

Optimized, 17-Minute GC Analysis of Semivolatiles

Using a 0.25mm ID Rtx®-5Sil MS Column

By Christopher English, Innovations Group Leader

- Excellent column for many methods, including US EPA methods 8270, 625, and 525.
- Greater on-column sample capacity, longer lifetimes than columns with thinner phase films.
- Analysis optimized for scanning mass spectrometers (ion trap or quadrupole).

Restek Innovations chemists have evaluated many combinations of stationary phase, column dimensions, and analytical conditions for analyzing environmental semivolatile compounds such as those listed in US Environmental Protection Agency Method 8270. Using a typical benchtop quadrupole mass spectrometer, we have achieved a 15-minute analysis, while maintaining a scan rate of at least 5 scans per target analyte.¹ Time-of-flight mass spectrometers (TOFMS) make analysis times under 9 minutes achievable,² because they can scan more than 100 times faster than quadrupole instruments.

After developing this analysis on a 0.18mm ID, 0.36µm column,³ our chemists decided to experiment with a column of standard ID and phase film dimensions (0.25mm ID / 0.50µm film), in an attempt to establish a similarly rapid analysis on a larger bore column. The column they chose was a 30m x 0.25mm ID x 0.5µm Rtx®-5Sil MS column. The target compound list included our 8270 MegaMix™ and Appendix IX Mix #2 mixes, plus internal standards and surrogates—a total of 117 compounds. Advantages of using a 0.25mm ID column with a 0.5µm phase film include increased sample capacity and longer column lifetime, combined with rapid analyses.

Injection Port Optimization

The first step in the experiment was to optimize conditions in the injection port. We found that the inlet liner and seal remain inert longer when we inject only 0.5µL of sample into the injection port. This increases the number of passing calibration checks per liner and seal, and so reduces instrument downtime. The key to maintaining sensitivity when injecting smaller amounts of sample is to attain the most efficient sample transfer possible: we determined a 2mm ID inlet liner most efficiently transfers 0.5µL samples.

Splitless hold time also is important; a change of only several seconds can significantly affect the amount of sample ultimately delivered onto the column. We discovered that a pulsed splitless time, using a 0.4-minute pulse at 30psi (normal column backpressure is 8.8psi at 50°C), dramatically improves sample transfer onto the column. Making the pulse longer than the splitless hold time allows excess solvent to be swept away quickly and dramatically sharpens resolution of the early eluting Method 8270 Appendix IX compounds, such as 1,4-dioxane.

Other Conditions

After optimizing conditions in the injection port, we adjusted other analytical conditions to deliver a fast, rugged analysis on a 0.25mm ID column. In combination, a constant flow of 1.1mL/min., a short initial hold time (0.5 min.) and a fast initial temperature ramp rate (25°C/min.) elute benzo(ghi)perylene in 16.5 minutes. The final temperature ramp rate is a relatively slow 4°C/min., to better resolve benzo(b)fluoranthene and benzo(k)fluoranthene.

With all conditions optimized, the 117 target compounds in our sample are well resolved by quantification ion in one analysis (Figure 1, page 6).

8270 MegaMix™ (76 components)

acenaphthene	2,4-dinitrophenol
acenaphthylene	2,4-dinitrotoluene
aniline	2,6-dinitrotoluene
anthracene	di- <i>n</i> -butyl phthalate
azobenzene**	di- <i>n</i> -octyl phthalate
benzo(a)anthracene	diphenylamine***
benzo(a)pyrene	fluorene
benzo(b)fluoranthene	fluoranthene
benzo(ghi)perylene	hexachlorobenzene
benzo(k)fluoranthene	hexachlorobutadiene
benzyl alcohol	hexachlorocyclopentadiene
benzyl butyl phthalate	hexachloroethane
bis 2-ethylhexyl adipate	indeno(1,2,3-cd)pyrene
bis(2-chloroethoxy)methane	isophorone
bis(2-chloroethyl)ether	1-methylnaphthalene
bis(2-chloroisopropyl)ether	2-methylnaphthalene
bis(2-ethylhexyl)phthalate	2-methylphenol
4-bromophenyl phenyl ether	3-methylphenol
carbazole	4-methylphenol
4-chloroaniline	naphthalene
4-chloro-3-methylphenol	2-nitroaniline
2-chloronaphthalene	3-nitroaniline
2-chlorophenol	4-nitroaniline
4-chlorophenyl phenyl ether	nitrobenzene
chrysene	2-nitrophenol
dibenzo(a,h)anthracene	4-nitrophenol
dibenzofuran	N-nitrosodimethylamine
1,2-dichlorobenzene	N-nitroso-di- <i>n</i> -propylamine
1,3-dichlorobenzene	pentachlorophenol
1,4-dichlorobenzene	phenanthrene
2,4-dichlorophenol	phenol
diethyl phthalate	pyrene
dimethyl phthalate	pyridine
2,4-dimethylphenol	2,3,4,6-tetrachlorophenol
1,2-dinitrobenzene	2,3,5,6-tetrachlorophenol
1,3-dinitrobenzene	1,2,4-trichlorobenzene
1,4-dinitrobenzene	2,4,5-trichlorophenol
4,6-dinitro-2-methylphenol	2,4,6-trichlorophenol

