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Low Level Determination of Polynuclear Aromatic Hydrocarbons in Environmental Samples Using GC/MS

N. Cleghorn, A. Loj, S. Zaworski

First Environmental Laboratories, Inc., Naperville, IL, USA

Low level analysis of PAHs is required to reach various clean-up limits for environmental regulations. The ability to maximize the GC/MS instrument conditions to meet lower reporting levels results in a more efficient and reliable determination of these analytes. The following analysis provides the necessary sensitivity and selectivity. The procedure requires that the parameters for GC as well as MS be fully optimized. Sensitivity is increased by introducing as much sample as possible onto the analytical column by using a "pressure-pulse" splitless injection. This method shows significant benefit over the traditional HPLC methods used for low level PAH analysis.

Polynuclear aromatic hydrocarbons (PAHs) in environmental samples must be analyzed at very low levels and identified accurately. Several problems are associated with SW-846 Method 8310, an HPLC method outlined by the US Environmental Protection Agency (EPA). One disadvantage of the HPLC method is a heavy dependence on retention time for compound identification. Identifying specific compounds in complex matrices is difficult when based solely on retention time data. For example, a single PAH compound is hard to distinguish in a sample that contains a large number of petroleum hydrocarbons.

The investigators were interested in the selectivity offered by mass spectrometry, and yet needed the sensitivity offered by traditional HPLC methodology. They found that three factors led to the successful use of gas chromatography/mass spectrometry (GC/MS) for PAH determinations:

- Newer generation GC/MS systems are more sensitive.
- Reporting limits can be decreased if more sample is introduced into the GC/MS system.
- Rapid analysis time can be accomplished with pressure programming.

GC/MS System

Newer generation MS systems are more sensitive than older systems. An older system can reach low detection limits if used in a selected ion mode during acquisition. However, full scan spectra provide a more assured identification of target compounds, allowing library search routines to be performed on non-target compounds. This enables the analyst to distinguish target compounds in difficult matrices.

As stated above, HPLC methodology relies heavily on retention time data for compound identification. With GC/MS, unique ions which have been isolated from the background matrix can be distinguished and used for quantitation. Samples from underground storage tanks are typically very complex, containing many petroleum hydrocarbons (Figure A). The potential for coeluting non-target analytes is extremely high.

Figure A. Typical Real-World Environmental Sample Chromatogram

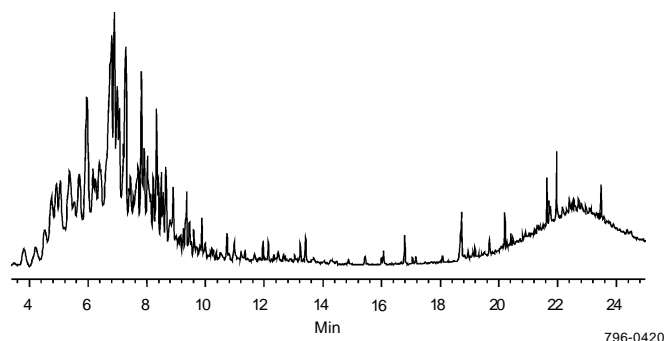


Figure provided by N. Cleghorn, A. Loj, S. Zaworski, First Environmental Laboratories, Inc., Naperville, IL, USA.

Sample Injection

Reporting limits can be decreased if more sample is introduced into the GC/MS system. This can be accomplished with a "pressure-pulse" injection. The injection port column head pressure is electronically controlled and can be programmed to begin the analysis at an elevated pressure. Increasing the column head pressure at the moment of injection forces more of the analyte onto the analytical column. The investigators used an initial pressure of 20psi (1.4kg/cm²), held for one minute, using splitless injection. The 20psi column head pressure produced a flow rate of 6.5mL/min. After one minute, the pressure was returned to a constant flow mode of approximately 1.0mL/min.

Additional analyte was introduced onto the GC by using a 2.0µL injection volume.

