Nine-Minute Analysis of Semivolatile Organic Compounds

Using an Rtx®-5Sil MS Capillary GC Column in Combination with TOFMS

by Frank Dorman, Ph.D., Director of Technical Development

- Monitor 81 analytes and internal standards in 9 minutes.
- Excellent resolution of critical target compounds.
- At least 20 scans for each peak.
- Use split injection, to minimize injection problems and extend reporting limits.

Analysts in many environmental laboratories struggle to increase sample throughput. Fast GC techniques have enabled analysis times to be decreased, but methods employing mass spectrometric detection often can't make use of these techniques, due to scan-speed limitations of commonly used instruments. While some manufacturers have improved the scan rates of their instruments, methods employing either quadrupole or ion-trap mass filters are limited by the residence time of an ion as it passes through the detector. In most cases, the scan-speed limitations of these devices preclude very rapid analyses of a wide range of compounds, such as the semivolatiles in environmental matrices, even though current capillary column and gas chromatograph technology would allow fast separations.

In order to adequately characterize a chromatographic peak as it elutes from the column, most methods require, at a minimum, 6 to 7 data points (scans) across the peak. Certainly, additional data points yield a better peak profile, and thus improved precision, so it is always better to have more than the 6 to 7 scan minimum. For a typical semivolatiles analysis, this correlates to a minimum scan rate of approximately 2 scans/second, with peak widths of 3 to 5 seconds considered "typical." It is important to note that this rate must be maintained over the entire expected mass range, or identifications, especially for unknown compounds, will be compromised. As faster GC techniques are investigated, peak widths are reduced and, as a result, the detector struggles to collect data at a rate that is fast enough to adequately characterize the peak profile. Unfortunately, for most GC/MS systems, this dictates a total analysis time of about 15 minutes, or longer, given the characteristics of most instruments used in this application.

In a recent collaboration, Restek and LECO Corporation developed a much faster analysis of common semivolatile organic compounds by taking advantage of both fast GC column technology and the speed of acquisition of the time-of-flight mass spectrometer (TOFMS). Using a 10 meter, 0.18μm ID, 0.18μm film Rtx®-5Sil MS fast GC column (phase optimized for semivolatiles analysis; low bleed) and TOFMS, the analysis time for this separation was less than 10 minutes, and at least 20 scans were recorded for each peak. Table 1 lists the retention times for the semivolatile target compounds, in seconds, and each compound had approximately a 1-second peak width at the base.

Figure 1 is the total ion chromatogram of a mid-level calibration standard of these compounds, analyzed under the conditions listed with the figure. Another valuable benefit of TOFMS is that there is a sensitivity improvement relative to most scanning instruments, enabling the analyst to use split injection. Split injection typically creates fewer maintenance issues than splitless injection, due to the much shorter residence time of the analytes in the injector, and produces narrower peaks, increasing resolution. For this analysis, theTOFMS system offers sensitivity sufficient to allow calibration beyond the 20 to 160ng/μL "normal" calibration range, to a range of 0.2 to 160ng/μL, even at a 50:1 split ratio, thus allowing laboratories to extend reporting limits (sensitivity) to lower levels.

Finally, extracts of actual samples were analyzed using this method, and results were compared to values obtained by a commercial environmental laboratory using conventional GC/MS. The results compared well, even for samples with high levels of non-target contaminants. Detailed information about this work is available on request, and will be presented at the 2005 Pittsburgh Conference.[1]

If your laboratory is analyzing semivolatile organic compounds by GC/MS, and you are interested in significantly increasing sample throughput by reducing analysis time to less than 10 minutes, we urge you to request a copy of the complete report of this work, and/or attend our presentation at the Pittsburgh Conference.

