Application Note

Environmental

GC/MS Analysis of Semivolatile Organic Compounds Using an Agilent J&W VF-5ms Intuvo GC Column

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Abstract

To show the performance of the Agilent J&W VF-5ms Intuvo GC column, this Application Note exhibits the stability of this column ramped at maximum speed (250 °C/min) to 330 °C for several hours. US Environmental Protection Agency (EPA) Method 525 standard mixtures were tested using an Agilent Intuvo 9000 GC and an Agilent 5977B MSD coupled system with J&W VF-5ms Intuvo GC columns. Good linearity and repeatability were demonstrated. The Intuvo 9000 GC system with a J&W VF-5ms Intuvo GC column can easily meet the demanding quality control criteria established by US EPA Method 525.2.

Introduction

US EPA Method 525.2[1] is one of the most commonly used methods for semivolatile organic compounds in drinking water. The method features many analytical challenges, including target compounds of varying polarity and stabilities. The analysis of basic or acidic semivolatile environmental pollutants at low concentrations places significant demands on the analytical instrument and gas chromatographic column.

The J&W VF-5ms column is an inert 5 % phenylmethyl column for increased sensitivity, accuracy, and instrument uptime. The column has the lowest guaranteed bleed specification of 1 pA at 325 °C (30 m × 0.25 mm, 0.25 µm). The J&W VF-5ms Intuvo GC column is based on a standard VF-5ms GC column, and is manufactured for the Intuvo 9000 GC system applications. The stability performance of the J&W VF-5ms Intuvo GC column was evaluated at 330 °C in this study. Columns were cycled in an Intuvo 9000 GC-FID system from 100 °C, ramped at maximum speed (250 °C/min) to 330 °C (five minutes) with a total cycle time of approximately 10 minutes (including cooling). Columns were taken out every 500 to 1,000 cycles, and tested for leakage and chromatographic behavior using an Intuvo 9000 GC with an Agilent 5977B MSD system (leakage was also tested using an Agilent helium leak detector). The film thickness demonstrates the phase stability (other column parameters are also stable during the test). Leakage was not detected until the column broke after several hours of heating at 330 °C. Breakage was observed between 389 and 1,462 hours at 330 °C for n = 5 tested columns. This was caused by thermal damage to polyimide on the outside of the fused silica column. This is normally observed after long periods of heating at high temperatures. No leaks were detected at the column coupling before breakage. This Application Note demonstrates that the J&W VF-5ms Intuvo GC column can easily achieve the demanding requirements of US EPA Method 525.2 using an Intuvo 9000 GC with a 5977B MSD system.

Experimental

Chemicals and standards

All EPA 525.2 standards were obtained from ANPEL Scientific Instrument Co. Ltd (Shanghai, China). The GC/MS performance check solution included decafluorotriphenylphosphine (DFTPP), endrin, and 4,4'-DDT, 5 ng/µL each in methylene chloride.

The EPA 525.2 regulated semivolatile organic compound (SVOC) mixture (p/n M-525-REG-EA) was prepared at concentrations of 0.1 to 10 ppm in dichloromethane, containing 5 ppm of ISTDs (acenaphthylene-d_{10}, phenanthrene-d_{10}, and chrysene-d_{12}) and SSs (1,3 dimethyl-2-nitrobenzene, pyrene-d_{10}, triphenyl phosphate, and perylene-d_{12}).

The standards were selected to provide a representative mixture for EPA 525.2. Standards were prepared at a concentration of 2 ppm in dichloromethane, containing 5 ppm of ISTDs (acenaphthylene-d_{10}, phenanthrene-d_{10}, and chrysene-d_{12}) and SSs (1,3 dimethyl-2-nitrobenzene, pyrene-d_{10}, triphenyl phosphate, and perylene-d_{12}). Pentachlorophenol is present at four times the other analyte concentrations, as described in EPA 525.2. Table 1 lists the compounds in the SVOC test mix.

The Agilent GC test mix 82 was diluted to a concentration of 100 µg/mL in dichloromethane. Table 2 lists the compounds in the Agilent GC test mix 82.

Instrumentation

Tables 3 and 4 describe the method instrumentation.

Table 1. Target compounds, surrogates, and internal standards.

