Fast Analysis of Polynuclear Aromatic Hydrocarbons Using Agilent Low Thermal Mass (LTM) GC/MS and Capillary Flow Technology QuickSwap for Backflush

Application Note

Environmental

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Abstract

Cycle time for GC-MS analysis of polynuclear aromatic hydrocarbons (PAHs) in soil and sediment samples was improved dramatically through the combined use of a narrow-bore (180-µm id) column installed in an LTM module and capillary column backflushing with QuickSwap. Improvements were achieved while maintaining resolution. Agilent Capillary Flow Technology enabled column backflushing to remove low-volatility material from the capillary column, reducing bakeout and maintenance time. The method resulted in increased sample throughput and lab productivity, while maintaining analytical performance.

Agilent Technologies

Introduction

The analysis of polycyclic (polynuclear) aromatic hydrocarbons (PAHs) by GC-MS is one of the most important applications in environmental analysis. In most reference methods, 16 target PAHs of particular toxicity and carcinogenicity are monitored, ranging from naphthalene (eluting first, MW = 128) to benzo(ghi)perylene (eluting last, MW = 276). Typically, PAH analyses are performed with a 30 m × 0.25 mm id × 0.25 µm 5% phenyldimethyl siloxane columns (for example, Agilent J&W HP-5MS or J&W DB-5MS) using a temperature program from 40–50 °C to 300–320 °C in 20 to 30 minutes of analysis time. The analysis of PAHs, therefore, covers the whole boiling point range of semivolatiles as typically covered in U.S. EPA Methods 525, 625, and 8270. These methods include compounds such as polychlorinated biphenyls (PCBs), phthalates, phenols, and most GC-amenable pesticides (for example, organochlorine, triazines, and organophosphorous). Any combination of these compounds is potentially present in PAH samples, in addition to hydrocarbon fuels and oils, complicating analysis of target PAHs. The use of mass spectrometers is required to facilitate reliable identification and quantitation.

Most labs are interested in maximizing lab efficiency and output. To this end, decreasing method analysis time and increasing sample throughput is often of interest. For this, columns of smaller diameter in combination with fast oven programming are an important option. However, a key challenge in PAH analysis is sufficient separation of key isomers (for example, benzo(b)fluoranthene and benzo(k)fluoranthene) since mass spectrometry is not able to differentiate them. Therefore, these isomers should be chromatographically separated, which requires columns of sufficient separation power and some careful choice in column flow and temperature ramp rates. Hence, it is important to use a tool like method translation software [1] to scale reference conditions appropriately.

Higher molecular-weight PAHs are potentially sensitive to cold spots and adsorption in the sample flow path. Problems with column connections, transfer line, source temperature, or activity in the inlet or column rapidly lead to peak tailing and loss of sensitivity. Although the compounds are considered apolar, PAH analysts find that frequent inlet, column, and source maintenance are needed when analyzing dirty samples (for example, sediment extract). A high source temperature (for example, ≥ 300 °C) and capillary column backflushing can greatly reduce the need for maintenance, thereby improving data quality and further increasing lab productivity.

In this application note, translation of a standard PAH method to a fast method using a 180-µm id column is demonstrated. To maximize sample throughput, fast column heating and cooling were further improved by using a low thermal mass (LTM) oven module. An Agilent Capillary Flow Technology QuickSwap capillary flow module was chosen for its ability to improve column replacement and system maintenance time, while providing the means to backflush the capillary column after the elution of the last PAH. As a result, low-volatility matrix compounds were efficiently removed, and maintenance interval greatly increased.

Experimental

Solutes and Sample

Tests were performed using a PAH standard mixture containing 16 PAHs in dichloromethane. The test mixture was obtained by dilution of a mixture in CH_2Cl_2/benzene (for example, Supelco, Bellefonte, PA, USA, cat no 48905, 2000 mg/mL) to 1 ng/µL (1 ppm) in dichloromethane.

A soil sample contaminated with mineral oil and PAHs was obtained from an environmental laboratory. 1 g of the soil was extracted in 20 mL dichloromethane (30 min ultrasonic treatment). This extract was filtered and analyzed directly as is typical in most high-volume environmental laboratories. The mineral oil concentration in the sample was approximately 5 g/kg. The concentrations of the PAHs were around 150 mg/kg for pyrene and fluoranthene and 5 to 10 mg/kg for the higher molecular-weight PAHs (for example, 9 mg/kg for benzo(a)pyrene). In the extract, the concentrations are 20 times lower (for example, 0.45 ng/µL for benzo(a)pyrene, assuming 100% extraction efficiency).

A sewage sludge sample (BCR-088, IRMM, Geel, Belgium) was also analyzed. 1 g of sludge was extracted in 20 mL of dichloromethane. The extract was filtered and analyzed directly. The sample contained concentrations of approximately 1 mg/kg of the higher molecular-weight PAHs (0.05 ng/µL benzo(a)pyrene in extract).

GC-MS Conditions

Analyses were performed on an Agilent 7890A GC – Agilent 5975C Series MSD system. The GC was equipped with an S/SI inlet, a QuickSwap device using a 17 cm × 110 µm id deactivated fused silica restrictor (G3185-60363), an AUX EPC module, and a LTM column module. The system configuration is diagrammed in Figure 1.

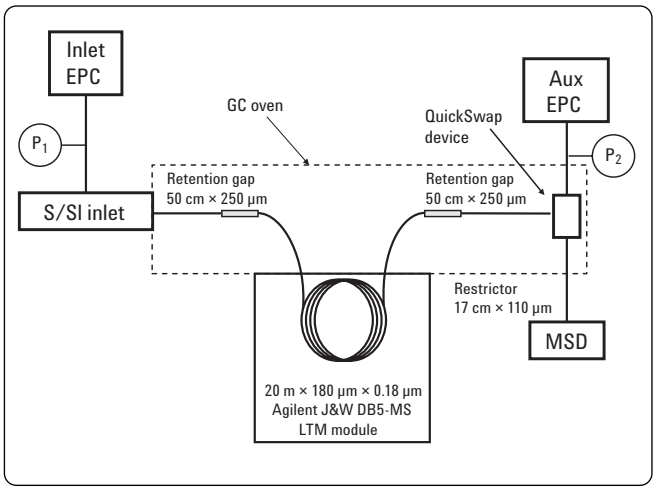

Figure 1. System configuration for fast GC analysis of PAHs using an LTM module and QuickSwap device for backflush.