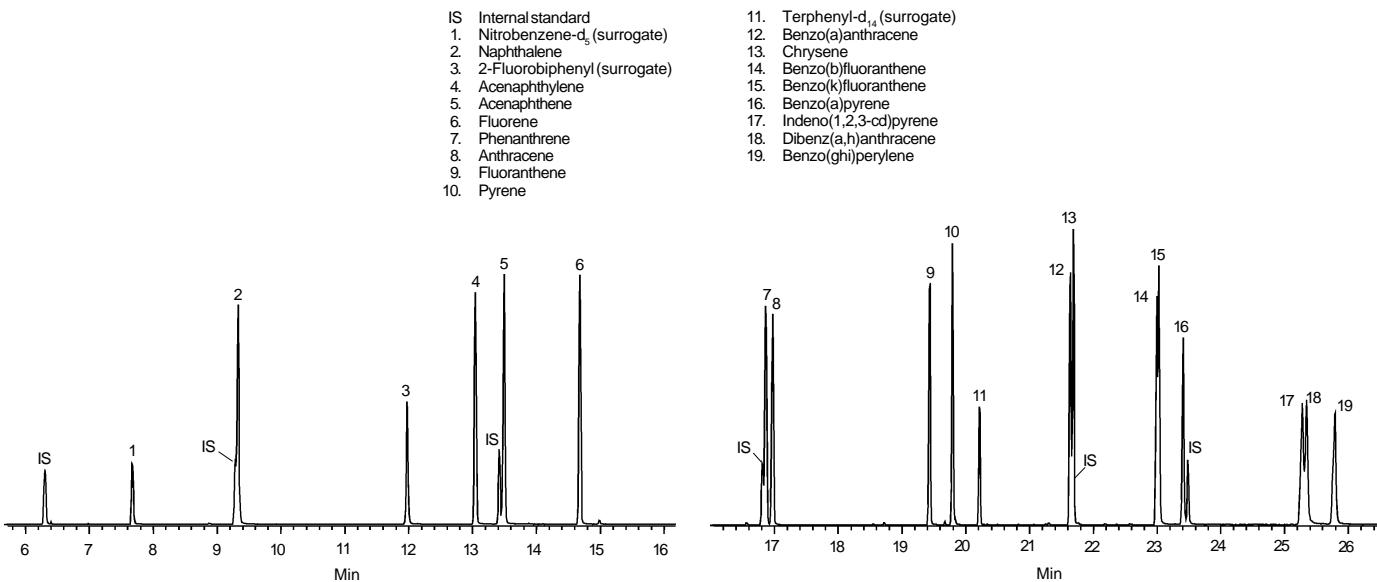
Analysis Time

To expedite the analysis, the investigators took advantage of the column pressure programming feature and ramped the column pressure as the oven temperature increased. The parameters were

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Figure B. Total Ion Chromatogram of PAHs

Column: PTE-5, 30m x 0.32mm ID, 0.25µm film
 Cat. No.: 24143
 Col. Temp.: 50°C (3 min) to 200°C at 10°C/min to 290°C at 20°C/min
 Carrier: 1.0mL/min
 Det.: mass spec (HP 5972)



796-0421, 0422

Figure provided by N. Cleghorn, A. Loj, S. Zaworski, First Environmental Laboratories, Inc., Naperville, IL, USA.

Table 1. Response Factors of PAHs by Method 8270 (Low Level)

Compound	Calibration Level (µg/mL)						Mean	%RSD
	0.25	0.50	1.0	5.0	20.0	30.0		
1,4-Dichlorobenzene-d ₄	Int. std.							
Nitrobenzene-d ₅ (surrogate)	0.377	0.399	0.402	0.388	0.394	0.430	0.4	4.46
Naphthalene-d ₈	Int. std.							
Naphthalene	1.250	1.117	1.135	1.094	1.046	1.108	1.1	6.08
2-Fluorobiphenyl (surrogate)	1.655	1.495	1.476	1.429	1.429	1.540	1.5	5.67
Acenaphthylene	1.971	1.878	1.913	1.867	1.831	1.952	1.9	2.80
Acenaphthene-d ₁₀	Int. std.							
Acenaphthene	1.221	1.140	1.205	1.114	1.082	1.156	1.2	4.60
Fluorene	1.333	1.272	1.328	1.272	1.237	1.339	1.3	3.25
Phenanthrene-d ₁₀	Int. std.							
Phenanthrene	1.193	1.150	1.132	1.096	1.057	1.110	1.1	4.18
Anthracene	1.100	1.056	1.091	1.077	1.032	1.081	1.1	2.32
Fluoranthene	1.145	1.070	1.107	1.115	1.081	1.158	1.1	3.11
Pyrene	1.653	1.568	1.613	1.566	1.470	1.634	1.6	4.16
Terphenyl-d ₄ (surrogate)	0.983	0.885	0.914	0.908	0.887	0.983	0.9	4.86
Benzo(a)anthracene	1.436	1.355	1.333	1.304	1.234	1.371	1.3	5.07
Chrysene	1.335	1.278	1.283	1.233	1.168	1.303	1.3	4.62
Chrysene-d ₁₂	Int. std.							
Benzo(b)fluoranthene	1.151	1.091	1.174	1.165	1.045	1.163	1.1	4.59
Benzo(k)fluoranthene	1.040	1.024	1.004	1.027	1.084	1.222	1.1	7.56
Benzo(a)pyrene	1.072	0.985	1.016	1.057	1.038	1.145	1.1	5.22
Perylene-d ₂	Int. std.							
Indeno(1,2,3-cd)pyrene	0.928	0.875	0.877	0.899	0.958	1.085	0.9	8.46
Dibenzo(a,h)anthracene	0.824	0.792	0.854	0.890	0.896	1.007	0.9	8.53
Benzo(ghi)perylene	0.959	0.953	0.965	0.971	0.971	1.083	1.0	5.00