No.	Compound	*m/z*
1	Isophorone	82
2	1,3-Dimethyl-2-nitrobenzene(SS)	134
3	Dichlorvos	109
4	Hexachlorocyclopentadiene	237
5	Dimethyl phthalate	163
6	2,6-Dinitrotoluene	165
7	Acenaphthylene	152
8	Acenaphthene-d_{10} (IS1)	164
9	2-Chlorobiphenyl	188
10	2,4-Dinitrotoluene	165
11	Diethyl Phthalate	149
12	Fluorene	166
13	Propachlor	120
14	α-BHC	181
15	2,3-Dichlorobiphenyl	222/152
16	Hexachlorobenzene	284
17	Simazine	201/186
18	Atrazine	200/215
19	β-BHC	181
20	Pentachlorophenol	266
21	γ-BHC	181
22	Diazinone	137/179
23	Phenanthrene-d_{10} (IS2)	188
24	Phenanthrene	178
25	Anthracene	178
26	δ-Lindane	181
27	2,4,5-Trichlorobiphenyl	256
28	Metribuzin	198
29	Alachlor	160
30	Heptachlor	100
31	Di-*n*-butyl phthalate	149
32	2,2',4,4'-Tetrachlorobiphenyl	292
33	Metolachlor	162
34	Aldrin	66
35	Cyanazine	225/68
36	Heptachlor epoxide	81
37	2,2',3',4,6-Pentachlorobiphenyl	326
38	γ-Chlordane	373
39	Butachlor	176/160
40	Pyrene-d_{10} (SS)	212
41	Pyrene	202
42	α-Chlordane	375/373
43	Endosulfan I	195
44	*trans*-Nonachlor	409
45	*p,p'*-DDE	246
46	2,2',4,4',5,6'-Hexachlorobiphenyl	360
47	Dieldrin	79
48	Endrin	67/81
49	Endosulfan II	195
50	*p,p'*-DDD	235/165
51	Endrin aldehyde	67
52	Endosulfan sulfate	272
53	Benzyl butyl phthalate	149
54	*p,p'*-DDT	235/165
55	*Bis*(2-ethylhexyl) adipate	129
56	Triphenyl phosphate(SS)	326/325
57	Endrin ketone	67/317
58	2,2',3,3',4,4',6'-Heptachlorobiphenyl	394/396
59	Benz[a]anthracene	228
60	Chrysene-d_{12} (IS3)	240
61	2,2',3,3',4,5',6,6'-Octachlorobiphenyl	430/428
62	Chrysene	228
63	Methoxychlor	227
64	*Bis*(2-ethylhexyl) phthalate	149
65	*cis*-Permethrin	183
66	*trans*-Permethrin	183
67	Benzo[b]fluoranthene	252
68	Benzo[k]fluoranthene	252
69	Benzo[a]pyrene	252
70	Perylene-d12(SS)	264
71	Indeno[1,2,3-cd]pyrene	276
72	Dibenz[a,h]anthracene	278
73	Benzo[ghi]perylene	276

Table 2. Target compounds in GC test mix 82.

No.	Component
1	1,2-Pentanediol
2	1-Octanol
3	*n*-C11
4	2,6-Dimethylphenol
5	2,6-Dimethylaniline
6	*n*-C12
7	Naphthalene
8	1-Decanol
9	*n*-C13
10	Decanoic acid ME

Table 3. GC/MSD method for chromatographic test with text mix 82.

Instruments	Intuvo 9000 GC and 5977B MSD
Column	J&W VF-5ms Intuvo GC column, 30 m × 0.25 mm, 0.25 µm (p/n CP8944-INT)
Carrier gas	Helium, constant flow mode, 1.2 mL/min
Inlet	250 °C, split mode, 1:100
Oven	120 °C (10 minutes)
Guard Chip	Track oven
MSD	EI, scan
Transfer line	250 °C
MS temperature	230 °C (source); 150 °C (quadrupole)
Injection	1 µL

Results and discussion

Column stability test

Columns were lifetime tested on an Intuvo 9000 GC-FID system. Figure 1 shows an example of the test profile.

Table 4. Intuvo 9000 GC and 5977B MSD method for US EPA 525.2 test mix.

Column	J&W VF-5ms Intuvo GC column, 30 m × 0.25 mm, 0.25 µm (p/n CP8944-INT)
Carrier gas	Helium, constant flow mode, 36 cm/s at 40 °C
Inlet	Split/splitless 300 °C, splitless mode, purge 50 mL/min at 0.5 minutes
Oven	40 °C, at 30 °C/min to 165 °C (2.3 minutes), 10 °C/min to 320 °C (5 minutes)
Guard Chip	Track oven
MSD	EI, scan/SIM
Transfer line	300 °C
Drawout plate	6 mm
MS temperature	300 °C (source); 180 °C (quadrupole)
Scan mode	Mass range (45 to 450 amu)
Tune	DFTPP
Injection	1 µL

