environmental

#59125

Applicationsnote

Improving throughput of semivolatile GC/MS analysis using a performance-based measurement system, Rtx®-5Sil MS column, and Uniliner® inlet liner.

Restek has developed a GC/MS method for analyzing semivolatile compounds (e.g., US Environmental Protection Agency [EPA] Method 8270) that will help increase productivity in the lab. The changes include modifying the final extract volume, using a drilled Uniliner® liner, optimizing GC analysis conditions, and modifying the calibration curve to offset the increased extract volume. Following is an explanation of each modification.

1) Increase the final extract volume from 1mL to 5mL.

Increasing the final extract volume will dilute the nonvolatile material extracted from the sample, resulting in less contamination to the injection system and analytical column. This has the potential to allow the GC/MS to stay in calibration longer, and to reduce maintenance time and expense. Also, the increased extract volume will result in better recoveries of low-boiling compounds that may be lost when the extract is concentrated to 1mL.

2) Replace the splitless inlet liner with a drilled Uniliner® liner.

When the sample is injected into the injection port, it expands and comes into contact with the bottom of the injection port. This may cause adsorption or breakdown of the active compounds in the sample. A drilled Uniliner® liner (Figure 1) can be used in place of a standard splitless liner to significantly reduce sample exposure to the injection port. This unique inlet liner can be used for both direct and splitless injections. Because the column is sealed to the liner with a press-tight connection, there is no chance for any sample contact with metal surfaces below the liner. The small hole located on the side of the Unliner® liner allows carrier gas to be routed through the split vent line during the splitless purge operation of the injection system. Because the drilled Uniliner® liner directs more of the sample onto the column, less discrimination of high molecular weight compounds occurs.

Figure 1

The drilled Uniliner® liner provides more accurate results.

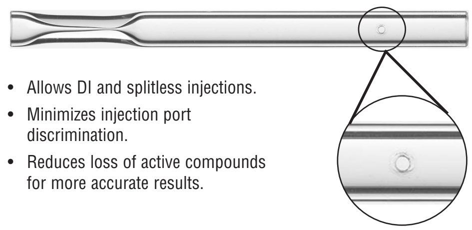
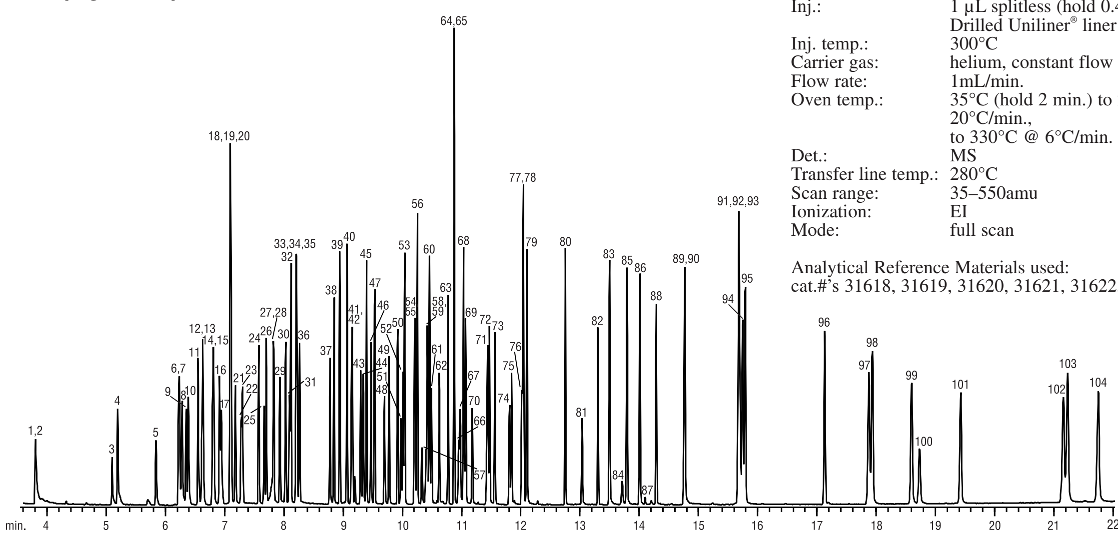


Figure 2

The Rtx®-5Sil MS column, combined with a Siltek™-treated drilled Uniliner® liner, exhibits excellent peak shape and response for semivolatile compounds.

