RESTEK environmental

Applications note

Analysis of Polycyclic Aromatic Hydrocarbons (PAHs) Using Rtx®-5Sil MS and Rtx®-CLPesticides2 Capillary Columns

Analysis of polycyclic aromatic hydrocarbons (PAHs) is a very common method in environmental laboratories. US Environmental Protection Agency (EPA) Method 8100 requires gas chromatograph/flame ionization detection (GC/FID) to quantitate PAHs found in extracts from soil, water, or biological samples. This method requires the use of a dual-column system, because most samples often contain hydrocarbon interferences. Confirmational analysis increases the confidence of proper identification and quantitation of the PAHs. Good resolution is necessary for proper quantitation; the most difficult compound pairs to resolve are benzo(b)/benzo(k)fluoranthene and indeno(1,2,3-cd)pyrene/dibenzo(a,h)anthracene. Short analysis time is another key consideration for most laboratories. By decreasing analysis time, sample throughput is increased and the lab benefits from a cost savings.

Primary Analysis

For this analysis, the primary analytical stationary phase is a 5% diphenyl/95% dimethyl-polysiloxane polymer. The Restek Rtx®-5Sil MS column is an equivalent phase and is recommended for this analysis (Fig. 1). While selectivity is similar to 5% diphenyl/95% dimethyl-polysiloxane columns, the proprietary silarylene stationary phase of the Rtx®-5Sil MS column is designed to produce very low bleed.

Confirmational Analysis

Confirmational analysis is a technique that requires two analytical columns of different selectivities, resulting in different retention times of target or interfering compounds. These differences can improve quantitative and qualitative reliability through peak verification. The confirmational column recommended by Restek for this analysis is the Rtx®-CLPesticides2 column (Fig. 2). Quantitative reliability for this analysis is maintained because the stationary phases differ in selectivity, resulting in retention time shifts of both PAHs and interference compounds.

Resolution of PAHs

Resolution between benzo(b)fluoranthene and benzo(k)fluoranthene and indeno(1,2,3,-cd)pyrene and dibenzo(a,h)anthracene is essential for quantitation when using an FID. To achieve excellent resolution of these peak pairs, the carrier gas, column flow rate, and temperature program must all be optimized. And, to achieve even better quantitative reliability, it is recommended to clean sample extracts following EPA Method 3630 (silica gel) prior to analysis.

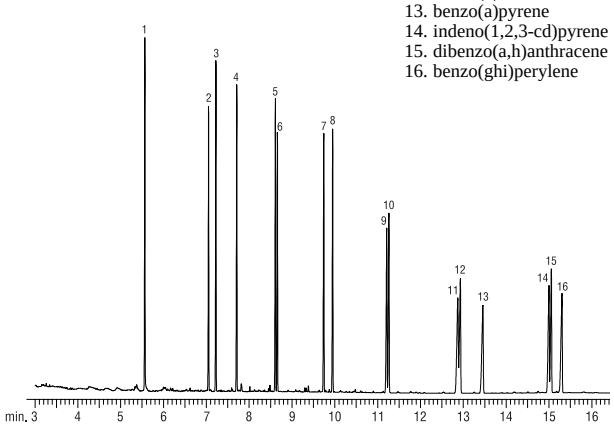
Optimizing Carrier Gas Flows

The resolution of PAHs can be increased and the overall analysis time reduced by using hydrogen carrier gas at high flow rates. For this application hydrogen is a better choice than helium because it is more efficient at higher flow rates. And, if used in the constant flow mode, the best separation and fastest analysis time can be achieved. (Constant pressure mode is not recommended because the flow rate will decrease as the oven temperature is increased. This could result in a loss of resolution for the later eluting PAHs and a longer analysis time.)

The optimum carrier gas flow rate for the 30m, 0.25mm ID, 0.25µm Rtx®-5Sil MS column is less than 1mL/min. However, by increasing the flow rate to 4mL/min. for the analysis of PAHs, the separation of the isomer pairs is increased and the analysis time is reduced to less than 17 minutes (Figure 1). The Rtx®-CLPesticides2 confirmation column can separate these compounds under identical conditions (Figure 2). Again, the faster flow rate (4mL/min.) improves separation and reduces analysis time to less than 18 minutes.

Figure 1–The Rtx®-5Sil MS column exhibits excellent resolution of polycyclic aromatic hydrocarbons including benzo(b)/benzo(k)fluoranthene in less than 16 minutes.

1. naphthalene
2. acenaphthylene
3. acenaphthene
4. fluorene
5. phenanthrene
6. anthracene
7. fluoranthene
8. pyrene
9. benzo(a)anthracene
10. chrysene
11. benzo(b)fluoranthene
12. benzo(k)fluoranthene
13. benzo(a)pyrene
14. indeno(1,2,3-cd)pyrene
15. dibenzo(a,h)anthracene
16. benzo(ghi)perylene



GC_EV00595

Rtx®-5Sil MS 30m, 0.25mm ID, 0.25µm (cat.# 12723)
Sample: 50µg/mL 610 PAH Mix standard (cat.# 31011) in carbon disulfide
Inj.: 1.0µL splitless (hold 2 min.), 2mm splitless w/ wool inlet liner (cat.# 20829)
Inj. temp.: 330°C
Carrier gas: hydrogen, 4mL/min constant flow
Oven temp.: 40°C (hold 2 min.) to 250°C @25°C/min. to 265°C @5°C/min. to 300°C (hold 4 min.) @25°C/min.
Det.: FID @350°C