Reference analyses were performed on a 30 m × 0.25 mm id × 0.25 µm Agilent J&W DB-5MS column, installed in the GC oven. For the fast method, a 20 m × 0.18 mm id × 0.18 µm J&W DB-5MS was used in LTM column format (p/n 121-5522LTM). Two pieces of 50 cm × 250 µm id deactivated fused silica tubing were used to connect the S/SI inlet to the column and from the column to the Quick-Swap device.

The final conditions for the 180-µm id column with backflushing are listed in Table 1.

Table 1. GC-MS Setpoints for Fast PAH Analysis Using a Low Thermal Mass Oven and QuickSwap Device for Backflush

Injection	1 µL, splitless mode, 280 °C
S/SI pressure program (He) (column inlet)	213 kPa (0.9 min), 60 kPa/min → 351 kPa, 7.5 kPa/min → 392 kPa (1.5 min), 600 kPa/min → 10 kPa (6 min)
AUX 1 (QuickSwap device, He) (column outlet)	28 kPa (10 min), 600 kPa/min → 250 kPa (6 min)
GC oven temperature	300 °C isothermal (17 min)
LTM oven program (translation of reference)	40 °C (0.9 min), 87 °C/min → 240 °C, 11 °C/min → 300 °C (8.35 min)
MS	SIM/Scan mode
Scan	50 to 300 *m/z*, samples = 2[1]
SIM	See Table 2
Transfer line	280 °C
Solvent delay	2.70 min
MS temperatures	Source = 300 °C, Quad = 150 °C
Run table events	MS off at 10 min

Table 2. SIM Table

Group	Start time (min)	Ion (*m/z*)	Dwell time (msec)
1	2.70	128	50
2	3.00	152, 153, 154, 165, 166	25
3	3.65	178	50
4	4.20	202	50
5	5.00	228	50
6	6.50	252	50
7	8.50	276, 278	50

Results and Discussion

For reference, a mixture containing 16 PAHs at 1 ppm in dichloromethane was analyzed using the typical 30 m × 0.25 mm id × 0.25 µm J&W DB-5MS column. The column temperature was programmed from 40 °C (2 min) at 40 °C/min to 240 °C and then at 5 °C/min to 300 °C (11 min hold). A low initial temperature is typically applied when a low-boiling solvent such as dichloromethane is used in order to allow recondensation (solvent focusing) in the column. Higher initial temperatures can be used if higher-boiling solvents are used. With higher initial temperatures, both the run time and the cool-down time of the GC are reduced; however, method translations are only valid with the same starting temperature used in the reference method.

The reference chromatogram of the standard mixture is shown in Figure 2. The critical pair benzo(b)fluoranthene/benzo(k)fluoranthene (peaks 11 and 12), eluted at 15 minutes, with sufficient resolution for quantification. The last solute, benzo(ghi)perylene, eluted at 19.7 minutes.

Next, the method was translated using GC Method Translation software [1] for the 20 m × 180 µm id × 0.18 µm column. Since separation power scales with length/diameter, the separation power of this column is very similar to that of the reference column. Through method translation, the inlet pressure and oven temperature program were scaled for the new column in fast analysis mode (one of the possible presets in the software). The resulting conditions are listed in Table 1. The predicted speed gain was a factor 2.17.

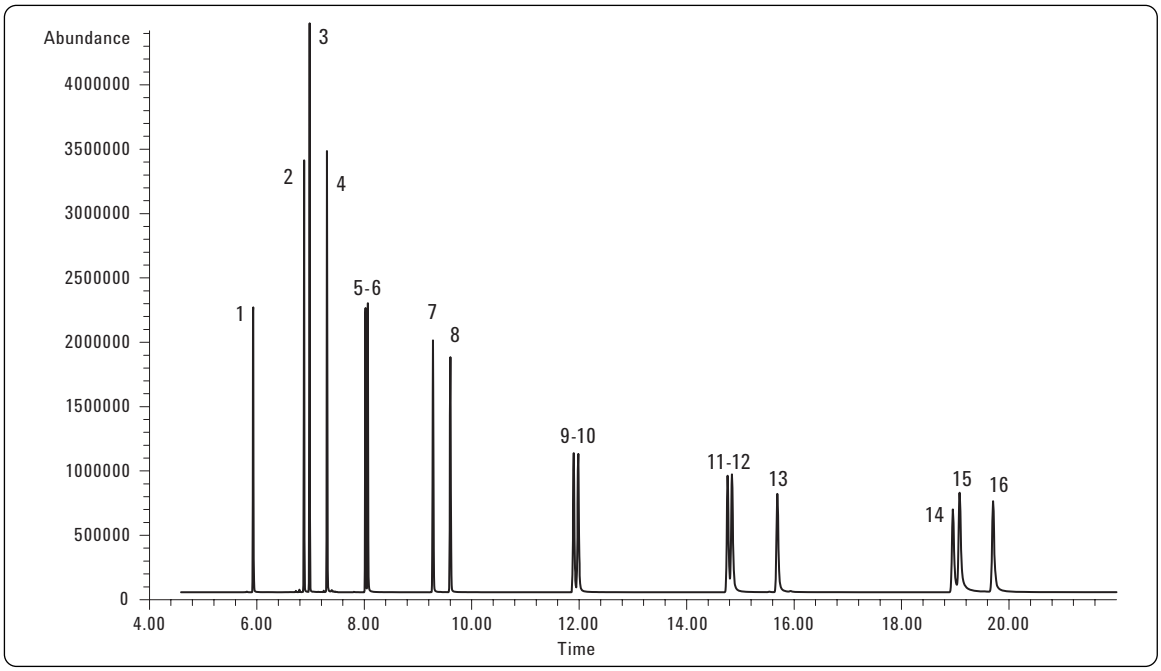

Figure 2. Reference total ion chromatogram for conventional system configuration and method conditions. Peak identities are listed in Table 3.