See page 3 for peak list.



Rtx®-5Sil MS, 30m, 0.25mm ID, 0.25µm (cat.# 12723)

Sample:	16µg/mL in methylene chloride, IS @ 8µg/mL
Inj.:	1 µL splitless (hold 0.4 min.), Drilled Uniliner® liner (cat.# 21054)
Inj. temp.:	300°C
Carrier gas:	helium, constant flow
Flow rate:	1mL/min.
Oven temp.:	35°C (hold 2 min.) to 260°C @ 20°C/min., to 330°C @ 6°C/min. (hold 1 min.)
Det.:	MS
Transfer line temp.:	280°C
Scan range:	35–550amu
Ionization:	EI
Mode:	full scan

Analytical Reference Materials used:
cat.#'s 31618, 31619, 31620, 31621, 31622, 31206, 31062, 31063

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3) Use a thin-film column by reducing the concentration of calibration standards.

A thin-film Rtxfi-5Sil MS column can reduce the analysis time to less than 22 minutes for the compounds listed in EPA Method 8270 (see compound list for Figure 2, p.3). The Rtxfi-5Sil MS column features a silarylene stationary phase that exhibits lower bleed and optimized separation of semivolatile compounds. Usually, a thinner film column has less sample capacity than a thicker film column, which can lead to column overload. To prevent column overload, the concentration of the calibration standards should be reduced by $^1/_5$, so that the on-column concentration ranges from 4ng to 32ng. Table I shows the response factors and linearity of active and late-eluting semivolatile compounds. Also, reducing the standard concentration by a factor of 5 off-sets the increased extract volume, resulting in the same reporting limits.

4) Optimize oven temperature programming.

A multi-ramp GC temperature program can optimize the separation of critical compound pairs. Increasing the initial hold time helps resolve early-eluting compounds; then a fast ramp rate can be used through non-critical areas, and a lower ramp rate used to elute later compounds. Extracted ion chromatograms of the closely eluting compounds show resolution between them (Figure 3).

5) Calibration Curve

We used $^1/_5$ the recommended concentration level of Method 8270 1 L injection of 4, 10, 16, 24, and 32ppm standard. The internal standards were also reduced to $^1/_5$ the concentration and are at 8ppm. As seen in Figure 2, the 16ng on-column injection shows excellent signal-to-noise ratio, and low column bleed and injection port discrimination.

Conclusion

A number of techniques can be used to increase sample throughput for the analysis of semivolatile compounds. Increasing extract volume will reduce preparation time and injection port contamination. Using a drilled Unilinerfi injection port liner results in a more inert sample pathway and eliminates injection port discrimination. In addition, the use of a thin-film column reduces analysis time helping laboratories increase sample output.

Table I

Response factors and linearity of active and late-eluting semivolatile compounds.