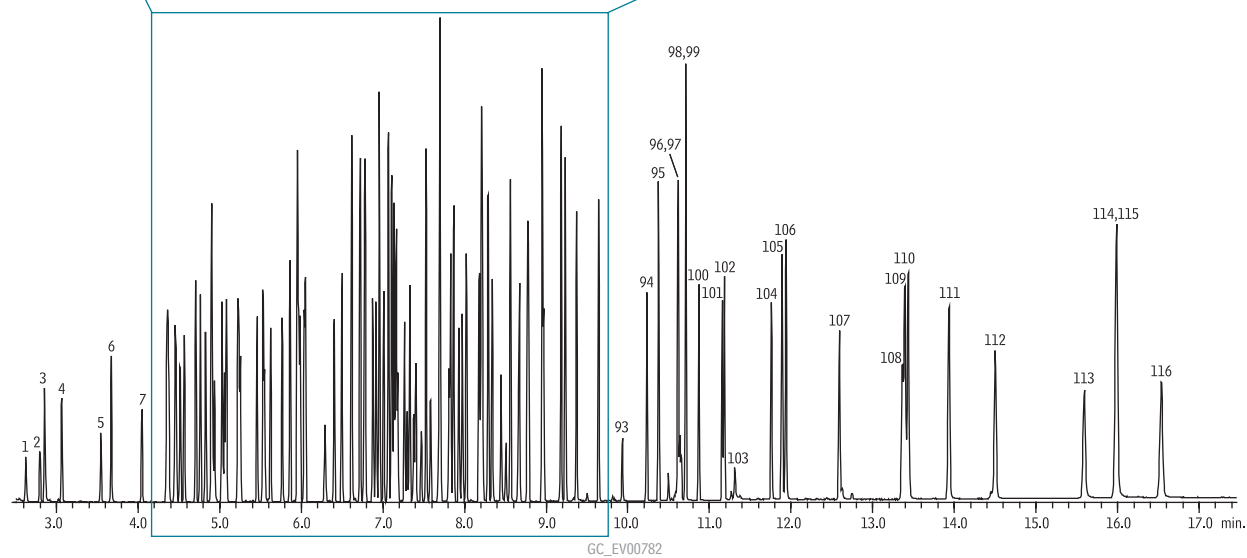
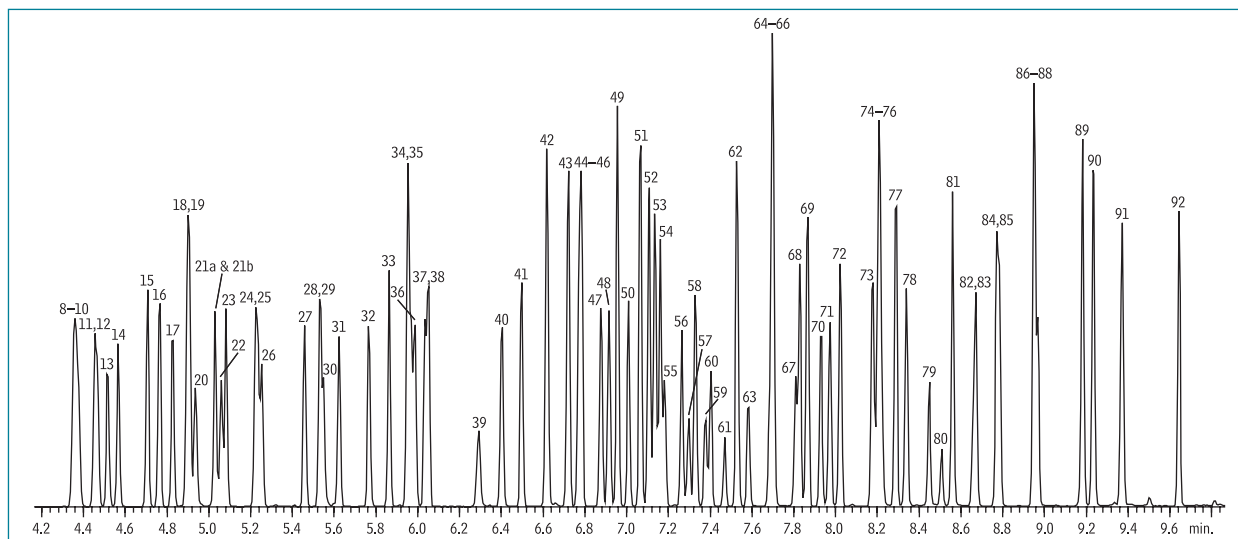
1,000µg/mL each in methylene chloride, 1mL/ampul*
cat. # 31850 (ea.)