The resulting chromatogram is shown in Figure 3. Comparing this chromatogram with the one in Figure 2, one can see that very similar resolution is obtained in about half of the retention time. Benzo(ghi)perylene elutes at 9.3 minutes, which corresponds well to the predicted retention time of 9.1 minutes (19.7/2.17). As expected, the resolution of benzo(b)fluoranthene and benzo(k)fluoranthene was similar to the separation obtained on the standard column. Resolution was maintained, while analysis time was reduced by a factor of 2.

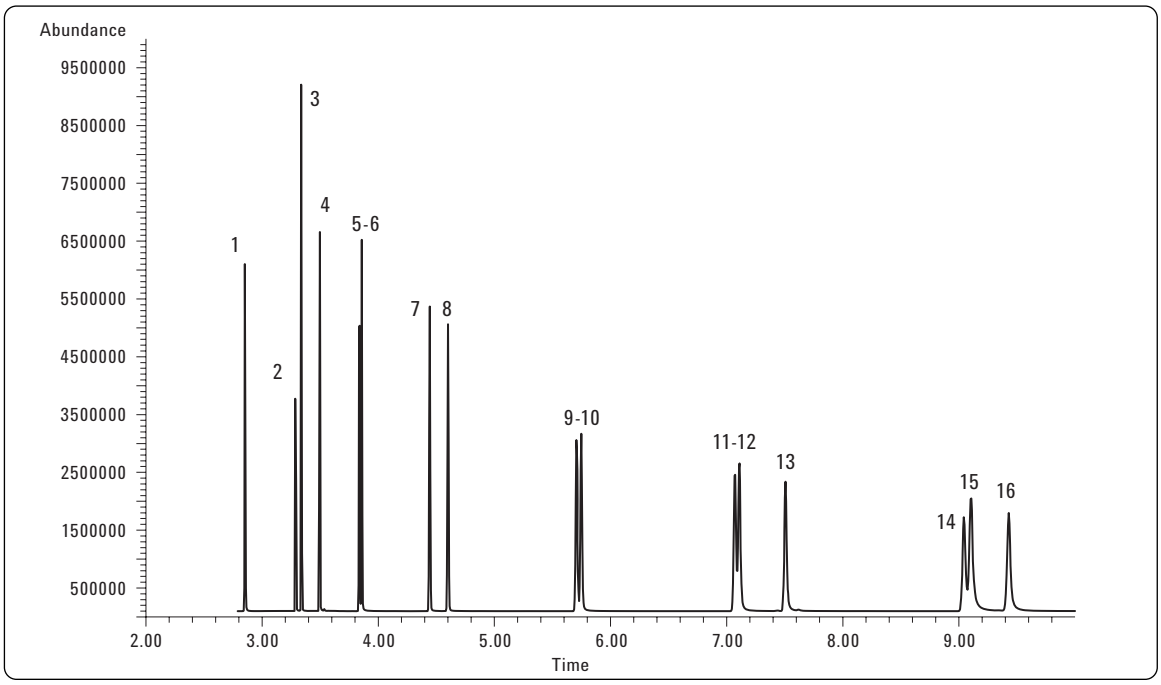

Figure 3. Fast PAH method using 20 m × 0.18 mm id × 0.18 µm Agilent J&W DB-5MS LTM column and BF at 10 minutes. SIM chromatogram shown.

Using these conditions, a backflush can be initiated at 10 minutes. To accomplish backflush, inlet pressure was dropped to 10 kPa and outlet pressure (AUX 1, QuickSwap device) was raised to 250 kPa while the column temperature was maintained at 300 °C. These conditions resulted in efficient backflush of solutes in about 7 minutes. This time was found to be required (under the stated pressure conditions) for effective removal of sample contamination (mineral oil). During backflush, the mass spectrometer detector was switched off.

Retention time and peak area repeatability were tested by analyzing a series of six standard samples using the fast GC-MS (SIM/Scan) method in combination with backflushing. The results are given in Tables 3 and 4. The repeatability of retention times was excellent, with an average standard deviation of 0.001 minute (typically < 0.01% RSD). This confirms that the heating of the capillary column in the LTM oven is uniform. Also, the peak area repeatability was excellent (2% RSD on average) and similar to results obtained using splitless injection in combination with standard GC-MS conditions.

Table 3. Retention Time Repeatability of Target PAH Compounds Using the Fast Analysis Method

Order of elution	Compound name	Mean t_R (min)	σ	% RSD
1	Naphthalene	2.850	0.000	0.00
2	Acenaphthylene	3.280	0.000	0.00
3	Acenaphthene	3.326	0.000	0.00
4	Fluorene	3.481	0.000	0.00
5	Phenanthrene	3.825	0.000	0.01
6	Anthracene	3.846	0.000	0.00
7	Fluoranthene	4.429	0.001	0.01
8	Pyrene	4.583	0.001	0.01
9	Benz(a)anthracene	5.654	0.001	0.02
10	Chrysene	5.693	0.001	0.01
11	Benzo(b)fluoranthene	6.979	0.001	0.02
12	Benzo(k)fluoranthene	7.016	0.002	0.02
13	Benzo(a)pyrene	7.405	0.002	0.02
14	Indeno(123-cd)pyrene	8.910	0.002	0.02
15	Dibenz(ah)anthracene	8.968	0.002	0.02
16	Benzo(ghi)perylene	9.278	0.002	0.02
		Average	**0.001**	**0.01**