Compound	Ret. time (min.)	Int. Stnd. for quant.	m/z	4ppm RRF	10ppm RRF	16ppm RRF	24ppm RRF	32ppm RRF	Ave. RRF	5-point %RSD	4-point %RSD (w/o 4ppm)
N-nitrosodimethylamine	3.79	1	74	0.724	0.736	0.775	0.742	0.748	0.745	3	2
pyridine	3.80	1	79	1.055	0.951	1.058	0.967	1.004	1.007	5	5
aniline	6.28	1	93	1.777	1.773	1.962	1.933	1.946	1.878	5	5
N-nitroso-di-n-propylamine	7.12	1	169	0.776	0.746	0.801	0.740	0.770	0.767	3	4
benzoic acid	7.84	2	122	0.148	0.193	0.201	0.203	0.228	0.195	15	7
2,4-dichlorophenol	7.94	2	162	0.215	0.248	0.240	0.249	0.259	0.242	7	3
hexachlorocyclopentadiene	9.14	3	237	0.283	0.310	0.323	0.333	0.357	0.321	9	6
3-nitroaniline	10.21	3	138	0.323	0.318	0.343	0.339	0.348	0.334	4	4
2,4-dinitrophneol	10.34	3	184	0.110	0.139	0.156	0.155	0.169	0.146	16	8
4-nitrophenol	10.41	3	109	0.162	0.168	0.185	0.187	0.202	0.181	9	7
azobenzene	11.07	3	77	1.387	1.446	1.436	1.369	1.414	1.410	2	2
nitrosodiphenylamine	11.04	4	169	0.718	0.698	0.723	0.771	0.738	0.729	4	4
pentachlorophenol	11.81	4	266	0.094	0.122	0.132	0.132	0.146	0.125	15	7
benzidine	13.72	5	184	0.213	0.178	0.188	0.206	0.269	0.211	17	19
benzo(b)fluoranthene	17.88	6	252	1.344	1.448	1.504	1.506	1.628	1.486	7	5
benzo(ghi)perylene	21.76	6	276	1.341	1.428	1.492	1.488	1.593	1.468	6	5
ISTD											
1,4-dichlorobenzene-d14	6.62	1	152								
naphthalene-d8	8.10	2	136								
acenaphthene-d10	10.22	3	164								
phenanthrene-d10	12.02	4	188								
chrysene-d12	15.70	5	240								
perylene-d12	18.73	6	264								

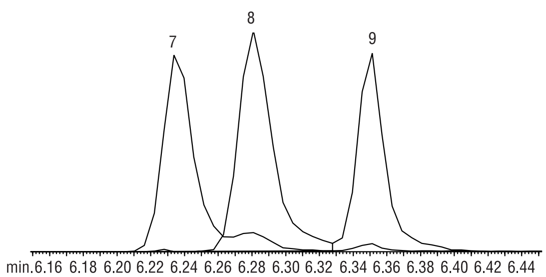
Peak List for Figure 2

1. N-nitrosodimethylamine
2. pyridine
3. methyl methanesulfonate
4. 2-fluorophenol
5. ethyl methanesulfonate
6. phenol-d6
7. phenol
8. aniline
9. bis(2-chloroethyl)ether
10. 2-chlorophenol
11. 1,3-dichlorobenzene
12. 1,4-dichlorobenzene-d4
13. 1,4-dichlorobenzene
14. 1,2-dichlorobenzene
15. benzyl alcohol
16. 2-methylphenol
17. bis(2-chloroisopropyl)ether
18. acetophenone
19. 4-methylphenol/3-methylphenol
20. N-nitroso-di-*n*-propylamine
21. hexachloroethane
22. nitrobenzene-d5
23. nitrobenzene
24. isophorone
25. 2-nitrophenol
26. 2,4-dimethylphenol
27. bis(2-chloroethoxy)methane
28. benzoic acid
29. 2,4-dichlorophenol
30. 1,2,4-trichlorobenzene
31. naphthalene-d8
32. naphthalene
33. 2,6-dichlorophenol
34. 4-chloroaniline
35. hexachloropropene
36. hexachlorobutadiene
37. 4-chloro-3-methylphenol
38. isosafrole
39. 2-methylnaphthalene
40. 1-methylnaphthalene
41. hexachlorocyclopentadiene
42. 1,2,4,5-tetrachlorobenzene
43. 2,4,6-trichlorophenol
44. 2,4,5-trichlorophenol
45. 2-fluorobiphenyl
46. safrole
47. 2-chloronaphthalene
48. 2-nitroaniline
49. 1,4-naphthoquinone
50. dimethylphthalate
51. 1,3-dinitrobenzene
52. 2,6-dinitrotoluene
53. acenaphthylene
54. acenaphthene-d10
55. 3-nitroaniline
56. acenaphthene
57. 2,4-dinitrophenol
58. pentachlorobenzene
59. 4-nitrophenol
60. dibenzofuran
61. 2,4-dinitrotoluene
62. 2,3,4,6-tetrachlorophenol
63. diethyl phthalate
64. fluorene
65. 4-chlorophenyl phenyl ether
66. 4-nitroaniline
67. 4,6-dinitro-2-methylphenol
68. diphenylamine
69. azobenzene
70. 2,4,6-tribromophenol
71. phenacetin
72. 4-bromophenyl phenyl ether
73. hexachlorobenzene
74. pentachlorophenol
75. pentachloronitrobenzene
76. phenanthrene-d10
77. dinoseb
78. phenanthrene
79. anthracene
80. di-*n*-butylphthalate
81. 4-nitroquinoline-1-oxide
82. isodrin
83. fluoranthene
84. benzidine
85. pyrene
86. *p*-terphenyl-d14
87. aramite
88. chlorbenzilate
89. kepone
90. butyl benzyl phthalate
91. benzo(a)anthracene
92. 3,3'-dichlorobenzidine
93. chrysene-d12
94. chrysene
95. bis(2-ethylhexyl)phthalate
96. di-*n*-octyl phthalate
97. benzo(b)fluoranthene
98. benzo(k)fluoranthene
99. benzo(a)pyrene
100. perylene-d12
101. 3-methylcholanthrene
102. indeno(1,2,3-cd)pyrene
103. dibenzo(a,h)anthracene
104. benzo(ghi)perylene