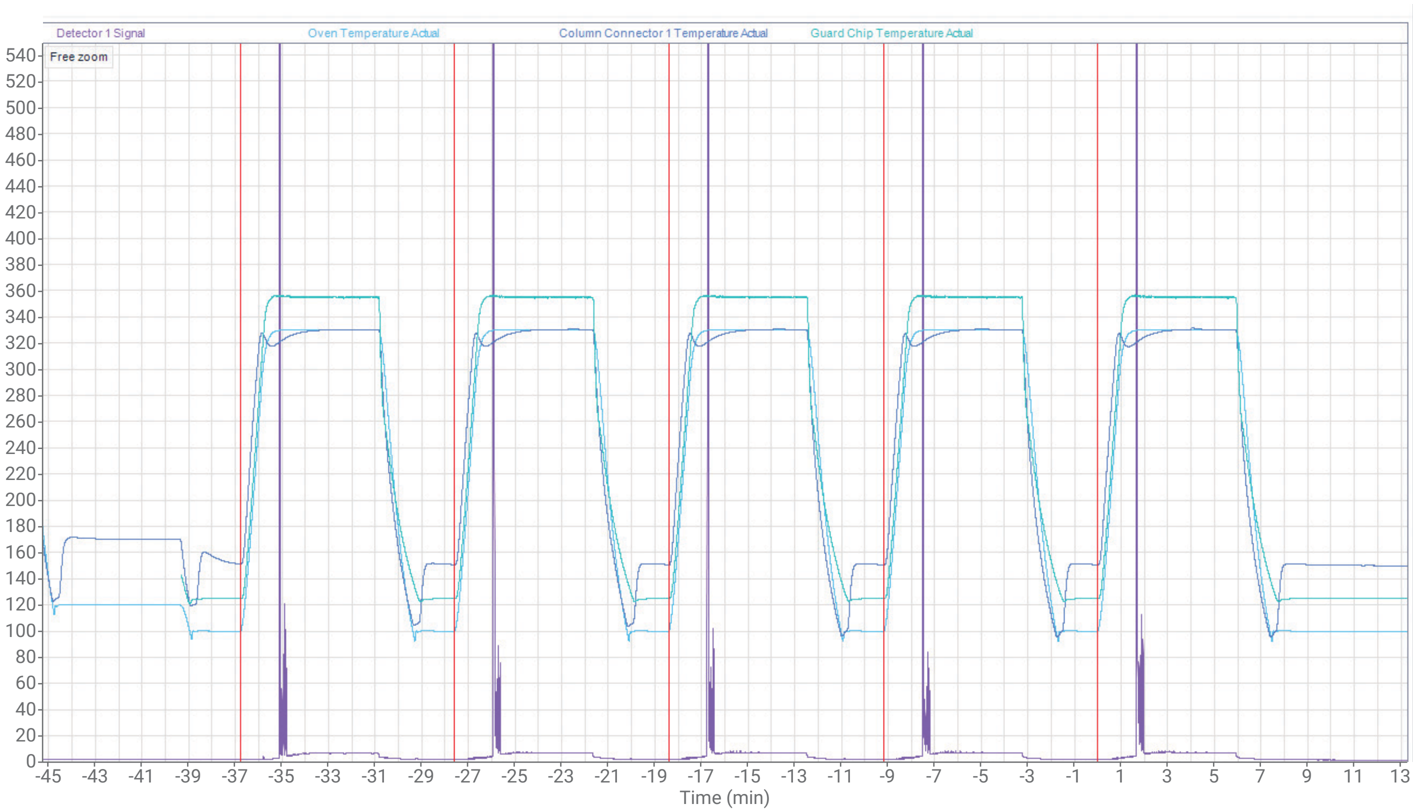


Figure 1. Thermal cycling profile of an J&W VF-5ms Intuvo GC column from 100 to 330 °C at 250 °C/min.

After cycling, the columns were transferred for testing to the Intuvo 9000 GC and 5977 GC/MSD combined system. As an example, Figure 2 shows column 5 giving a stable performance (inertness and separation) during the lifetime test. It also proves that the reinstallation of the column gives reproducible retention times.

Figure 3 shows the stability of the J&W VF-5ms Intuvo GC columns (n = 5) tested at 330 °C. The normalized film thickness is plotted based on the variation in k of the decanoic acid methyl ester, initially normalized at 0.25 µm for all columns.

