Full-Scan Low-Level Polynuclear Aromatic Hydrocarbon Analysis Using the Agilent Technologies 6890/5973 inert Gas Chromatograph/Mass Selective Detector

Application

Environmental

Author

Mike Szelewski

Agilent Technologies, Inc.

2850 Centerville Road

Wilmington, DE 19808-1610

USA

Abstract

The analysis of polynuclear aromatic hydrocarbons presents challenges due to the tendency of the polynuclear aromatic hydrocarbons to adsorb on surfaces in the chromatographic system. This results in calibrations that are not linear and the need to run selected ion monitoring for low-level analysis. The Agilent Technologies 6890/5973 inert gas chromatograph/mass selective detector system is designed for improved polynuclear aromatic hydrocarbons analysis using full scan while maintaining linearity across a wide calibration range.

Introduction

Polynuclear aromatic hydrocarbons (PAHs) are produced during combustion of organic material and are suspected carcinogens. The high amounts and widespread occurrence of these compounds in our environment requires reliable, sensitive, and very robust analytical methods.

PAHs, especially the high molecular weight ones, tend to be adsorbed on any active or cold site in a gas chromatographic system. Additionally occurring inlet discrimination often further reduces the number of compounds with higher boiling points that are transferred onto the column. Therefore, typical PAH analyses on a gas chromatography (GC) or gas chromatography/mass selective detector (GC/MSD) system show decreasing response and sensitivity with increasing molecular weight.

The Agilent 6890/5973 inert GC/MSD system has features to overcome this negative trend, including a new uncoated solid-source material and higher temperature filaments. Using a direct-connect inlet liner also improves chromatographic peak shape and sensitivity.

Many laboratories calibrate for PAHs from 0.1 to 10 ppm using Selected Ion Monitoring (SIM) for low level work. Historically, SIM has been necessary because of instrument sensitivity considerations and loss of PAHs at the lower concentration levels, although full scan data is preferred for further confirmation of the compounds.

This application note will show the performance of the Agilent 6890/5973 inert for PAHs using a calibration range of 0.1 to 10.0 ppm in full scan mode with linearity equal to that of many SIM methods.

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Table 1. Gas Chromatograph and Mass Spectrometer Conditions

GC	Agilent Technologies 6890

Inlet	EPC split/splitless
Mode	Pulsed splitless, 1 µL injected
Inlet temperature	300 °C
Pressure	12.64 psi
Pulse presssure	30.0 psi
Pulse time	0.30 min
Purge flow	30.0 mL/min
Purge time	1.0 min
Total flow	34.6 mL/min
Gas saver	Off
Gas type	Helium

Inlet liner	Direct Connect, deactivated, 4-mm id, Agilent part number G1544-80700

Oven

Oven ramp	°C/min	Next °C	Hold min
Initial		50	1.00
Ramp 1	25	200	0.00
Ramp 2	8	316	0.00

Total run time	21.50 min
Equilibration time	0.5 min
Oven max temp	325 °C

Column	Agilent Technologies HP-5MS part number 19091S-433
Length	30.0 m
Diameter	250 µm
Film thickness	0.25 µm

Mode	Constant flow
Flow	1.5 mL/min
Initial pressure	12.64 psi

Inlet	Front
Outlet	MSD
Outlet pressure	Vacuum

MSD	Agilent Technologies 5973 inert
Drawout lens	6-mm ultralarge aperture, Agilent part number G2589-20045
Solvent delay	3.00 min
EM voltage	Run at DFTPP tune voltage = 1000 V
Low mass	45 amu
High mass	450 amu
Threshold	0
Sampling	2
Scans/s	3.58
Quad temp	180 °C
Source temp	300 °C
Transfer line temperature	280 °C
Repeller voltage	DFTPP tune value
Emission current	DFTPP tune value = 34.6 µamp

Calibration standards

Calibration standards were diluted in dichloromethane from a stock mix of the 13 PAHs. The seven levels made were 10, 5, 2, 1, 0.5, 0.2 and 0.1 ppm. The perylene-d12 internal standard (ISTD) and the two surrogate standards, 1,3-dimethyl-2-nitrobenzene and triphenylphosphate, were added to each calibration level at 2.0 ppm.

Instrument Operating Parameters

The recommended instrument operating parameters are listed in Table 1. These are starting conditions that may have to be optimized.

The Agilent 6890 inlet temperature was set to 300 °C, instead of the typical 250 °C, to minimize compounds adsorbing on the liner surface. Pulsed injection was used to facilitate quantitative transfer of the heavier PAHs onto the column, minimizing inlet discrimination. Pulsed injection parameters are easily set in the ChemStation software and are automatically controlled by the electronic pneumatic control (EPC) module.

The Direct Connect inlet liner allows for complete transfer of analytes onto the column. The column inlet end attaches to the liner and minimizes analyte exposure to the stainless steel annular volume in the inlet.