Pittcon® presentation

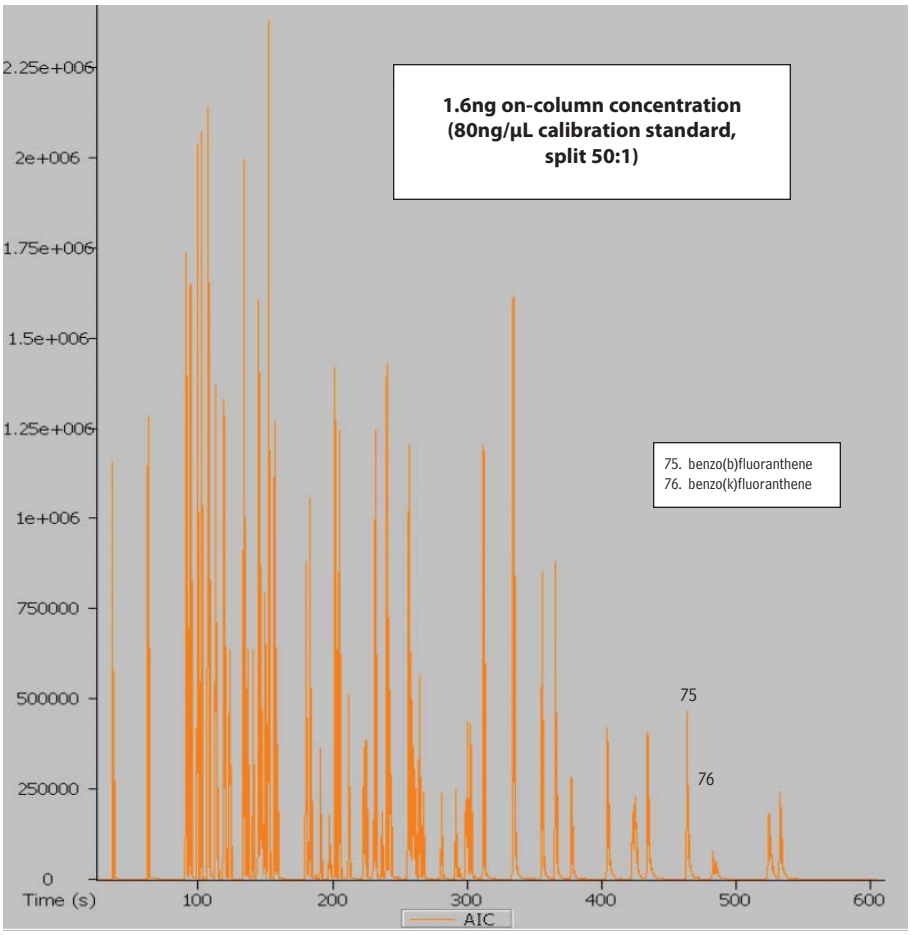
1. Improved Sensitivity and Analysis Time for Semivolatile Organic Compounds, Using GC-TOFMS: Can this Analysis Really be Performed in Less Than 10 Minutes? Frank L. Dorman, Jack W. Cochran (LECO Corporation), Gary B. Stidsen, Chris M. English, Michael S. Wittrig
PittCon 2005, Monday, Feb. 28. Oral Session 380, Room S210C, presentation 380-3, 2:10 pm.

Acknowledgement
This investigation was conducted in collaboration with Jack Cochran, Director of Separation Science, LECO Corporation, Las Vegas, NV.

Table 1 Absolute retention times for semivolatile target compounds, in seconds.