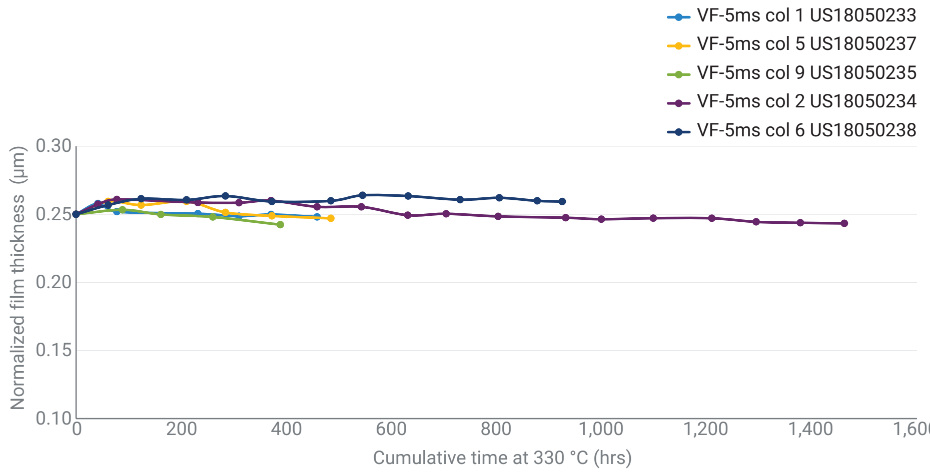


Figure 3. Film thickness stability of J&W VF-5ms Intuvo GC columns (n = 5) tested after cycling to 330 °C for several hours.

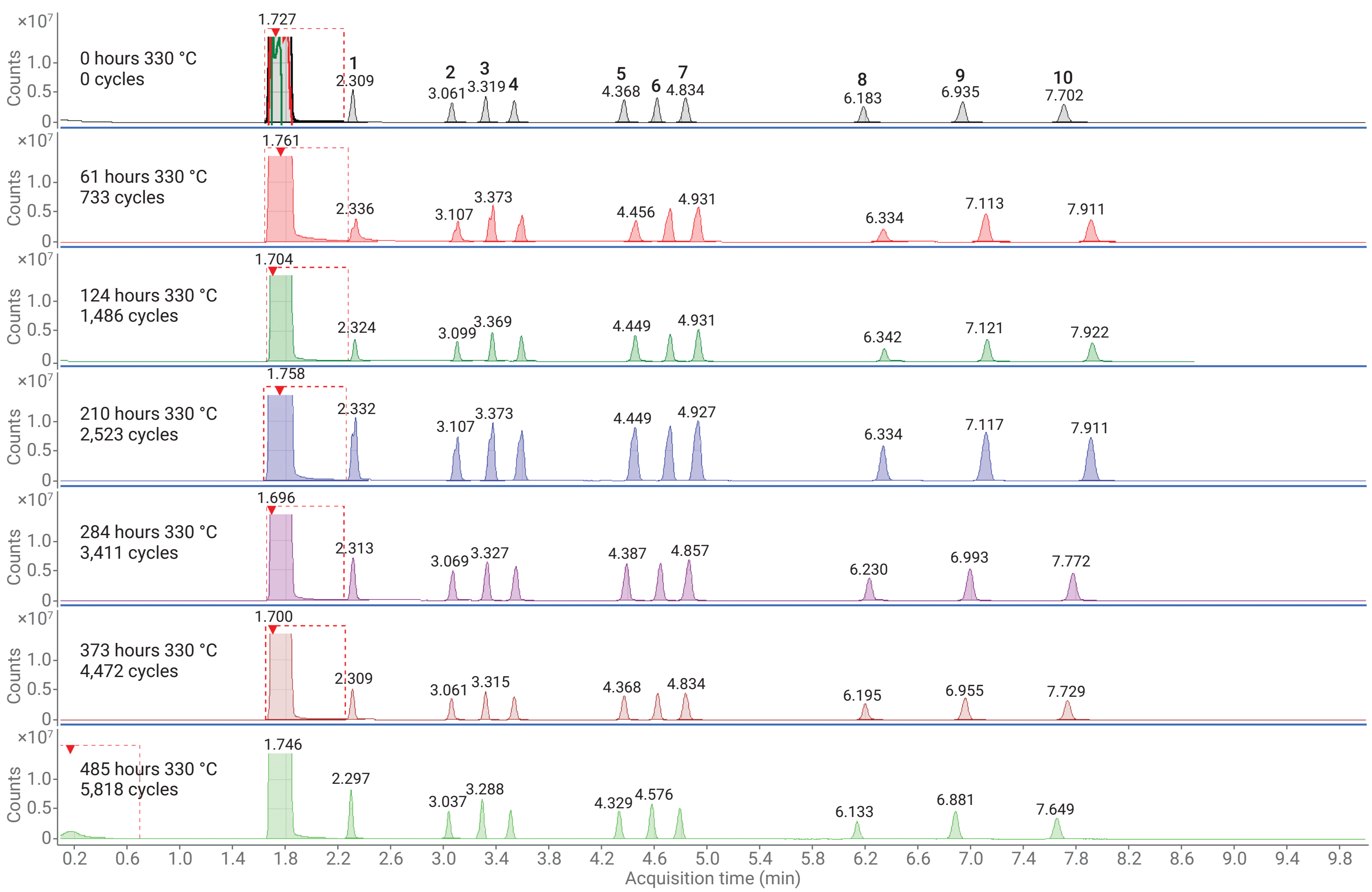
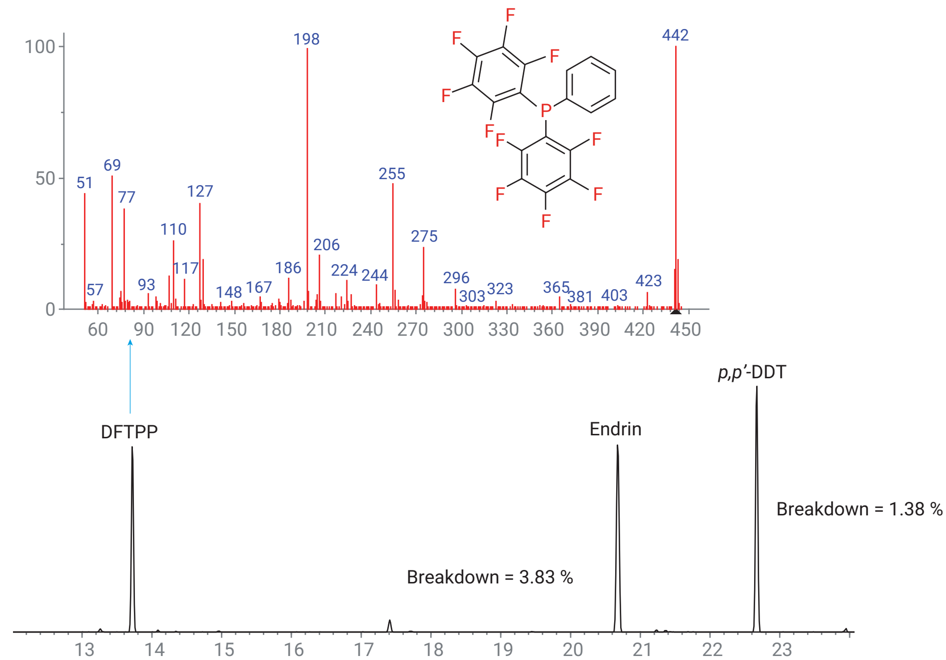