Table 4. Area Repeatability for Target PAHs

Order of elution	Compound name	Mean peak area	σ	% RSD
1	Naphthalene	2145022	45438.72	2.12
2	Acenaphthylene	2531734	57007.60	2.25
3	Acenaphthene	3410703	76081.85	2.23
4	Fluorene	3108369	66651.55	2.14
5	Phenanthrene	2341505	50290.78	2.15
6	Anthracene	2304885	46774.62	2.03
7	Fluoranthene	2598819	57961.99	2.23
8	Pyrene	2678698	58471.60	2.18
9	Benz(a)anthracene	2264966	58416.06	2.58
10	Chrysene	2597444	50507.12	1.94
11	Benzo(b)fluoranthene	2245073	50491.19	2.25
12	Benzo(k)fluoranthene	2954729	71902.33	2.43
13	Benzo(a)pyrene	2239967	57434.91	2.56
14	Indeno(123-cd)pyrene	1616395	56133.34	3.47
15	Dibenz(ah)anthracene	3065828	86273.62	2.81
16	Benzo(ghi)perylene	2511598	65387.08	2.60
			Average	**2.37**

Next, a real sample extract was analyzed with the fast method, applying backflushing at 10 minutes after elution of benzo(ghi)perylene. The chromatograms obtained in scan and SIM mode are shown in Figures 4 and 5. The chromatogram (Figure 4) shows the high background from mineral oil contamination of the sample. At 10 minutes, the drop in signal clearly signals the initiation of the backflush. Tests would later show that the mineral oil "hump" extends well after 24 minutes (ending temperature of 300 °C) when backflush is not used.

The SIM chromatogram in Figure 5 clearly shows the presence of PAHs in the sample (high concentration of phenanthrene through pyrene, lower concentrations of later-eluting PAHs; see inset).

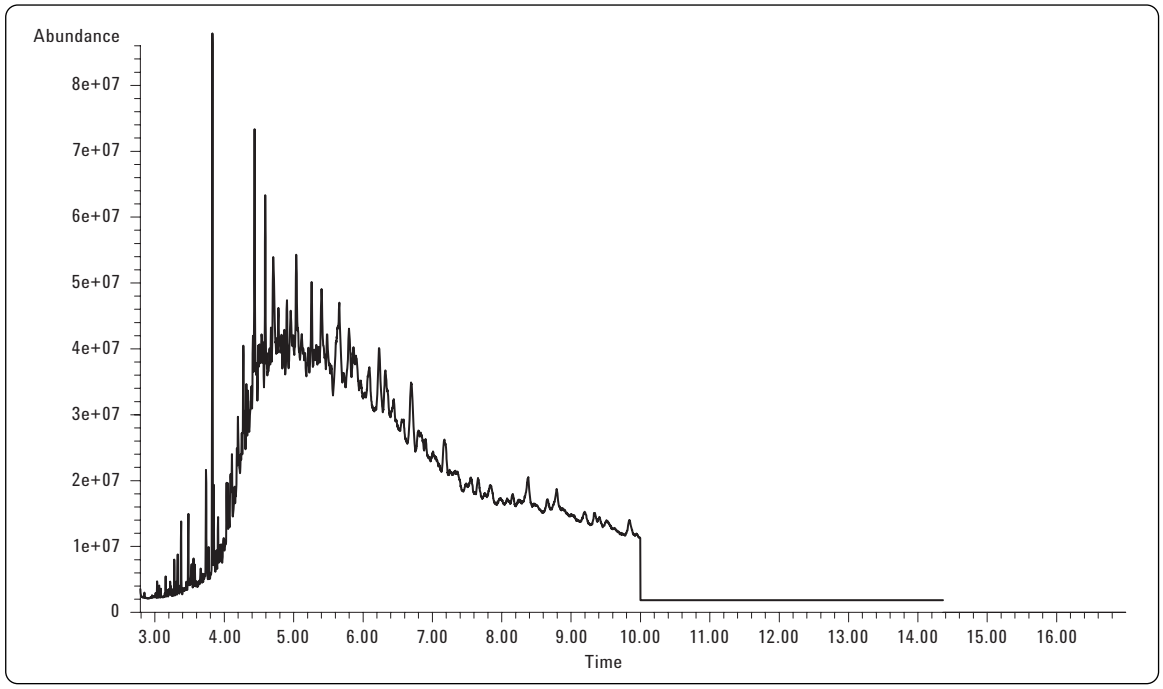

Figure 4. Sample (soil extract) with fast method and backflush at 10 minutes. Scan TIC shown.