Figure 3

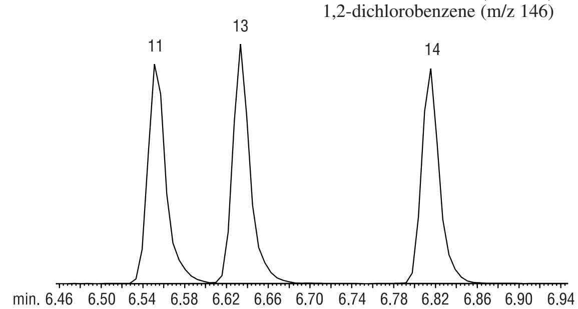
Extracted ion chromatograms show resolution of closely-eluting compounds.

phenol (m/z 94)
aniline (m/z 93)
bis(2-chloroethyl)ether (m/z 93)



GC_EV00562

1,3-dichlorobenzene (m/z 146)
1,4-dichlorobenzene (m/z 146)
1,2-dichlorobenzene (m/z 146)

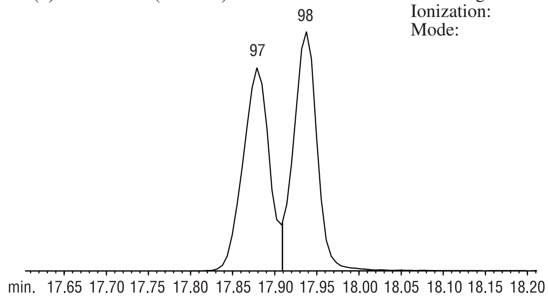


GC_EV00563

Rtx®-5Sil MS, 30m, 0.25mm ID, 0.25µm (cat.# 12723)

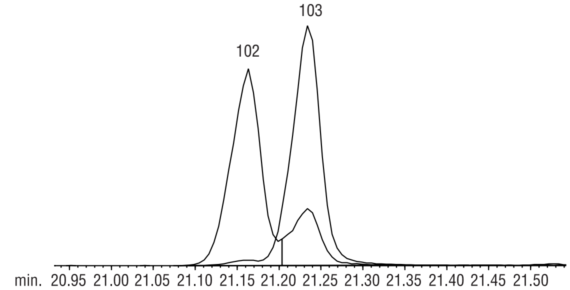
Sample:	16µg/mL in methylene chloride
Inj.:	1µL splitless (hold 0.4 min.), Drilled Uniliner® liner (cat.# 21054)
Inj. temp.:	300°C
Carrier gas:	1mL/min., constant flow
Linear velocity:	34cm/sec.
Oven temp.:	35°C (hold 2 min.) to 260°C @ 20°C/min., to 330°C @ 6°C/min. (hold 1 min.)
Det.:	MS
Transfer line temp.:	280°C
Scan range:	35–550amu
Ionization:	EI
Mode:	full scan

benzo(b)fluoranthene (m/z 252)
benzo(k)fluoranthene (m/z 252)



