RESTEK
Chromatography Products

Environmental Applications

Accurately Quantify PAHs Down to 5 pg On-Column

GC/MS SIM Analysis with the New Rxi®-5Sil MS Column

Introduction

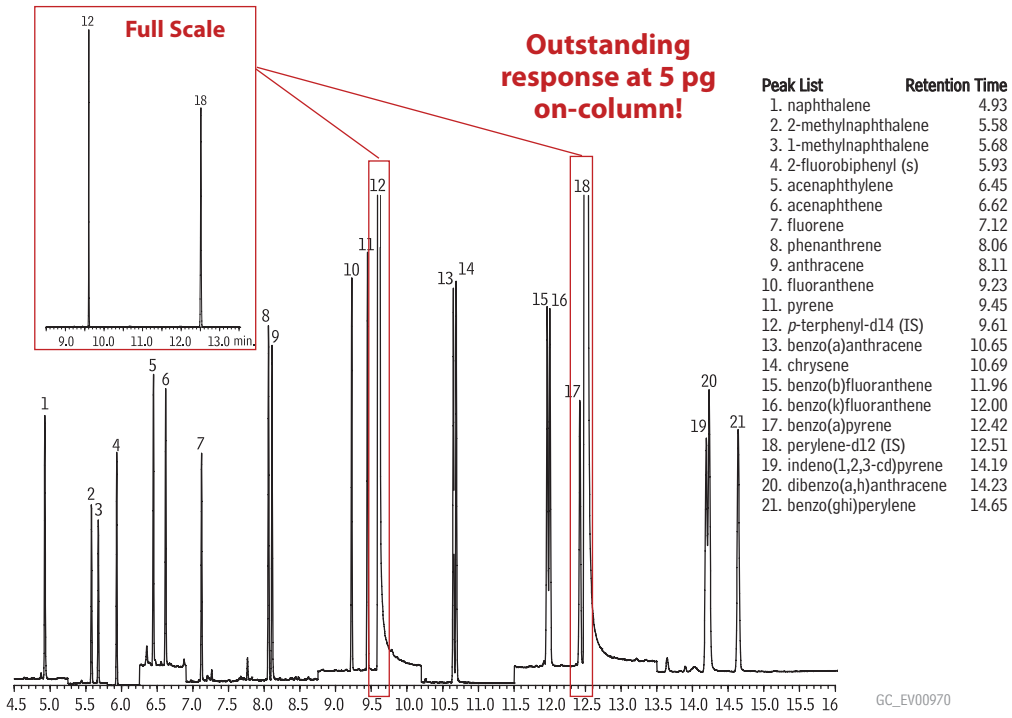
Polycyclic aromatic hydrocarbons (PAHs) are common environmental pollutants, affecting air, water, and soil quality. Although naturally occurring, human impact has created a steady increase in environmental levels of PAHs and their byproducts. PAHs are typically formed through the incomplete combustion of organic materials, such as wood, coal, and oil, but are also used in manufacturing of some medicines, plastics, and pesticides. Many PAHs are known or suspected carcinogens. The United States Environmental Protection Agency currently lists and mandates testing of the 16 PAHs they deem most hazardous.

Many chromatographic methods are available to analyze these pollutants. The gas chromatographic techniques typically used are often coupled with mass spectrometry. Laboratories performing low-level PAH analyses often utilize the single ion monitoring (SIM) function of GC/MS because of the sensitivity required to achieve typical regulatory or monitoring levels.

Method Parameters

For our SIM method we chose to use the new Rxi®-5Sil MS column. The Rxi®-5Sil MS stationary phase incorporates phenyl rings in the polymer backbone, which strengthens the siloxane chain, preventing thermal breakdown. The content of this aryl functionality has been adjusted so that its selectivity is similar to conventional 5% diphenyl/95% dimethyl phases. The low column bleed reduces the amount of noise

Figure 1 Excellent response and resolution of PAHs at 5 pg on-column in SIM mode.