Figure 2. The J&W VF-5ms Intuvo column 5 was tested with test mix 82, and showed stable performance (inertness and separation) over the course of the lifetime test (485 hours at 330 °C, 5,818 cycles).

EPA 525.2 method test

According to EPA Method 525.2, the GC/MS performance check solution, which contains 5 ng/µL of DFTPP, endrin, and 4,4'-DDT in methylene chloride, was tested using an Intuvo 9000 GC coupled with a 5977 GC/MSD with a J&W VF-5ms Intuvo GC column. The system must pass the DFTPP tune check; the degradation products of either endrin or DDT should be less than 20 %.



DFTPP

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Data File : performance-002.D
Acq On    : 30 Jul 2018   17:03
Operator  :
Sample    :
Misc      :
ALS Vial  : 1    Sample Multiplier: 1

Integration File: events.e

Method    : D:\MassHunter\GCMS\4\methods\9000GC-EPA525.M
Title     :
Last Update  :

Spectrum Information: Scan 866
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Target Mass	Rel. to Mass	Lower Limit%	Upper Limit%	Rel. Abn%	Raw Abn	Result Pass/Fail
51	198	30	60	51.2	5613	PASS
68	69	0.00	2	0.0	0	PASS
69	198	0.00	100	40.6	4452	PASS
70	69	0.00	2	0.0	0	PASS
127	198	30	60	46.5	5099	PASS
197	198	0.00	1	0.0	0	PASS
198	198	100	100	100.0	10956	PASS
199	198	5	9	6.6	727	PASS
275	198	10	30	28.4	3111	PASS
365	198	1	100	4.2	459	PASS
441	443	0.01	100	89.2	1818	PASS
442	198	39	100	91.3	10004	PASS
443	442	17	23	20.4	2037	PASS

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Figure 4. Chromatogram of GC/MS performance check solution using a J&W VF-5ms Intuvo GC column.