Data obtained by N. Cleghorn, A. Loj, S. Zaworski, First Environmental Laboratories, Inc., Naperville, IL, USA.

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Table 2. Detection Limits of PAHs in Soil

Compound	Spike Amt. (µg/mL)	Mean (µg/mL)	Std. Dev.	MDL (µg/mL)	% RSD	Reps
Nitrobenzene-d ₅ (surr)	10.00	6.29	0.34	0.99	3.41	9
2-Fluorobiphenyl (surr)	10.00	5.87	0.28	0.81	2.81	9
Terphenyl-d ₁₄ (surr)	10.00	9.30	0.47	1.37	4.71	9
Naphthalene	0.50	0.34	0.02	0.06	3.92	9
Acenaphthylene	0.50	0.32	0.02	0.06	4.05	9
Acenaphthene	0.50	0.34	0.02	0.06	4.14	9
Fluorene	0.50	0.37	0.03	0.08	5.49	9
Phenanthrene	0.50	0.50	0.02	0.05	3.70	9
Anthracene	0.50	0.40	0.01	0.04	2.67	9
Fluoranthene	0.50	0.50	0.02	0.07	4.60	9
Pyrene	0.50	0.52	0.02	0.06	4.35	9
Benzo(a)anthracene	0.50	0.49	0.02	0.06	4.41	9
Chrysene	0.50	0.50	0.03	0.08	5.46	9
Benzo(b)fluoranthene	0.50	0.53	0.02	0.06	4.19	9
Benzo(k)fluoranthene	0.50	0.50	0.05	0.14	9.38	9
Benzo(a)pyrene	0.50	0.44	0.02	0.06	4.22	9
Indeno(1,2,3-cd)pyrene	0.50	0.49	0.03	0.09	6.28	9
Dibenz(a,h)anthracene	0.50	0.51	0.03	0.09	5.96	9
Benzo(ghi)perylene	0.50	0.52	0.03	0.09	6.32	9

Data obtained by N. Cleghorn, A. Loj, S. Zaworski, First Environmental Laboratories, Inc., Naperville, IL, USA.

set so that a constant flow of 1.0mL/min was maintained throughout the sample analysis. The analysis time was 30 minutes with these parameters (Figure B), using a PTE™-5 fused silica capillary column (30m x 0.32mm ID, 0.25µm film). The PTE-5 column was able to partially resolve the difficult-to-separate benzo(b)fluoranthene and benzo(k)fluoranthene, and separated benzo(a)anthracene and chrysene nearly to the baseline.

The working range of the analysis was 0.25 to 30µg/mL. A linear relationship is shown in the calibration curve (Table 1).

The investigators were able to meet all method limit requirements for low level detection. The data in Table 2 represent soil samples processed by Soxhlet extraction. Similar results have been observed for soil samples extracted by sonication, and for aqueous samples extracted by separatory funnel.

GC/MS provides significant benefit over traditional HPLC methods used for low level PAH analysis. It allows the use of full-scan mass spectra that aids interpretation of complex matrices, gives comparable low reporting limits that are typically less than 0.25µg/mL, and allows the analysis to be completed in 30 minutes.

Ordering Information:

Description	Cat. No.
PTE-5 Fused Silica Capillary Column	
30m x 0.32mm ID, 0.25µm film	24143
TCL Polynuclear Aromatic Hydrocarbons Mix	
16 PAHs at 20-1000µg/mL in 1 mL acetonitrile/methanol (90:10)	49156

Acknowledgment

This article was submitted by Neal Cleghorn, Adam Loj and Stan Zaworski, First Environmental Laboratories, Inc., Naperville, IL, USA.

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Fused silica columns manufactured under HP US Pat. No. 4,293,415.