The Agilent 5973 inert was tuned using the automatic DFTPP target tune, as required by some Government methods. The ultralarge aperture drawout lens was used to maintain linearity across the wide calibration range. Source temperature was set to 300 °C, which is now possible with the high temperature filaments. This higher source temperature in combination with the new source material produces better peak shapes for the PAHs.

Results

The system was calibrated at seven levels, 0.1, 0.2, 0.5, 1.0, 2.0, 5.0, and 10.0 ppm using full scan data acquisition. The total ion chromatogram (TIC) for the 0.2-ppm level is shown in Figure 1. Each calibration level contained 13 PAHs, perylene-d12 internal standard (ISTD) and the 2 surrogate standards, 1,3-dimethyl- 2-nitrobenzene and triphenylphosphate.

The relative response factor (RRF) was calculated automatically for each compound by the GC/MSD ChemStation software. Linearity was determined by calculating the percent relative standard deviation (%RSD) of the RRFs across the calibration range for each compound. This is also done automatically by the software in conjunction with Microsoft® Excel.

Linearity is shown in Table 2. The %RSD of the RRFs are shown for each of the PAHs. All RSDs are less than 5%. This level of performance is equal to that of most SIM methods for PAHs.
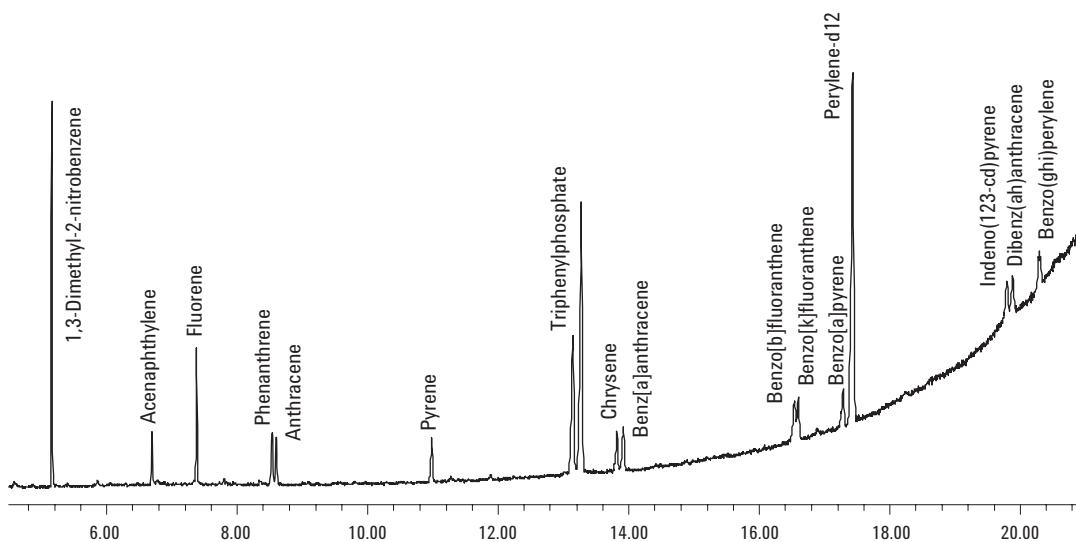

Figure 1. Thirteen PAHs at 0.2 ppm each with surrogates and ISTD at 2.0 ppm each.

As further proof of system inertness and sensitivity, a 0.01-ppm level spike was analyzed. This sample was quantitated against the seven level calibration curve using average response factor. The results are shown in Table 2. These results are excellent considering this is full scan data and the spike level was 10× lower than the lowest calibration point.

Table 2. %RSD of RRF from Seven Level Calibration and 0.01-ppm Spike Results

	%RSD	0.01 ppm Spike
Perylene-d12	3	–
1,3-dimethyl-2-nitrobenzene	1	2.100
Acenaphthylene	3	0.011
Fluorene	3	0.010
Phenanthrene	3	0.010
Anthracene	3	0.011
Pyrene	3	0.010
Triphenylphosphate	1	1.940
Chrysene	2	0.009
Benz[a]anthracene	3	0.010
Benzo[b]fluoranthene	2	0.009
Benzo[k]fluoranthene	4	0.010
Benzo[a]pyrene	2	0.010
Indeno(123-cd)pyrene	4	0.010
Dibenz(ah)anthracene	2	0.007
Benzo(ghi)perylene	3	0.011

Conclusions

The Agilent 6890/5973 inert shows much improved response and peak shape for PAHs due to the inert source material and higher allowable source temperature. This improved response gives better linearity across the calibration range. Analysis of PAHs can be accomplished using full scan data acquisition over a calibration range of 0.1 to 10 ppm, while maintaining performance similar to SIM methods.

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