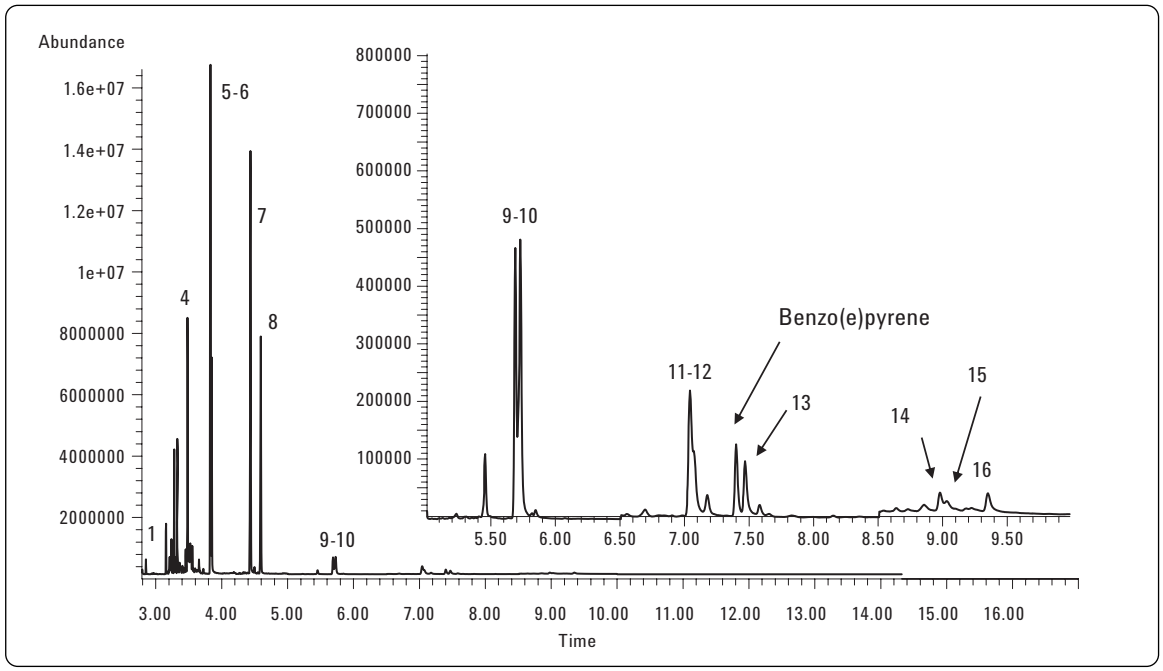

Figure 5. Sample (soil extract) with fast method and backflush at 10 minutes. SIM chromatogram shown with later portion expanded for better visibility.

A blank run was performed after the sample analysis with backflush. The resulting chromatogram in Figure 6 shows that no significant peaks were detected and that the background is flat, indicating that remaining mineral oil contamination was effectively removed with backflush.

One might question if the fast GC analysis (especially with temperature programming at 87 °C/min) in combination with SIM/Scan MS data acquisition mode results in enough data points per peak for accurate identification and quantification. The repeatability of peak areas, shown in Table 4, clearly demonstrates that the speed and repeatability of the Agilent 5975C Series MSD detection is excellent.

This is further illustrated in Figure 7, the AMDIS report for the detection of benzo(a)pyrene in the environmental sample. For this exercise, the scan data (as in Figure 3) were analyzed using AMDIS [2]. The upper window in Figure 7 shows overlaid TIC and extracted ion (*m/z* 252) chromatograms. The middle window confirms > 10 scans across the peak. The lower two windows show the raw spectrum and deconvolved spectrum, allowing unequivocal confirmation of the presence of benzo(a)pyrene in the sample. Even with the high background level, trace-level PAHs were reliably detected and confirmed.

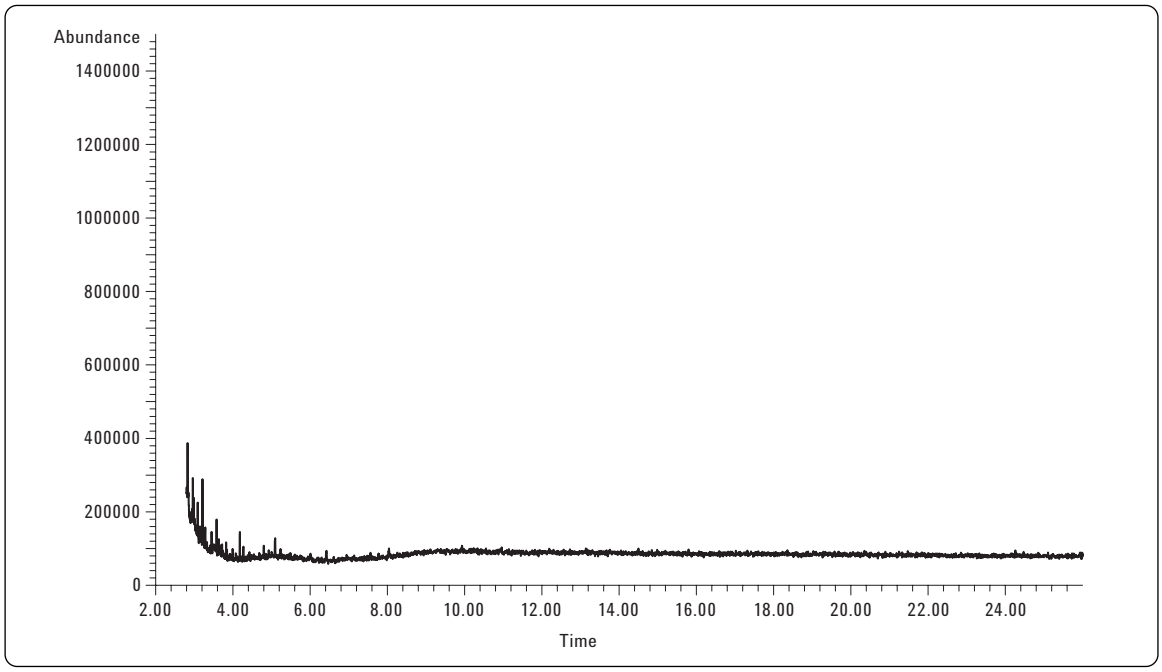

Figure 6. Blank SIM/Scan run after sample extract analysis using backflush. Scan chromatogram shows clean baseline free of contamination.