Figure 4 lists the measured DFTPP ion ratios along with the specified ratios. All measured ratios were within the required limits. The average percent degradation was 1.38 and 3.83 % for 4,4'-DDT and endrin, respectively. The system easily achieves the performance criteria specified in US EPA Method 525.2.

Figure 5 shows a typical chromatogram of a regulated semivolatile mixture tested on an Intuvo 9000 GC and 5977B MSD coupled system with a J&W VF-5ms Intuvo GC column. All 25 regulated compounds show excellent linearity in the 10 ng/mL to 10 µg/mL calibration range. The average correlation coefficient was 0.9978, and the RSD% of the relative response factors were from 5.5 to 13.9 %.

SS 1	1,3-Dimethyl-2-nitrobenzene
SS 2	Pyrene-d10
SS 3	Triphenyl phosphate
SS 4	Perylene-d12
IS 1	Acenaphthene-d10
IS 2	Phenanthrene-d10
IS 3	Chrysene-d12

No.	Compound	R^2
1	Hexachlorocyclopentadiene	0.9998
2	2,6-Dinitrotoluene	0.9969
3	2,4-Dinitrotoluene	0.9979
4	Propachlor	0.9983
5	Hexachlorobenzene	0.9948
6	Simazine	0.9950
7	Atrazine	0.9959
8	Lindane	0.9985
9	Metribuzin	0.9990
10	Alachlor	0.9989
11	Heptachlor	0.9979
12	Metolachlor	0.9988
13	Aldrin	0.9993

No.	Compound	R^2
14	Cyanazine	0.9987
15	Heptachlor epoxide	0.9991
16	γ-Chlordane	0.9945
17	Butachlor	0.9979
18	α-Chlordane	0.9975
19	*trans*-Nonachlor	0.9961
20	Dieldrin	0.9978
21	Endrin	0.9980
22	*Bis*(2-ethylhexyl) adipate	0.9981
23	Methoxychlor	0.9998
24	*Bis*(2-ethylhexyl) phthalate	0.9997
25	Benzo[a]pyrene	0.9989

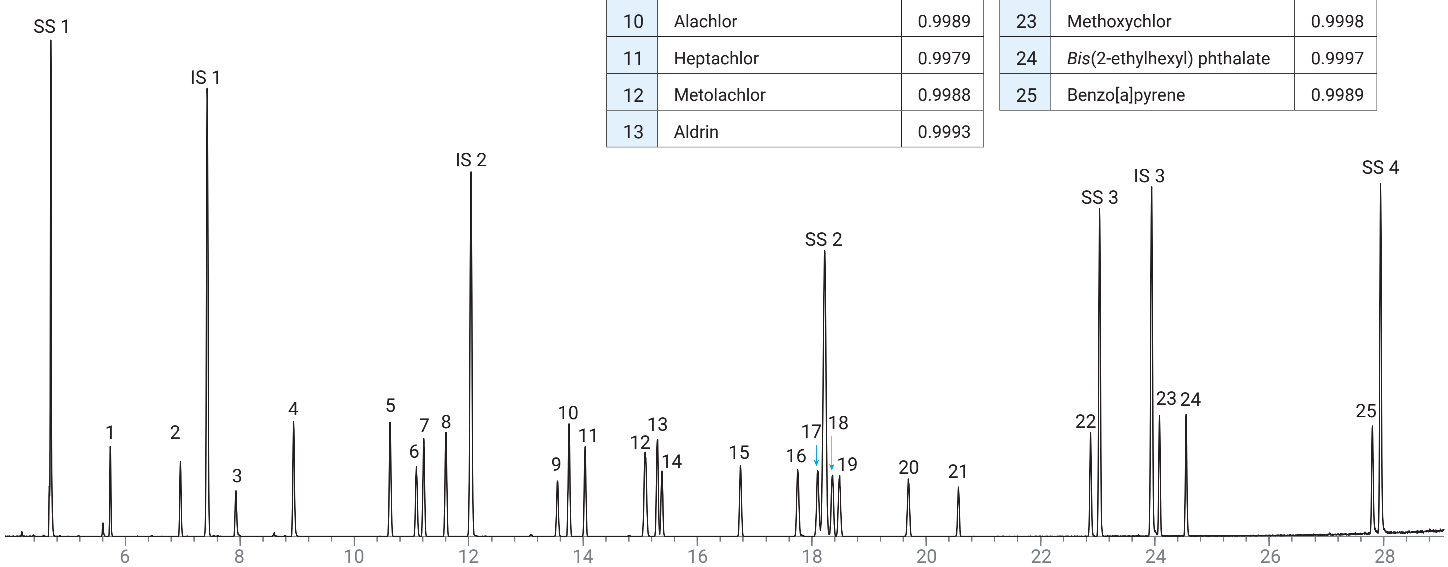

Figure 5. TIC of the regulated semivolatile mixture using a J&W VF-5ms Intuvo GC column.

