Application Note

Environmental Exposure

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Analysis of European Union Polyaromatic Hydrocarbons (EUPAH) with the Agilent 8890 GC

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Abstract

This Application Note describes a method for the analysis of polyaromatic hydrocarbons (PAHs) by GC/MS. Critical PAH pairs could successfully be resolved, and reproducible calibration of certain PAHs was achieved. An Agilent 8890A GC, an Agilent 5977 GC/MSD, and an Agilent 7693A automatic liquid sampler were used in combination with an Agilent J&W DB-EUPAH column.

Introduction

The analysis of PAH compounds is commonly performed in many laboratories with samples from agricultural or environmental sources. Members of this compound class are considered to be human health hazards. The European Union (EU) has identified 16 priority PAHs for regulatory analysis, known as the EUPAH list. GC analysis of these compounds is challenging because the compound list includes multiple sets of structural isomers. In addition to the separation challenges associated with isomers, these PAH compounds have demonstrated a tendency to adsorb to surfaces within a GC flowpath. This effect commonly increases with target compound molecular weight. In addition to activity challenges, lower volatility organic compounds can exhibit inlet discrimination, creating a bias within results and affect reproducibility for a method.

Several Agilent improvements have been introduced to minimize effects due to inlet discrimination, decrease surface area for compounds to adsorb, and shift maintenance actions from reactive to preventive. Ultra Inert inlet liners are designed to better transfer active compounds to the column. Enhancements in column technology have resulted in analyte-specific column phases, such as the DB-EUPAH used in this study[1]. To further complement available consumable options, the 8890A GC provides onboard diagnostics and setpoint entry and control. Help and learning files can also be accessed through both a capacitive touch screen interface a and a web user interface (UI) for local or remote convenience.

Experimental

An 8890A GC configured with a multimode inlet (MMI), a 5977A GC/MSD, and a 7693A automatic liquid sampler (ALS) were used in the workflow. Agilent MassHunter GC/MS software was used to process the data presented here. A vial of EUPAH calibration standard was diluted with isooctane (Sigma-Aldrich, Chromosolv Grade, >99.5 %) to create an eight-point calibration range of 0.1–10 ppm. The 5977 MSD extractor source was modified to include a 9-mm extraction lens, and the mass filter was used in selective ion monitoring (SIM) mode.

Table 1 lists the consumables used in this study.

Experimental testing has concluded that, for PAH compounds, a hotter source temperature[2] and large aperture extractor lens[3] greatly assist with linearity, and performance with a minimal trade-off in sensitivity. When adjusting source and quadrupole temperatures for a method, allowing substantial time for thermal equilibration of the MSD and re-tuning at the new temperature setpoints will preclude delays and inconsistencies due to temperature changes. Tables 2 and 3 provide extended method setpoints.

Table 1. Consumables used for EUPAH data acquisition.

Description	Agilent part number
EUPAH certified standard (250 µg/mL)	5190-0487
Autosampler syringe (10 µL)	G4513-80203
Advanced Green inlet septa (green)	5183-4761
Ultra Inert splitless inlet liner with wool	5190-2293
Agilent J&W DB-EUPAH column (30 m × 250 µm, 0.25 µm)	122-9632
Extractor source large diameter lens (9 mm)	G3870-20449

Table 2. Method conditions for EUPAH on an 8890 GC.

Parameter	Value
Syringe size	10 µL
Injection volume	1 µL
Inlet type	MMI
Inlet mode	Pulsed splitless
Inlet temperature	330 °C
Pulse pressure	40 psi
Pulse time	0.5 minutes
Purge flow	50 mL/min
Purge time	0.9 minutes
Septum purge	3 mL/min
Carrier gas	Helium
Column	DB-EUPAH p/n 122-9632, 30 m × 0.25 mm, 0.25 µm
Oven equilibration	1 minute
Oven program	80 °C for 2 minutes, 40 °C/min to 225 °C, hold 6 minutes 2.5 °C/min to 330 °C, hold 4.5 minutes
GC cycle time	58.25 minutes
MSD transfer line	320 °C

Table 3. Analysis conditions for EUPAHs on an 5977 GC/MSD (extractor).