Peak List	Retention Time
1. naphthalene	4.93
2. 2-methylnaphthalene	5.58
3. 1-methylnaphthalene	5.68
4. 2-fluorobiphenyl (s)	5.93
5. acenaphthylene	6.45
6. acenaphthene	6.62
7. fluorene	7.12
8. phenanthrene	8.06
9. anthracene	8.11
10. fluoranthene	9.23
11. pyrene	9.45
12. *p*-terphenyl-d14 (IS)	9.61
13. benzo(a)anthracene	10.65
14. chrysene	10.69
15. benzo(b)fluoranthene	11.96
16. benzo(k)fluoranthene	12.00
17. benzo(a)pyrene	12.42
18. perylene-d12 (IS)	12.51
19. indeno(1,2,3-cd)pyrene	14.19
20. dibenzo(a,h)anthracene	14.23
21. benzo(ghi)perylene	14.65

Column:	Rxi®-5Sil MS, 30m, 0.25mm ID, 0.25µm (cat.# 13623)
Sample:	PAH mix, 1µL of 0.005µg/mL (IS 2µg/mL) SV Calibration Mix #5 (cat.# 31011) 1-methylnaphthalene (cat.# 31283) 2-methylnaphthalene (cat.# 31285) 2-fluorobiphenyl (cat.# 31091)
Inj.:	1.0µL (5pg on-column concentration), 4mm Drilled Uniliner® (hole near top) inlet liner (cat.# 21055-200.5), pulsed splitless: pulse 20psi @ 0.2 min., 60mL/min. @ 0.15 min.
Inj. temp.:	300°C
Carrier gas:	helium, constant flow
Flow rate:	1.4mL/min.
Oven temp.:	50°C (hold 0.5 min.) to 290°C @ 25°C/min. to 320°C @ 5°C/min.
Det.:	MS
Transfer line temp:	290°C
Ionization:	EI
Mode:	SIM

contributed by the column, thereby increasing the signal-to-noise ratio of the analytical system. Increased sensitivity and subsequently lower detection limits are direct results of the improved signal-to-noise ratios. The silarylene polymer not only exhibits improved thermal stability and reduced bleed, but it also shows improved separation for aromatic compounds, such as PAHs.

Analytical conditions were set to optimize resolution of critical pairs and reduce discrimination of high molecular weight analytes. We chose a 4mm Drilled Uniliner® inlet liner with wool, since direct injection using this liner provides near complete transfer of sample analytes to the column. The Drilled Uniliner® inlet liner also eliminates analyte exposure to cold spots and potentially active metal components in the injection port, assuring complete transfer of the higher molecular weight PAHs, which otherwise tend to adsorb in these areas. To improve the quantification of high molecular weight compounds we chose a column with a thin film thickness (0.25µm) and set the injection port temperature to 300°C. A pulsed splitless injection technique was used to maximize the transfer of analytes onto the column. The pressure pulse has proven to be a very effective injection technique for trace level analyses and also helps minimize discrimination against the high molecular weight components. Finally, the ion source and quadrupole temperatures of the instrument were set at 290°C and 180°C, respectively. This increase in detector temperatures, from the defaults of 230°C and 150°C, yields better peak shapes and responses for the PAHs.

Results

These run conditions produced excellent resolution and response for all of the target analytes in a run time of less than 16 minutes. Figure 1 shows the SIM trace at 0.005 µg/mL (5 pg on column). The system was calibrated at eight levels, from 0.005 to 10 µg/mL in single ion monitoring mode. The SIM acquisition program used for this analysis is shown in Table I. Each calibration standard contained eighteen target PAHs, two internal standards (p-terphenyl-d14 and perylene-d12), and the surrogate (2-fluorobiphenyl). At each level, the relative response factor (RRF) was calculated for all compounds and linearity was determined by calculating the percent relative standard deviation (%RSD) for all response factors, as shown in Table II. The %RSDs for all compounds are in the low single digits with an average for all compounds of 4.7%.

Table I Single ion monitoring program.

Group	Time	Ion(s)	Dwell (ms)
1	4.00	128	100
2	5.25	142	100
3	5.80	172	100
4	6.25	152	100
5	6.90	166	100
6	7.60	178	100
7	8.75	202, 244	100
8	10.2	228	100
9	11.5	252, 264	100
10	13.5	276, 278	100

Table II PAH relative response factors and %RSD for calibration standards (0.005-10 µg/mL).