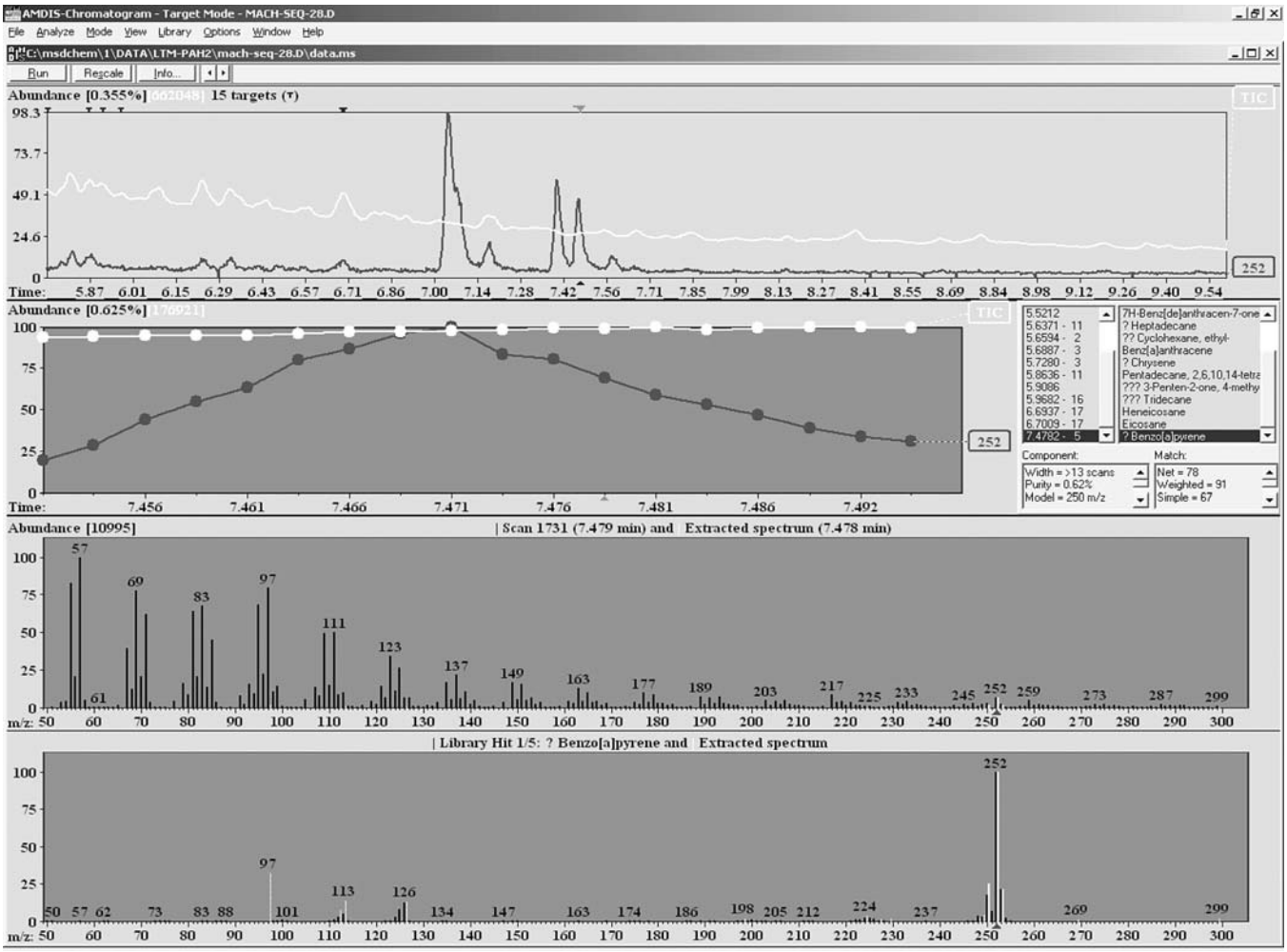

Figure 7. AMDIS report on the detection of benzo(a)pyrene in soil extract in the presence of mineral oil.

An additional sequence of multiple runs without backflush was performed to illustrate the benefits of backflushing for elimination of sample carryover. Sample extract was analyzed with the LTM oven module programmed to 300 °C and held for 11 minutes (17 minutes total run time). An example TIC chromatogram is shown in Figure 8. It can be seen that the mineral oil envelope extends to 17 minutes (and beyond).

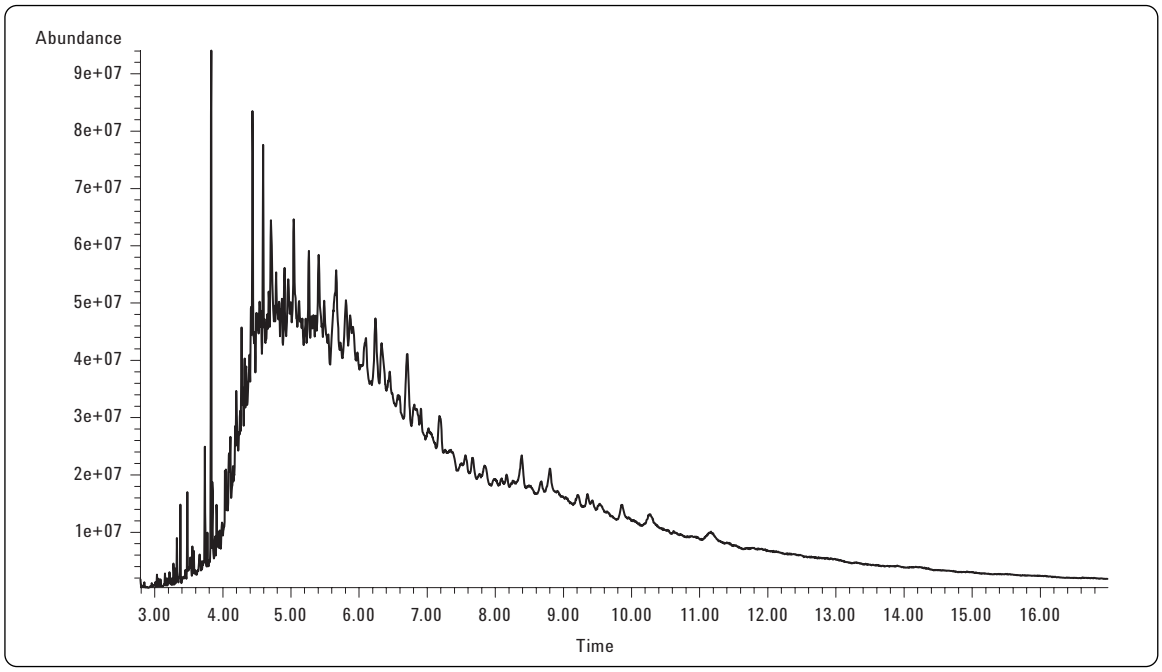

Figure 8. Soil extract analyzed without backflush. Scan chromatogram shows contribution of high mineral oil content in the extract.