Parameter	Value
Source	Extractor - 9-mm lens
Hi Vacuum pump	Turbo
Mode	SIM
Tune	etune
Source temperature	325 °C
Quad temperature	200 °C

To minimize the occurrence of inlet discrimination, Ultra Inert splitless liners containing glass wool were used in the inlet. Also, a pressure pulse was applied for a short time after the injection. Pulsed pressure techniques are often implemented in trace-level analysis to more effectively transfer the injection components to the column. This can also provide better control of solvent expansion after vaporization in the GC inlet liner.

Results and discussion

Figure 1 shows an example chromatogram, with Figure 2 displaying expanded captures of critical pairs and calculated resolution values.

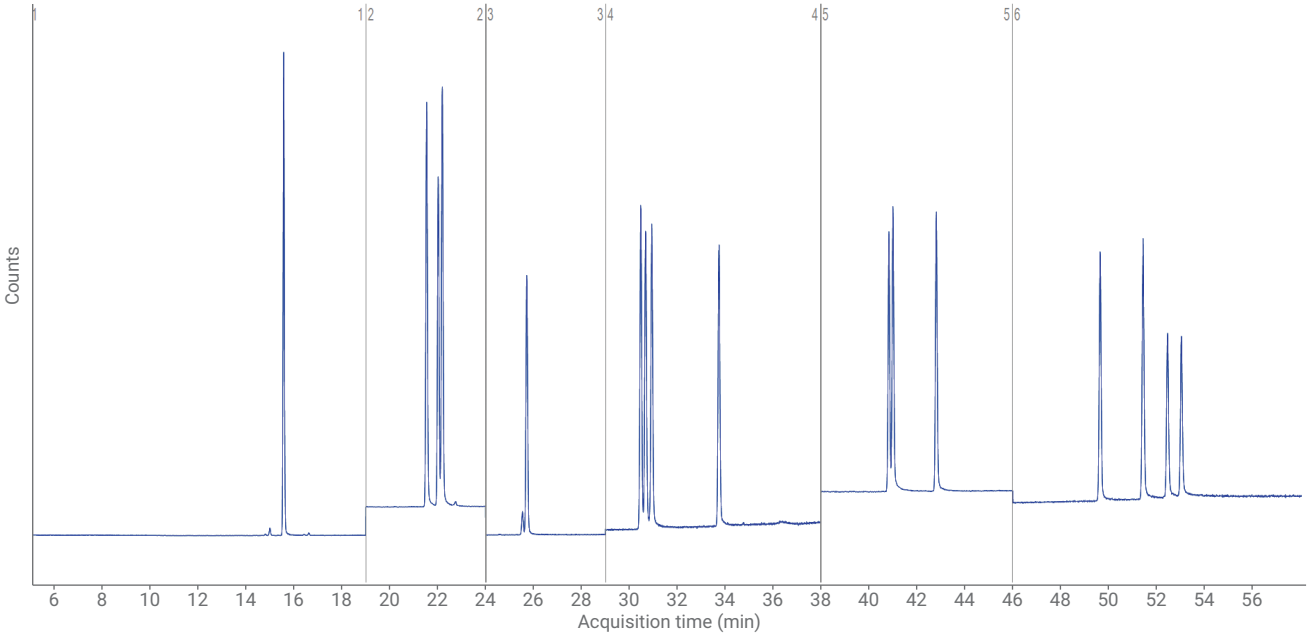

Figure 1. Resulting time-segmented SIM chromatogram of an EUPAH standard (1 ppm).