	Relative Response Factor									
Compound	0.005	0.01	0.05	0.1	0.5	1	5	10	Avg	%RSD
p-Terphenyl-d14 (IS)	-	-	-	-	-	-	-	-	-	-
Naphthalene	0.825	0.778	0.822	0.785	0.760	0.774	0.771	0.721	0.779	4.28
2-Methylnaphthalene	0.539	0.518	0.556	0.525	0.512	0.524	0.521	0.495	0.524	3.42
1-Methylnaphthalene	0.503	0.478	0.518	0.483	0.470	0.481	0.476	0.455	0.483	4.05
2-Fluorobiphenyl (SS)	0.689	0.664	0.691	0.680	0.664	0.679	0.669	0.608	0.668	3.93
Acenaphthylene	0.879	0.838	0.917	0.887	0.868	0.899	0.904	0.856	0.881	3.00
Acenaphthene	0.541	0.508	0.544	0.522	0.508	0.522	0.514	0.482	0.518	3.80
Fluorene	0.700	0.662	0.709	0.677	0.659	0.679	0.668	0.627	0.673	3.80
Phenanthrene	1.108	1.049	1.119	1.068	1.028	1.050	1.022	0.953	1.050	4.97
Anthracene	1.052	0.962	1.043	1.003	0.981	1.013	0.993	0.921	0.996	4.27
Fluoranthene	1.239	1.161	1.254	1.206	1.166	1.195	1.171	1.093	1.185	4.25
Pyrene	1.364	1.254	1.355	1.295	1.256	1.284	1.247	1.155	1.276	5.20
Perylene-d12 (IS)	-	-	-	-	-	-	-	-	-	-
Benzo(a)anthracene	1.111	0.980	1.086	1.054	1.048	1.087	1.090	1.017	1.059	4.12
Chrysene	1.153	1.041	1.116	1.073	1.057	1.078	1.043	0.951	1.064	5.59
Benzo(b)fluoranthene	1.282	1.039	1.183	1.146	1.139	1.185	1.204	1.144	1.165	5.92
Benzo(k)fluoranthene	1.327	1.119	1.223	1.189	1.183	1.229	1.225	1.136	1.204	5.35
Benzo(a)pyrene	1.037	0.967	1.146	1.083	1.038	1.089	1.134	1.080	1.072	5.36
Indeno(1,2,3-cd)pyrene	1.457	1.224	1.379	1.366	1.333	1.387	1.471	1.424	1.380	5.69
Dibenzo(a,h)anthracene	1.195	1.027	1.150	1.180	1.094	1.164	1.233	1.173	1.152	5.56
Benzo(ghi)perylene	1.331	1.118	1.238	1.263	1.140	1.192	1.244	1.190	1.215	5.68

Conclusion

The Rxi®-5Sil MS column allows for a very broad calibration range, in this case 2,000-fold from 5 pg to 10 ng while maintaining exceptional linearity. Using the Rxi®-5Sil MS column and an optimized temperature program is an excellent solution to the challenges posed by SIM PAH analyses.

Product Listing

Rxi®-5Sil MS Columns (fused silica)

(low polarity Crossbond® silarylene phase; selectivity close to 5% diphenyl/95% dimethyl polysiloxane)

- Ultra-low bleed.
- Exceptional inertness.
- Reproducible performance, column after column.

ID	df (µm)	temp. limits	15-Meter	30-Meter	60-Meter
0.25mm	0.10µm	-60 to 330/350°C	13605	13608	
0.25mm	0.25µm	-60 to 330/350°C	13620	13623	13626
	0.50µm	-60 to 330/350°C	13635	13638	
	1.00µm	-60 to 325/350°C	13650	13653	13697

similar **phases**

DB-5MS, VF-5ms,
CP-Sil 8 Low-Bleed/MS

Rxi®-5Sil MS with Integra-Guard®

- Extend column lifetime.
- Eliminate leaks with a built-in retention gap.
- Inertness verified by isothermal testing.