	Compound	T_R (sec.)
1.	N-nitrosodimethylamine	36.5
2.	2-fluorophenol	62.7
3.	phenol-d6	90.9
4.	phenol	91.3
5.	2-chlorophenol-d4	93.9
6.	bis(2-chloroethyl) ether	94.2
7.	2-chlorophenol	94.5
8.	1,3-dichlorobenzene	99.6
9.	1,4-dichlorobenzene-d4	101.8
10.	1,4-dichlorobenzene	102.4
11.	1,2-dichlorobenzene-d4	107.0
12.	1,2-dichlorobenzene	107.6
13.	benzyl alcohol	108.1
14.	2-methylphenol	112.9
15.	bis(2-chloroisopropyl) ether	113.7
16.	N-nitrosodipropylamine	118.8
17.	4-methylphenol	119.3
18.	hexachloroethane	119.8
19.	nitrobenzene-d5	123.1
20.	nitrobenzene	123.9
21.	isophorone	134.1
22.	2-nitrophenol	136.7
23.	2,4-dimethylphenol	140.7
24.	bis(2-chloroethoxy) methane	145.0
25.	2,4-dichlorophenol	146.8
26.	benzoic acid	148.0
27.	1,2,4-trichlorobenzene	149.8
28.	naphthalene-d8	151.6
29.	naphthalene	152.5
30.	4-chloroaniline	156.8
31.	hexachlorobutadiene	159.1
32.	4-chloro-3-methyl phenol	180.3
33.	2-methylnaphthalene	183.4
34.	hexachlorocyclopentadiene	190.9
35.	2,4,6-trichlorophenol	197.5
36.	2,4,5-trrichlorophenol	198.5
37.	2-fluorobiphenyl	201.7
38.	2-chloronaphthalene	205.1
39.	2-nitroaniline	212.1
40.	dimethyl phthalate	222.9
41.	acenaphthylene	223.5
42.	2,6-dinitrotoluene	224.8
43.	acenaphthene-d10	230.3
44.	3-nitroaniline	231.6
45.	acenaphthene	231.9
46.	2,4-dinitrophenol	236.6
47.	dibenzofuran	240.3
48.	4-nitrophenol	242.2
49.	2,4-dinitrotoluene	243.0
50.	fluorene	256.0
51.	diethyl phthalate	256.7
52.	4-chlorophenyl phenyl ether	258.5
53.	4-nitroaniline	260.2
54.	4,6-dinitro-2-methylphenol	261.3
55.	N-nitrosodiphenylamine	264.6
56.	2,4,6-tribromophenol	267.4
57.	4-bromophenyl phenyl ether	280.8
58.	hexachlorobenzene	281.0
59.	pentachlorophenol	291.5
60.	phenanthrene-D10	299.0
61.	phenanthrene	300.2
62.	anthracene	302.6
63.	carbazole	312.2
64.	dibutyl phthalate	334.5
65.	fluoranthene	355.7
66.	pyrene	365.7
67.	*p*-terphenyl-d14	377.5
68.	butyl benzyl phthalate	404.4
69.	benzo(a)anthracene	423.0
70.	chrysene-d12	423.4
71.	chrysene	424.6
72.	3,3'-dichlorobenzidine	425.4
73.	bis(2-ethylhexyl) phthalate	434.3
74.	di-*n*-octyl phthalate	463.6
75.	benzo(b)fluoranthene	470.2
76.	benzo(k)fluoranthene	471.4
77.	benzo(a)pyrene	483.0
78.	perylene-d12	485.1
79.	indeno(1,2,3-cd)pyrene	524.4
80.	dibenzo(a,h)anthracene	526.0
81.	benzo(ghi)perylene	533.0

Figure 1 Monitor 81 semivolatile compounds and internal standards in 9 minutes.



Column:	Rtx®-5SilMS, 10m x 0.18mm x 0.18µm, cat.# 42703
Sample:	1µL containing SV Calibration Mix #1 (cat.# 31007), SV Calibration Mix #2 (cat.# 31008), SV Calibration Mix #3 (cat.# 31009), SV Calibration Mix #4 (cat.# 31010), SV Calibration Mix #5 (cat.# 31011), SV Calibration Mix #7 (cat.# 31013), 3,3'-Dichlorobenzidine (cat.# 31026); acids, bases, and neutrals 80ng each, internal standards 50ng each.
Inj.:	1uL, split, 4mm Siltek® treated inlet liner with Siltek® treated wool, 250ºC, split ratio 50:1, 25 sec. solvent delay
Carrier gas:	helium
Flow rate:	2mL/min., constant flow
Oven:	40ºC (0.1 min.) to 340ºC @ 30ºC/min. (no hold)
Mass spectrometer:	LECO Pegasus 3 ToF-MS
Source temp.:	250ºC
Electron ionization:	70 eV
Stored mass range:	35 - 500 u
Acquisition rate:	20 spectra/sec.
Total run time:	10 min.

Rtx®-5Sil MS Columns (fused silica)

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

ID	df (µm)	temp. limits	10-Meter	20-Meter
0.18mm	0.18	-60 to 325°C	42703	42702
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

Dr. Frank Dorman will present this information in detail at the 2005 Pittsburgh Conference in Orlando, FL. See Reference 1 on page 8 for details.

Reference Mixes

Use the mixes listed in the conditions for Figure 1, or replace the six SV calibration mixes with 8270 MegaMix™.

8270 MegaMix™ (76 components)

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

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

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

[1]1,2-diphenylhydrazine (8270-listed analyte) decomposes to azobenzene (mix component).
[2]N-nitrosodiphenylamine (8270-listed analyte) decomposes to diphenylamine (mix component).

3,3'-Dichlorobenzidine

3,3'-dichlorobenzidine

2,000µg/mL in methanol, 1mL/ampul
cat. # 31026 (ea.)

please note

Many other calibration mixes, internal standards, and surrogates for analysis of semivolatile compounds are described in our catalog and on our website.