*3-methylphenol and 4-methylphenol concentration is 500µg/mL.

**1,2-diphenylhydrazine (8270-listed analyte) decomposes to azobenzene (mix component).

***N-nitrosodiphenylamine (8270-listed analyte) decomposes to diphenylamine (mix component).

Figure 1 117 semivolatile compounds rapidly eluted and well resolved using a 0.25mm ID x 0.50µm Rtx®-5Sil MS column.



1. 1,4-dioxane	39. ε-caprolactam	78. azobenzene
2. N-nitrosodimethylamine	40. 4-chloro-3-methylphenol	79. 2,4,6-tribromophenol
3. pyridine	41. isosafrole (<i>cis</i>)	80. 1,3,5-trinitrobenzene
4. ethyl methacrylate	42. 2-methylnaphthalene	81. phenacetin
5. methyl methanesulfonate	43. 1-methylnaphthalene	82. diallate
6. 2-fluorophenol	44. hexachlorocyclopentadiene	83. 4-bromophenyl phenyl ether
7. ethyl methanesulfonate	45. isosafrole (<i>trans</i>)	84. hexachlorobenzene
8. phenol-d6	46. 1,2,4,5-tetrachlorobenzene	85. atrazine
9. phenol	47. 2,4,6-trichlorophenol	86. pronamide
10. benzaldehyde	48. 2,4,5-trichlorophenol	87. pentachlorophenol
11. aniline	49. 2-fluorobiphenyl	88. pentachloronitrobenzene
12. bis(2-chloroethyl)ether	50. 2-chloronaphthalene	89. phenanthrene
13. pentachloroethane	51. biphenyl	90. anthracene
14. 2-chlorophenol	52. safrole	91. carbazole
15. 1,3-dichlorobenzene	53. 1-chloronaphthalene	92. di- <i>n</i> -butylphthalate
16. 1,4-dichlorobenzene	54. diphenyl ether	93. 4-nitroquinoline-N-oxide
17. benzyl alcohol	55. 2-nitroaniline	94. isodrin
18. 2-methylphenol	56. 1,4-naphthoquinone	95. fluoranthene
19. 1,2-dichlorobenzene	57. 1,4-dinitrobenzene	96. pyrene
20. bis(2-chloroisopropyl)ether	58. dimethylphthalate	97. benzidine
21a. 4-methylphenol	59. 1,3-dinitrobenzene	98. <i>p</i> -terphenyl-d14
21b. 3-methylphenol	60. 2,6-dinitrotoluene	99. Aramite
22. N-nitroso-di- <i>n</i> -propylamine	61. 1,2-dinitrobenzene	100. chlorobenzilate
23. acetophenone	62. acenaphthylene	101. benzyl butyl phthalate
24. hexachloroethane	63. 3-nitroaniline	102. bis(2-ethylhexyl)adipate
25. nitrobenzene-d5	64. 2,4-dinitrophenol	103. Kepone
26. nitrobenzene	65. acenaphthene	104. bis(2-ethylhexyl)phthalate
27. isophorone	66. 4-nitrophenol	105. benzo(a)anthracene
28. 2,4-dimethylphenol	67. 2,4-dinitrotoluene	106. chrysene
29. 2-nitrophenol	68. pentachlorobenzene	107. di- <i>n</i> -octyl phthalate
30. diallate (isomer)	69. dibenzofuran	108. 7,12-dimethylbenzo(a)anthracene
31. bis(2-chloroethoxy)methane	70. 2,3,5,6-tetrachlorophenol	109. benzo(b)fluoranthene
32. 2,4-dichlorophenol	71. 2,3,4,6-tetrachlorophenol	110. benzo(k)fluoranthene
33. 1,2,4-trichlorobenzene	72. diethyl phthalate	111. benzo(a)pyrene
34. naphthalene	73. 4-chlorophenyl phenyl ether	112. 3-methylcholanthrene
35. 4-chloroaniline	74. 4-nitroaniline	113. dibenzo(a,j)acridine
36. 2,6-dichlorophenol	75. fluorene	114. indeno(1,2,3- <i>cd</i>)pyrene
37. hexachloropropene	76. 4,6-dinitro-2-methylphenol	115. dibenzo(a,h)anthracene
38. hexachlorobutadiene	77. diphenylamine	116. benzo(ghi)perylene

