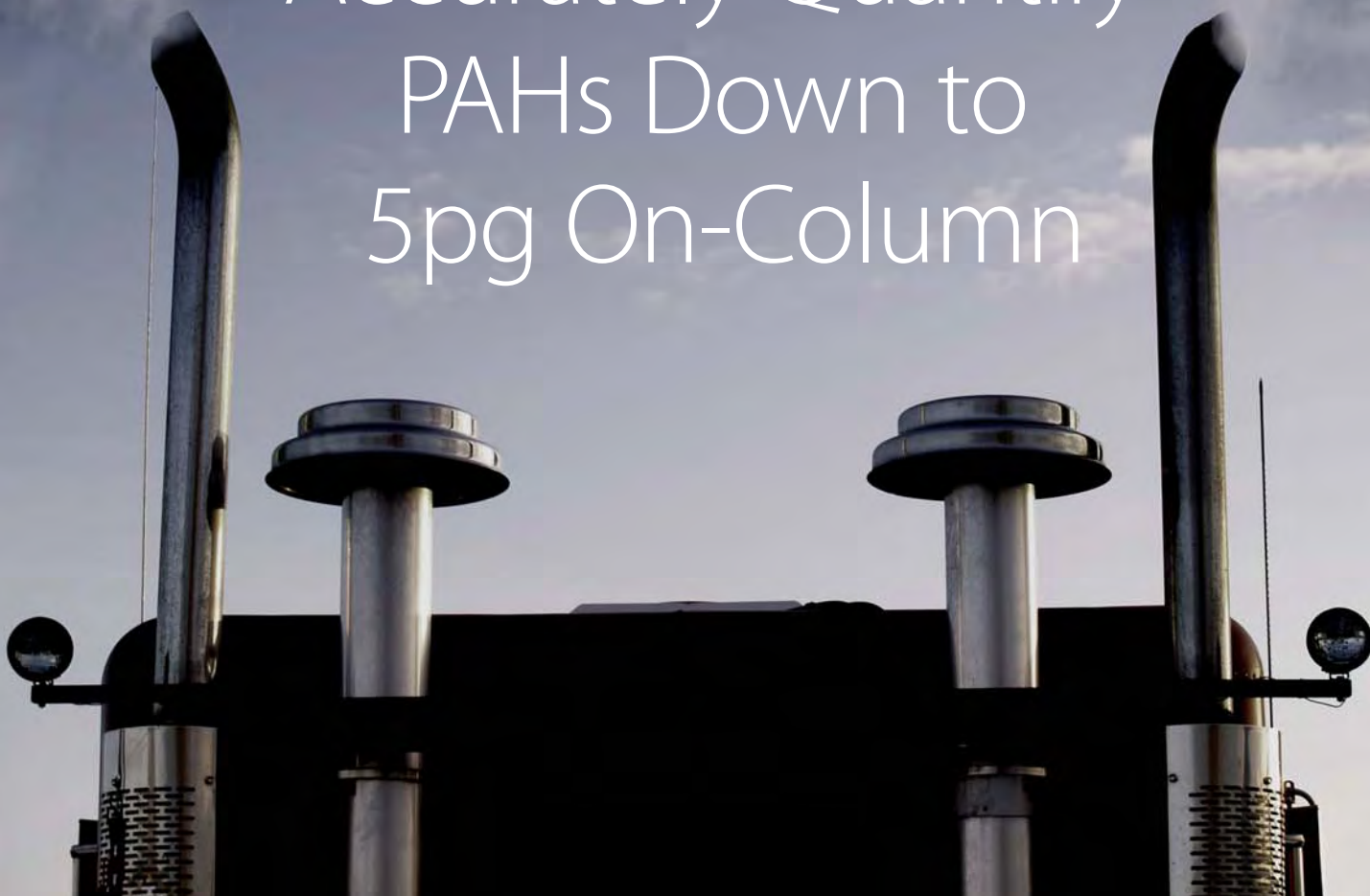


Accurately Quantify PAHs Down to 5pg On-Column



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

By Robert Freeman, Environmental Innovations Chemist

- Excellent linearity across a broad calibration range.
- Ideal for trace level analyses.
- Low bleed at high temperatures, for better overall response and lower detection limits.

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 chromatographic methods are available to analyze these pollutants. 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.