Next, a blank run was performed. The chromatogram in Figure 9 shows that a significant portion of the mineral oil remained in the column even after the extended hold at the higher temperature. Comparing the upper and lower chromatograms in Figure 9 (plotted with the same scale) clearly illustrates the efficacy of backflushing.

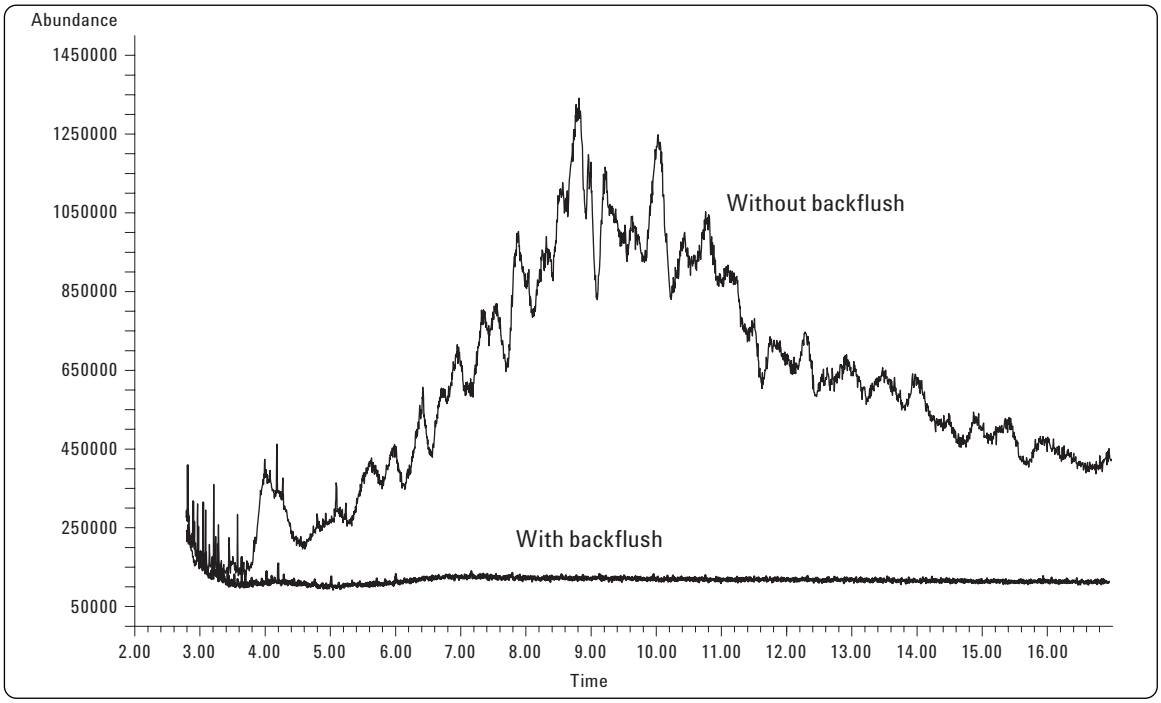

Figure 9. Blank run following the soil extract run without backflush (Figure 7). The upper TIC chromatogram shows high background carryover of matrix remaining on column after run. Bottom chromatogram is from Figure 6 (blank after method with backflush).

The standard mixture was then run after an analysis of sample extract without backflush. The resulting TIC chromatogram of the standard in Figure 10 shows several potential interferences from sample carryover in and among the PAH peaks. These contaminants are absent when backflushing is included in the method.

The extract of a sewage sludge was also analyzed. The sludge was contaminated with low-volatility plant material, phthalates, and linear alkyl sulphonates (LASs). A sequence was programmed wherein a 1-ppm PAH reference standard was analyzed first followed by 10 runs of the sewage sludge extract using backflush, one reference standard, another 10 runs of the sewage sludge extract without backflush, and a final reference standard. The chromatograms of the reference samples are overlaid in Figure 11. The two chromatograms of the references before and after the sample analyses using backflush match perfectly and show a low baseline without ghost peaks. The last reference sample chromatogram (after 10 runs of sample without backflush) shows a significantly higher background, including ghost peaks.

From this test, it is clear that low-volatility material is not removed by the standard process of keeping the column at 300 °C for 7 minutes. By backflushing, this material is effectively removed. This improves not only the quality of the data, but also reduces or eliminates the need to trim the column due to accumulation of contaminants, a typical maintenance procedure for those running extracts without backflush. This demonstration should serve to assuage concerns about the use of LTM modules with dirty samples. This had been a concern in the past because the format does not accommodate column trimming.