Column: Rtx®-5Sil MS 30m, 0.25mm ID, 0.50µm (cat.# 12738)
Sample: US EPA Method 8270D Appendix IX mix
8270 MegaMix™ (cat.# 31850)
Appendix IX Mix #2 (cat.#31806)
Acid Surrogate Mix (4/89 SOW) (cat.# 31063)
B/N Surrogate Mix (4/89 SOW) (cat.# 31062)
Inj.: 0.5µL, splitless, 100ppm each compound (50ng on column)
2mm Cyclo double gooseneck splitless inlet liner
(cat.# 20907), 0.3 min. splitless hold time, 0.4 min.
pressure pulse @ 30psi
Inj. temp.: 250°C
Carrier gas: helium, constant flow
Flow rate: 1.1mL/min.
Oven temp.: 50°C (hold 0.5 min.) to 310°C @ 25°C/min. (hold 0 min.)
to 330°C @ 4°C/min. (hold 4 min.)
Det.: MS
Det. temp.: 280°C
Transfer line temp.: 280°C
Scan range: 35-550 amu
Solvent Delay: 1 min.
Tune: DFTPP
Ionization: EI
Instrument: Agilent 6890 / 5973

Conclusions

Complex mixtures of semivolatiles can be resolved on an Rtx®-5Sil MS column in a conventional 30m x 0.25mm ID x 0.50µm configuration, without sacrificing the speed associated with shorter, thin phase film columns, and with greater sample capacity. Restek can provide the columns, reference mixes, inlet and other accessories, and technical help you need for reliable, problem-free analyses of semivolatiles by US EPA or other methodology.

References

1. *Fast Analysis of Semivolatile Organic Analytes*, Restek Advantage, 2004, Vol.2 p.2.
 2. *Nine-Minute Analysis of Semivolatile Organic Compounds*, Restek Advantage, 2005, Vol.1 p. 8.
 3. *Fast GC/MS Analysis of Semivolatile Organic Compounds*, Restek Advantage, 2005, Vol 1 p. 14.
- References available on request.

Appendix IX Mix #2 (32 components)

acetophenone	hexachloropropene
Aramite	isodrin
atrazine	isosafrole (<i>cis</i> & <i>trans</i>)
benzaldehyde	kepone
biphenyl	3-methylcholanthrene
ε-caprolactam	methyl methanesulfonate
chlorobenzilate	1,4-naphthoquinone
1-chloronaphthalene	4-nitroquinoline-N-oxide
diallate	phenacetin
dibenzo(a,i)acridine	pentachloroethane
2,6-dichlorophenol	pentachloronitrobenzene
7,12-dimethylbenzo(a)anthracene	pronamide
1,4-dioxane	safrole
diphenyl ether	1,2,4,5-tetrachlorobenzene
ethyl methacrylate	1,3,5-trinitrobenzene
ethyl methanesulfonate	

1,000µg/mL each in methylene chloride, 1mL/ampul
cat. # 31806 (ea.)

Acid Surrogate Mix (4/89 SOW)

2-fluorophenol	2,4,6-tribromophenol
phenol-d6	

2,000µg/mL each in methanol, 1mL/ampul
cat. # 31025 (ea.)

10,000µg/mL each in methanol, 1mL/ampul
cat. # 31063 (ea.)

10,000µg/mL each in methanol, 5mL/ampul
cat. # 31087 (ea.)

B/N Surrogate Mix (4/89 SOW)

2-fluorobiphenyl	<i>p</i> -terphenyl-d14
nitrobenzene-d5	

1,000µg/mL each in methylene chloride, 1mL/ampul
cat. # 31024 (ea.)

5,000µg/mL each in methylene chloride, 1mL/ampul*
cat. # 31062 (ea.)

5,000µg/mL each in methylene chloride, 5mL/ampul*
cat. # 31086 (ea.)

*Requires warming and sonication before use.

Rtx®-5Sil MS Columns (fused silica)

(Selectivity equivalent to Crossbond® 5% diphenyl / 95% dimethyl polysiloxane)

ID	df (µm)	temp. limits	length	cat. #
0.18mm	0.18	-60 to 325°C	20-Meter	42702
0.18mm	0.36	-60 to 330/350°C	20-Meter	42704
0.25mm	0.25	-60 to 330/350°C	30-Meter	12723
0.25mm	0.50	-60 to 330/350°C	30-Meter	12738