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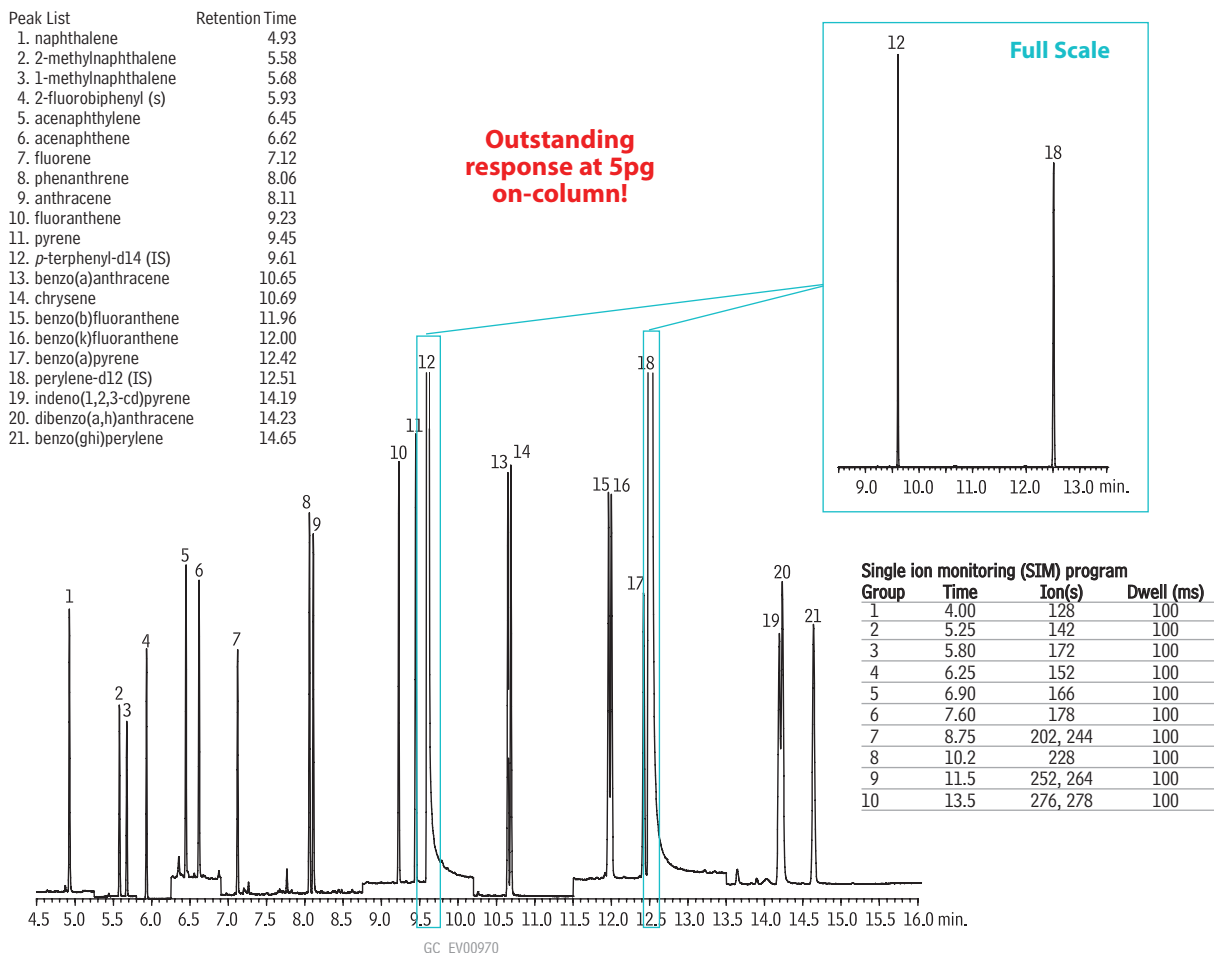
Accurately Quantify PAHs Down to 5pg On-Column *Continued from page 3.*

Method Parameters

For our SIM method we chose to use the new Rxi®-5Sil MS column. This stationary phase incorporates phenyl rings in the polymer backbone, which strengthens the siloxane chain, preventing thermal breakdown. This low bleed column is similar in selectivity to 5% diphenyl/95% dimethyl phases, but offers improved signal-to-noise ratios, resulting in increased sensitivity and subsequently lower detection limits. 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. To improve the quantification of high molecular weight compounds we chose 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 is an 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 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.

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



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

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 0.005µg/mL (5pg on column). The system was calibrated at eight levels, from 0.005 to 10µg/mL in single ion monitoring mode. The SIM acquisition program used for this analysis is shown in Figure 1. 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%.

The Rxi®-5Sil MS column allows for a very broad calibration range, in this case 2000-fold from 5pg to 10ng 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.

Table I Relative response factors and %RSD for calibration standards (0.005-10µg/mL).

Compound	Relative Response Factor								Avg	%RSD
	0.005	0.01	0.05	0.1	0.5	1	5	10		
<i>p</i>-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

SV Calibration Mix #5 / 610 PAH Mix

(16 components)

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

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

1-Methylnaphthalene

1,000µg/mL in methanol, 1mL/ampul
cat. # 31283

2-Methylnaphthalene

1,000µg/mL in methylene chloride, 1mL/ampul
cat. # 31285

2-Fluorobiphenyl


2,000µg/mL in methylene chloride, 1mL/ampul
cat. # 31091

Rxi®-5Sil MS Columns (fused silica)

(Crossbond®, selectivity close to 5% diphenyl/95% dimethyl polysiloxane)

ID	df (µm)	temp. limits	length	cat. #
0.25mm	0.25	-60 to 330/350°C	30-Meter	13623

Direct Injection Liners for Agilent GCs (For 0.25/0.32/0.53mm ID Columns)

ID* x OD & Length (mm)	qty.	cat.#
Drilled Uniliner® (hole near top)		
4.0 ID x 6.3 OD x 78.5	ea.	21054
4.0 ID x 6.3 OD x 78.5	5-pk.	21055
4.0 ID x 6.3 OD x 78.5	25-pk.	20998

Drilled Uniliner® (hole near top) w/ Wool

4.0 ID x 6.3 OD x 78.5	ea.	21054-200.1
4.0 ID x 6.3 OD x 78.5	5-pk.	21055-200.5
4.0 ID x 6.3 OD x 78.5	25-pk.	20998-214.25

*Nominal ID at syringe needle expulsion point.