as well as the ability to perform targeted and nontargeted analyses in tandem.

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