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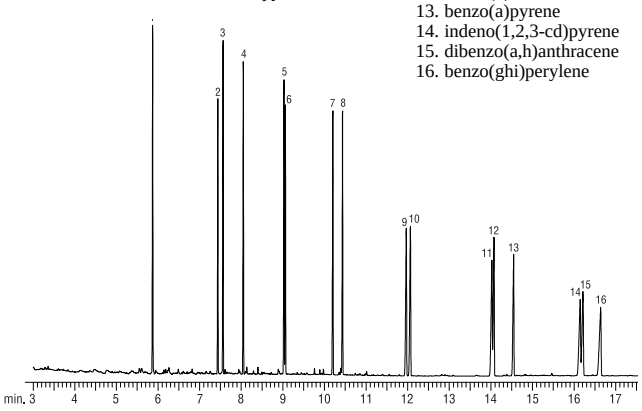
Optimizing Temperature Program

Optimizing the temperature program also contributes to better resolution of closely eluting peak pairs and shortens analysis times. The temperature program in Figures 1 and 2 achieves baseline resolution of indeno(1,2,3-cd)pyrene and dibenzo(a,h)anthracene, and excellent resolution of benzo(b)fluoranthene and benzo(k)fluoranthene, while still keeping the analysis time under 18 minutes. Because the column flow rate and temperature program for both columns is the same, the analysis can be run simultaneously on the primary and confirmation columns.

Figure 2–The Rtx®-CLPesticides column is an excellent confirmational column for polycyclic aromatic hydrocarbon analysis.

1. naphthalene
2. acenaphthylene
3. acenaphthene
4. fluorene
5. phenanthrene
6. anthracene
7. fluoranthene
8. pyrene
9. benzo(a)anthracene
10. chrysene
11. benzo(b)fluoranthene
12. benzo(k)fluoranthene
13. benzo(a)pyrene
14. indeno(1,2,3-cd)pyrene
15. dibenzo(a,h)anthracene
16. benzo(ghi)perylene



GC_EV00596

Rtx®-CLPesticides2 30m, 0.25mm ID, 0.20µm (cat.# 11323)
Sample: 50µg/mL 610 PAH Mix standard (cat.# 31011) in carbon disulfide
Inj.: 1.0µL splitless (hold 2 min.), 2mm splitless w/ wool inlet liner (cat.# 20829)
Inj. temp.: 330°C
Carrier gas: hydrogen, 4mL/min constant flow
Oven temp.: 40°C (hold 2 min.) to 250°C @25°C/min. to 265°C @5°C/min. to 300°C (hold 4 min.) @25°C/min.
Det.: FID @350°C

Reducing Discrimination

Reduced response of the higher molecular weight PAHs is caused by discrimination in the injection port. In extreme cases the response of the last three PAH compounds may be lost completely. Discrimination will vary by injection port design. Chromatograms generated using a Perkin Elmer Autosys GC system exhibit minimal discrimination (Figures 1 and 2). The area ratio of naphthalene (peak 1) is ~2:1 compared to benzo(ghi)perylene (peak 16).

Several modifications can be made to reduce discrimination: increasing injection port temperature to improve vaporization; increasing the splitless hold time; and using a drilled Uniliner® inlet sleeve. The design of the drilled Uniliner® creates a seal between the liner and the column, which reduces the loss of high molecular weight compounds and thereby improves their response. The drilled Uniliner® has a small hole drilled at the top of the liner that allows it to work with small-diameter columns and electronic pressure control (EPC) injection systems.

Conclusion

PAH analysis by US EPA Method 8100 can be improved by choosing the appropriate analytical columns and by optimizing the temperature program, carrier gas type, and column flow rates. When operating under the conditions listed for Figures 1 and 2, the Rtx®-5Sil MS and the Rtx®-CLPesticides2 columns yield excellent resolution and short analysis times for PAHs.

Rtx®-5Sil MS Columns (-60 to 330/350°C)

30m	0.25mm ID	0.25µm	cat.# 12723
30m	0.32mm ID	0.25µm	cat.# 12724

Rtx®-CLPesticides2 Columns (-60 to 310/330°C)

30m	0.25mm ID	0.20µm	cat.# 11323
30m	0.32mm ID	0.25µm	cat.# 11324

Method 610–Polynuclear Aromatic Hydrocarbons Mix

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 CH_2Cl_2, 1mL/ampul

	Each	5-pk.	10-pk.
	31011	31011-510	
w/data pack	31011-500	31011-520	31111

Inlet Liners

For Agilent GCs

Drilled Uniliner® *(4.0mm ID, 6.3mm OD, 78.5mm length)*		
	21054 (ea.)	21055 (5-pk.)

Siltek™ Drilled Uniliner® *(1.0mm ID, 6.3mm OD, 78.5mm length)*		
	21390-214.1 (ea.)	21391-214.5 (5-pk.)

For PE GCs

Auto SYS Splitless w/Wool *(2.0mm ID, 6.2mm OD, 92.1mm length)*		
20829 (ea.)	20830 (5-pk.)	20831 (25-pk.)

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