Description	qty.	cat.#	price
30m, 0.25mm ID, 0.25µmµm Rxi-5Sil MS w/5m Integra-Guard Column	ea.	13623-124	
30m, 0.25mm ID, 0.25µmµm Rxi-5Sil MS w/10m Integra-Guard Column	ea.	13623-127	

SV Calibration Mix #5 / 610 PAH Mix

(16 components)

acenaphthene
acenaphthylene
anthracene
benzo(a)anthracene
benzo(a)pyrene
benzo(b)fluoranthene
benzo(k)fluoranthene
benzo(ghi)perylene
chrysene
dibenzo(a,h)anthracene
fluoranthene
fluorene
indeno(1,2,3-cd)pyrene
naphthalene
phenanthrene
pyrene

2,000µg/mL each in methylene chloride, 1mL/ampul
cat. # 31011 (ea.)

1-Methylnaphthalene

1-methylnaphthalene
1,000µg/mL in methanol, 1mL/ampul
cat. # 31283 (ea.)

2-Methylnaphthalene

2-methylnaphthalene
1,000µg/mL in methylene chloride, 1mL/ampul
cat. # 31285 (ea.)

2-Fluorobiphenyl

2-fluorobiphenyl
2,000µg/mL in methylene chloride, 1mL/ampul
cat. # 31091 (ea.)

Method 525.2 Fortification Recovery Standard

p-terphenyl-d14
1,000µg/mL in methylene chloride, 1mL/ampul
cat. # 31828 (ea.)

Method 525.2 Internal Standard Mix

(3 components)

acenaphthene-d10
chrysene-d12
phenanthrene-d10

1,000µg/mL each in acetone, 1mL/ampul
cat. # 31825 (ea.)

4.0mm ID Drilled Uniliner® Inlet Liner with Hole near Top w/ Wool

ID* x OD & Length	qty.	cat.#
Drilled Uniliner (hole near top), Intermediate Polarity (IP), Deact. Wool, Borosilicate Glass 4.0mm x 6.3mm x 78.5mm	5-pk.	21055-200.5

Restek's Ultra-Clean resin eliminates the hassle of cleaning and testing resin for air sampling.

Ultra-Clean Resin

Equivalent to XAD-2 Resin; Exclusively from Restek!

- For adsorbing semivolatiles in air.
- Cleaned, GC tested and certified.
- Available in 100 gram quantities.

Method	Applications
EPA TO-13A	PAHs in Ambient Air
ASTM D6209	PAHs in Ambient Air
EPA Method 23	Dioxins in Stationary Source Emissions
EPA Method 0010	Semivolatiles in Stationary Source Emissions

Although resin is an excellent adsorbent for trapping PAHs, it requires extensive clean-up because many of its impurities are PAH compounds. To enable you to eliminate time-consuming clean-up we do the cleaning for you! We test each batch of Ultra-Clean Resin by capillary GC/flame ionization detector to ensure cleanliness.

Feature	Benefit
Shipped precleaned to TO-13 method requirements.	Saves time.
In stock for immediate delivery.	No waiting.
Each batch is lot-tested.	Quality guaranteed, so you have confidence in your analyses.

Commonly Asked Questions

- Is Restek's Ultra-Clean resin really the same as XAD®-2 resin? Yes. Restek's resin has been manufactured to match the original XAD®-2 specifications of composition, pore size, and surface area. You will experience identical sampling performance for all semivolatile compounds.
- Does Restek's Ultra-Clean resin need to be baked-out prior to use? No. Restek's resin is precleaned and prebaked. Unlike other resins, Restek's resin is rigorously cleaned and baked prior to being bottled. When we say our Ultra-Clean resin is precleaned, you can count on it!
- Is Restek's Ultra-Clean resin safe when using an ECD detector? Yes. Restek's cleaning process involves a unique step that removes compounds that may show up on an electron capture detector (ECD).

Description	cat.#
Ultra-Clean Resin, 100 grams	24230

Quantity discounts available.

SDVB Resin

- Styrene/divinylbenzene, equivalent to XAD-2 resin.
- Untreated, packaged in 1kg plastic containers.
- Spherical, 20 to 60 mesh particles.

Description	qty.	cat.#
SDVB Resin	1kg	24053

Larger quantities available on request.

RESTEK

Lit. Cat.# EVAN1284

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