GC_EV00564

indeno(1,2,3-cd)pyrene (m/z 276)
dibenzo(a,h)antracene (m/z 278)



GC_EV00565

Product Listing

Rtx®-5Sil MS (Fused Silica)

(Equivalent selectivity of Crossbond® 5% diphenyl/95% dimethyl polysiloxane) Stable to 360°C

ID	df (µm)	temp. limits	15-Meter	30-Meter
0.25mm	0.10	-60 to 330/350°C	12705	12708
	0.25	-60 to 330/350°C	12720	12723
	0.50	-60 to 330/350°C	12735	12738
	1.00	-60 to 325/350°C	12750	12753
0.28mm	0.25	-60 to 330/350°C	12790	12793
	0.50	-60 to 330/350°C	12791	12794
	1.00	-60 to 325/350°C	12792	12795
0.32mm	0.10	-60 to 330/350°C	12706	12709
	0.25	-60 to 330/350°C	12721	12724
	0.50	-60 to 330/350°C	12736	12739
	1.00	-60 to 325/350°C	12751	12754
0.53mm	0.50	-60 to 320/340°C	12737	12740
	1.00	-60 to 320/340°C	12752	12755
	1.50	-60 to 310/330°C	12767	12770

Rtx®-5MS (Fused Silica)

(Crossbond® 5% diphenyl - 95% dimethyl polysiloxane) Stable to 360°C

ID	df (µm)	temp. limits	15-Meter	30-Meter	60-Meter
0.25mm	0.10	-60 to 330/350°C	12605	12608	12611
	0.25	-60 to 330/350°C	12620	12623	12626
	0.50	-60 to 330/350°C	12635	12638	12641
	1.00	-60 to 325/350°C	12650	12653	
0.32mm	0.10	-60 to 330/350°C	12606	12609	12612
	0.25	-60 to 330/350°C	12621	12624	12627
	0.50	-60 to 330/350°C	12636	12639	12642
	1.00	-60 to 325/350°C	12651	12654	
0.53mm	0.50	-60 to 320/340°C	12637	12640	
	1.00	-60 to 320/340°C	12652	12655	
	1.50	-60 to 310/330°C	12667	12670	

Innovative Integra-Guard™ Columns

ID	Length	Suffix #	ID	Length	Suffix #
0.25mm	5m	-124	0.32mm	5m	-125
	10m	-127		10m	-128
0.28mm	5m	-243	0.53mm	5m	-126
	10m	-244		10m	-129

Drilled Uniliner® Liners for Agilent 6890 GCs (For 0.32/0.53mm ID Columns)

	Benefits/Uses:	ID**/OD & Length (mm)	cat.# ea.	cat.# 5-pk.
 **Drilled Uniliner®**	allows direct injection when using an EPC-equipped GC	4.0 ID 6.3 OD x 78.5	21054	21055

*** Nominal ID at syringe needle expulsion point.*

Merlin Microseal™ Septa

Microseal™ High-Pressure Septa 400 Series	Merlin#	Similar to Agilent#	cat.#
Nut kit (1 nut, fits 300 & 400 series septa)	403	5182-3445	22809
Standard kit (nut, 2 high-pressure septa)	404	Not offered	22810
Starter kit (nut, 1 high-pressure septum)	405	5182-3442	22811
High-pressure replacement septum (1 septum)	410	5182-3444	22812

Microseal™ Septa, 300 Series	Merlin#	Similar to Agilent#	cat.#
Standard kit (nut, 2 septa)	304	5181-8833	22813
Starter kit (nut, 1 septum)	305	5181-8816	22814
Microseal replacement septum (1 septum)	310	5181-8815	22815
Replacement PTFE washers (2-pk.)	311	5181-0853	22808