The SVOC test mix (target compounds at 2 ng/µL, IS/SS at 5 ng/µL) was analyzed with an Agilent 7890B GC and a 5977A GC/MSD with a J&W VF-5ms GC column. The same test mix was analyzed with an Intuvo 9000 GC and a 5977 GC/MSD with a similar GC column. In Figure 6, the J&W VF-5ms Intuvo GC column shows similar selectivity to a standard VF-5ms GC column.

Method 525.2 also specifies chromatographic performance requirements. Baseline resolution of phenanthrene and anthracene is required. Benz[a]anthracene and chrysene should also be separated by a valley whose height is less than 25 % of the average peak height of these two compounds. They are closely eluting compounds with the same quantitation ions. Figure 7 shows that the phenanthrene/anthracene and the benz[a]anthracene/chrysene critical pairs were 100 % baseline resolved on the J&W VF-5ms Intuvo GC column.

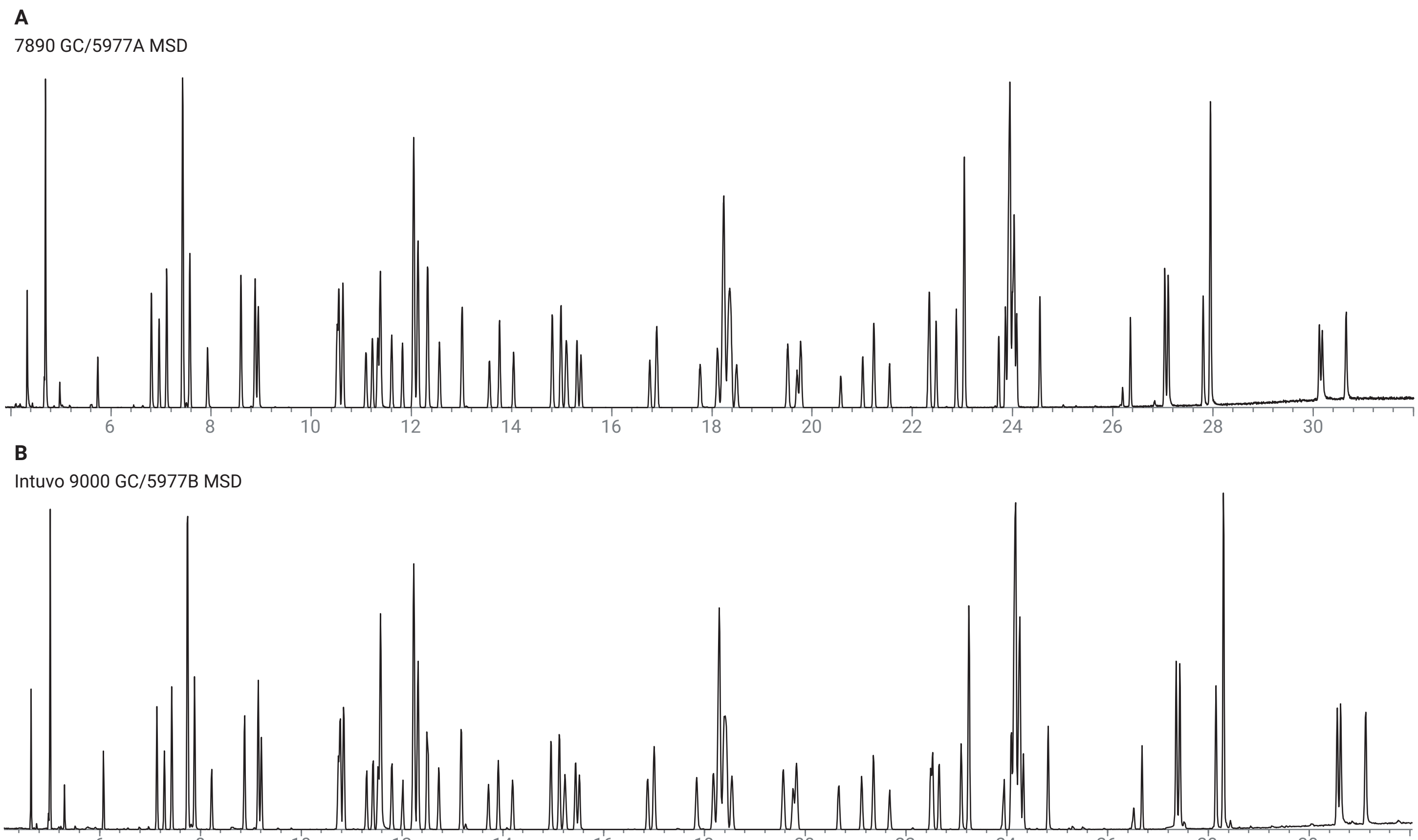

Figure 6. Overlaid chromatograms of the SVOC test mix using a 7890B GC with a 5977A MSD (A) and an Intuvo 9000 GC with a 5977B MSD (B).

Conclusion

This Application Note exhibits the stability of J&W VF-5ms Intuvo GC columns ramped at maximum speed (250 °C/min) to 330 °C for several hours. Column performance and film thickness were stable, and the column was leak tight even after extreme ramping conditions to high temperatures.