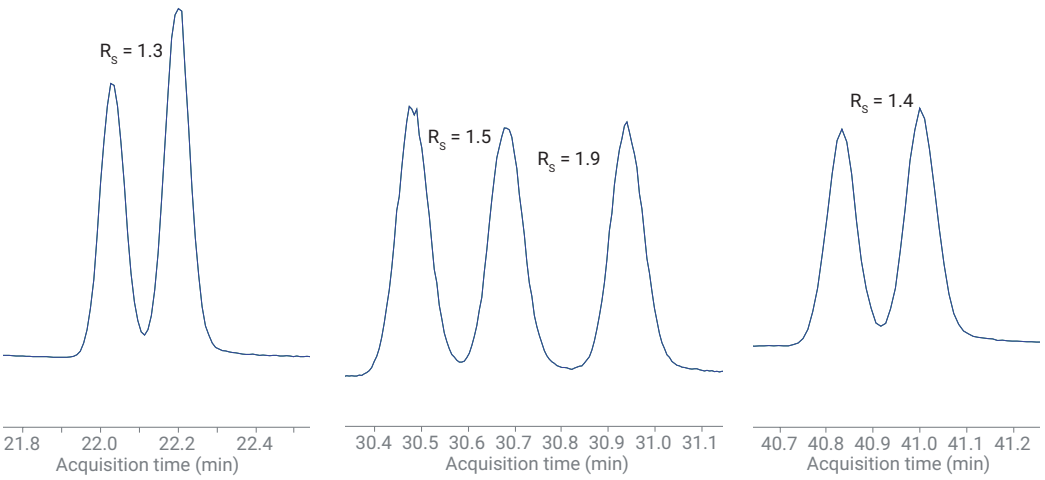

Figure 2. Resolution values for critical pairs for a 1 ppm standard injection. Resolution values were calculated using the following formula: $R_S = 1.18[\Delta RT/(\Sigma PW_{50})]$.

Standards for an eight-point calibration curve were analyzed, with bracketing blanks to evaluate carryover. While working in this concentration range, no carryover was observed. To check the precision of the calibration curve, two calibration check standards were analyzed immediately following the post calibration blanks. The calibration curve was generated using linear regression with inverse weighting, and Table 4 summarizes the coefficients of determination. Comparing the calculated amount found after calibration to the target amount in each standard generated accuracy within ±5 % for each calibration level for each compound in the mix.

Table 4. Linear correlations of calibration curves with inverse weighting applied.

Compound	R^2
Benzo[c]fluorene	0.9999
Benz[a]anthracene	0.9998
Cyclopenta[c,d]pyrene	0.9999
Chrysene	0.9998
5-Methylchrysene	0.9999
Benzo[b]fluoranthene	0.9997
Benzo[k]fluoranthene	0.9997
Benzo[j]fluoranthene	0.9999
Benzo[a]pyrene	0.9997
Indeno{1,2,3-cd]pyrene	0.9990
Dibenzo[a,h]anthracene	0.9997
Benzo[ghi]perylene	0.9999
Dibenzo[a,l]pyrene	0.9994
Dibenzo[a,e]pyrene	0.9997
Dibenzo[a,i]pyrene	0.9992
Dibenzo[a,h]pyrene	0.9994

The GC cycle time could be decreased by optimizing the temperature profile of the oven. An alternative is to convert this set of parameters to a smaller diameter column[4] using available tools such as the Agilent method translator. This software tool is built into the GC driver for users of Agilent data systems, and is available as a standalone tool accompanying the user documentation. Instructional videos for how to use this tool are available on the Agilent YouTube channel[5]. A best practice for improving cycle time is to start with a series of extended runs, demonstrating resolution between target compounds before accelerating the acquisition process. The extended runs should also be evaluated with matrix to determine if the additional components of a sample affect the chromatography.

Conclusion

This Application Note presents a method that resolves critical PAH pairs in the analyzed EUPAH standard, and precise calibration of constituent PAHs. Agilent has created a continuously evolving collection of products to assist customers in the development of robust analytical procedures while providing the flexibility to suit different levels of sample complexity, regulatory oversight, and user experience level. The 8890A GC is the newest addition to our suite of options. Providing onboard diagnostics, built-in help and learning files, maintenance counters, and a host of compatible complements, the 8890 GC combines the features of the past, as well as new and resourceful improvements for enhancing laboratory productivity.

References

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