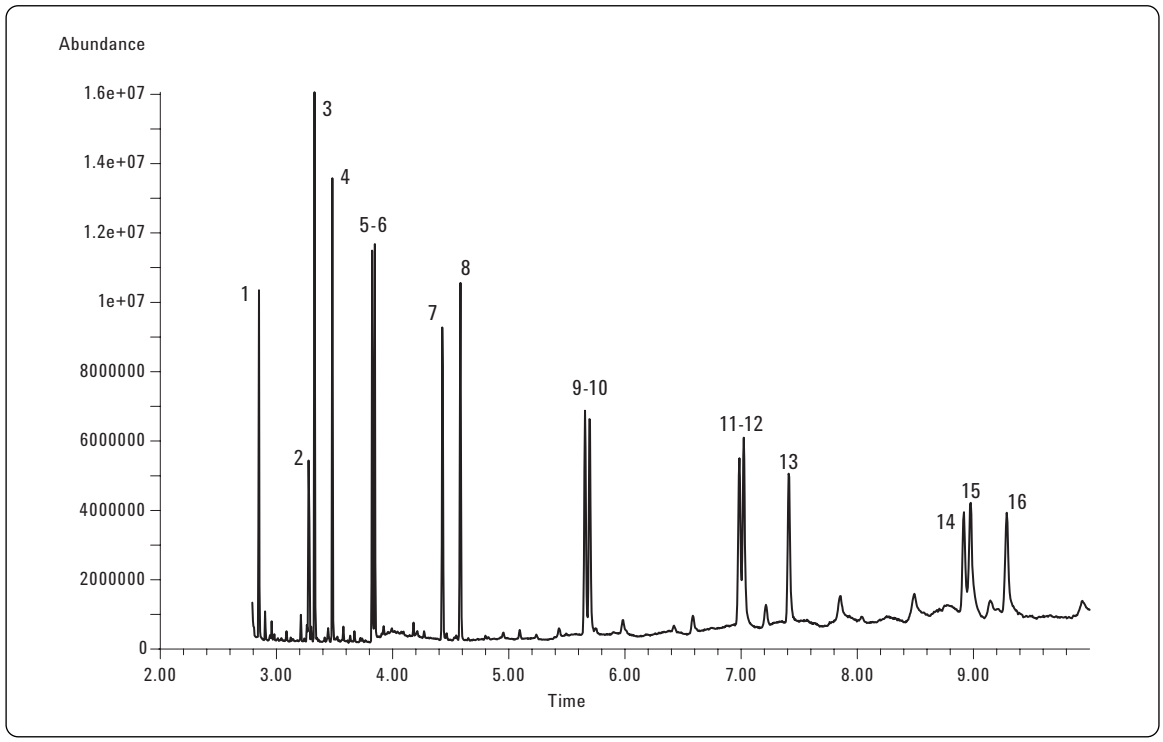

Figure 10. GC-MS scan chromatogram of 1-ppm PAH standard after sample extract analysis with no backflush.

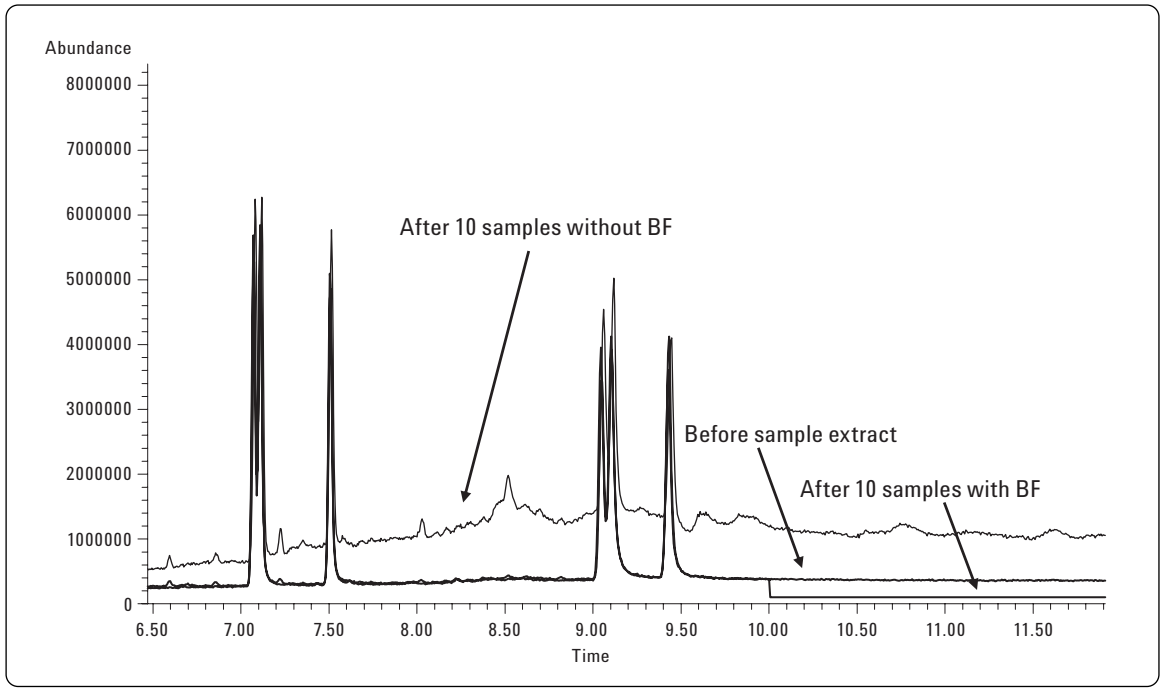

Figure 11. Standard analyses before and after analyzing sewage sludge extract with backflush and after analyzing sewage sludge extract without backflush.

A final review of improvements in analysis time revealed that the LTM column module provides an additional advantage of approximately 30% faster cooldown time compared to the conventional 7890A GC (even with fast cooling on). This further improves overall cycle time by one minute in addition to the savings from fast temperature ramp conditions and potential truncated run time from backflush.

Conclusions

A standard 25-minute method for the analysis of PAHs was translated to a fast GC-MS method using a narrow-bore column in an LTM column module. The resulting fast GC method decreased analysis time with elution of all PAHs within 10 minutes while maintaining resolution of critical isomers and method performance metrics.

The backflush capability afforded by using a Capillary Flow Technology QuickSwap capillary flow module resulted in efficient removal of high molecular-weight sample matrix and addresses prior concerns about column trimming with LTM columns. Faster run time, backflush, and faster cooldown combined in the new fast GC method with LTM significantly increase sample throughput and lab productivity while maintaining or improving data quality.

References

1. GC Method Translation Software available at http://www.chem.agilent.com.
2. AMDIS is an add-on to NIST Mass Spectral libraries. Information is available at http://chemdata.nist.gov/mass-spc/amdis/

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