Environmental

Accurately Quantify PAHs Down to 5pg On-Column

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

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

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 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.

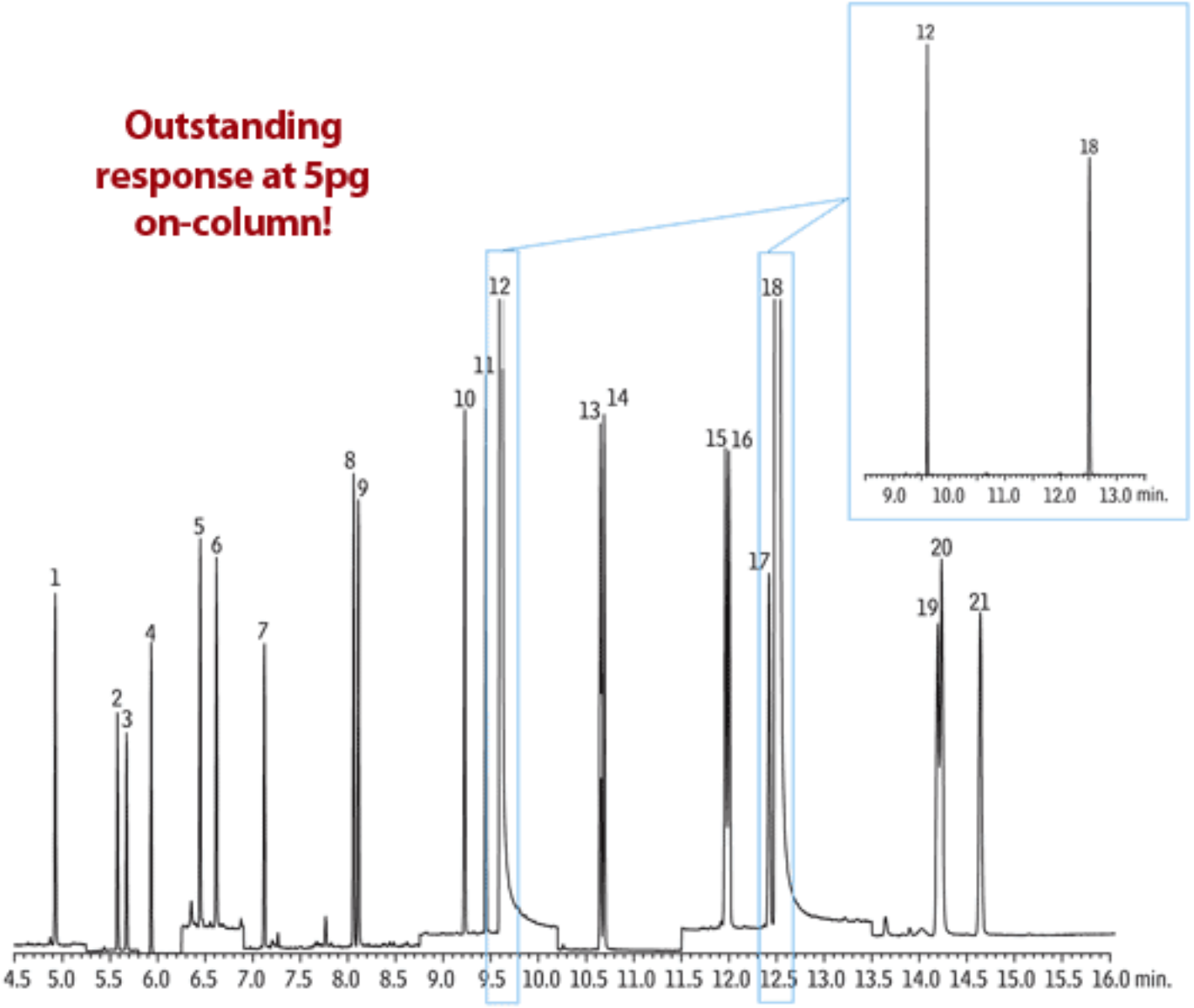
Analytical conditions were set to optimize resolution of critical pairs and reduce discrimination of high molecular weight analytes. We chose a 4mm Drilled Uniliner® inlet liner with wool, since direct injection using this liner provides near complete transfer of sample analytes to the column. The Drilled 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 (5pg 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%.

Figure 1: Excellent response and resolution of PAHs at 5pg 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 (SS)	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

GC_EV00970

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 (0.005-10µg/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 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.

RESTEK PRODUCTS

GC Columns Rxi®-5Sil MS (Fused Silica)