The analysis of basic or acidic semivolatile environmental pollutants at low concentrations places significant demands on the analytical instrument and gas chromatographic column. The J&W VF-5ms Intuvo GC column shows superior performance, repeatability, and exceptional thermal stability. This column provides excellent chromatographic performance for semivolatile compounds, including difficult-to-analyze active compounds at trace levels. In addition, the J&W VF-5ms Intuvo GC column demonstrates similar selectivity to standard VF-5ms columns in this study.

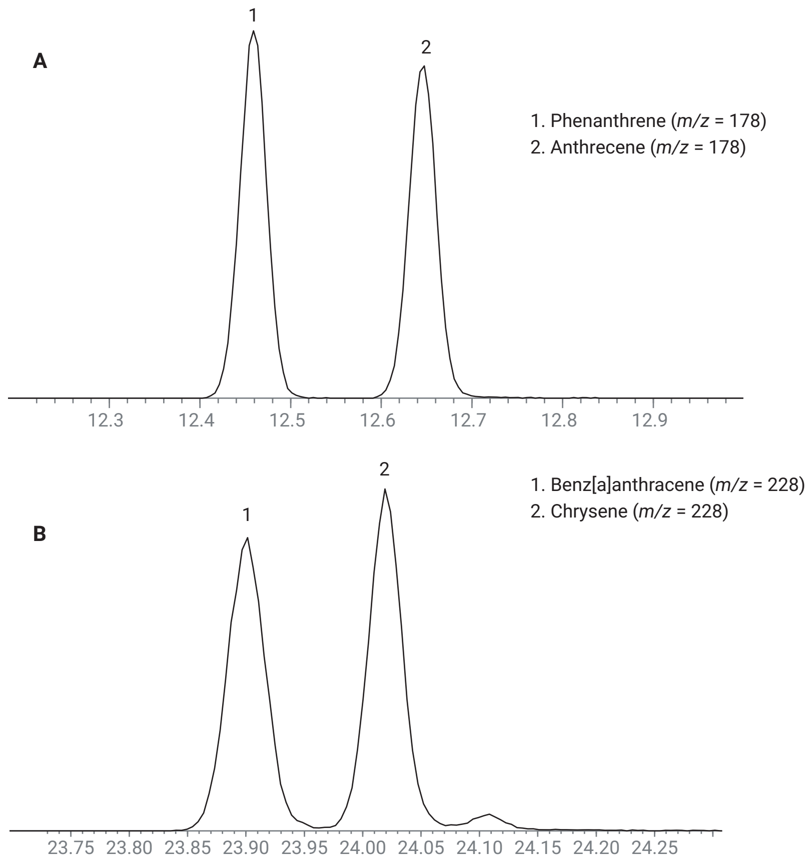

Figure 7. Resolution of critical pairs on a J&W VF-5ms Intuvo GC column.

References

1. US EPA Method 525.2, Methods for the Determination of Organic Compounds in Drinking Water Supplement III, National Exposure Research and Development U.S. EPA, Cincinnati, OH (August **1995**).
2. Endrin and DDT Stability Study for Drinking Water Method EPA 525.2 on the Intuvo. *Agilent Technologies Application Note*, publication number 5991-9277EN, **2018**.

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