APPLICATION NOTE

Analysis of Polycyclic Aromatic Hydrocarbons (PAHs) in Water Samples by GC-MS (SQ)

AN169.v1, February 2025, SCION Instruments

Introduction

Polycyclic aromatic hydrocarbons (PAHs) fall under the class of semi volatile organic compounds (SVOCs). PAHs are released into the environment by both human activity and natural processes (such as forest fires and volcanoes). PAHs are released by the burning of coal, wood and other solid forms of fuel, as well as being present in vehicle emissions and cigarette smoke.[1]

Gas chromatography/mass spectrometry (GC/MS) is a commonly used technique for the analysis of PAHs. PAHs are considered to be harmful to human health and therefore their presence within the environment requires monitoring.

PAHs are often tested independently as their own category or can fall under general SVOC testing.

SVOCs are likely to be found in products such as pesticides, oil-based products and fire retardants, SVOCs are able to be deposited on surfaces – unlike VOCs which are more likely to be monitored for in the air.[2] Some SVOCs are considered to be carcinogenic. Visit the SCION website to find our application note covering EPA method 8270E for full SVOC analysis.

Human exposure to PAHs can come from a number of sources including but not limited to: contaminated soil, drinking water and food that has been smoked or cooked using methods such as chargrilling.[3]

In this application note water samples will be analysed for PAHs using a 8500 GC with 8700 MS single quad (SQ) and 8400PRO autosampler.

Experimental

An internal standard was employed in this analysis to help improve the precision of results.

The internal standard solution was prepared by adding 500 µL of EPA 8270 semi volatile IS mix to a 100 mL volumetric flask and making to volume with DCM (500 µL of this working standard was added to each sample giving final IS concentration in all samples of 0.5 ppm).

A commercially available PAH standard containing 16 PAH compounds at 2000 µg/mL was used to prepare linearity samples at 6 concentrations: 1, 0.6, 0.3, 0.1, 0.01 and 0.005 µg/mL.

10 system precision samples were prepared in DCM at a concentration of 0.1 µg/mL.

Tap water samples were prepared by adding 100 mL of tap water to a Duran flask with 20 mL (19 mL for spiked samples) of dichloromethane (DCM), to spiked samples 1 mL of a 0.01 µg/mL PAH mix stock solution was added. 500 µL of internal standard was added to both spiked and blank tap water samples. The solutions were then stirred for 15 minutes by magnetic stirrer bar. 10 mL DCM was extracted and the samples concentrated under nitrogen gas to a volume of 0.5 mL and ran.

Instrument parameters can be found in Table 1.

Table 1 instrument parameters for GC-MS

GC Part	Settings
Injector	300°C Pulsed splitless injection Splitless time 1 min Pulse 25 psi for 0.75 min
Injection Volume	1.0 µL
Column	SCION-5MS 30m x 0.25mm x 0.25µm
Carrier Gas	Helium 1.5mL/min
Oven Program	50°C (hold 1.0 min), 10°C/min to 330°C (hold 1.0 min)
Run Time	30 min
Software	MSWS v 8.2.1
MS Part	**Settings**
MS transfer line temp	325°C
Ion source temp	350°C
MS mode	Electron Ionization
Delay collection time	5.00 min
Scan mode	SIM mode

The instrument method stated in Table 1 gave excellent specificity. All compounds resolved from each other and exhibited good peak shape.

Selective Ion Monitoring (SIM) was used in order to improve sensitivity of the system. A single quantifier ion was used for each compound, this was chosen as the most abundant ion for each PAH.

The 2nd and 3rd most abundant ions for each PAH were then employed as qualifier ions in order to assist with analyte confirmation and prevent false positive results. An example screenshot from MSWS showing quantifier and 2 qualifier ions for fluoranthene can be seen in Figure 1.

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Results

Table 2 shows the correlation coefficient and system precision (n=10) results for all compounds present within the PAH mix. Also shown are the chosen quantifier and qualifier ions for each compound.

The r^2 values of all compounds demonstrate excellent linearity, with all results >0.99. Typically it is the testing laboratories decision to define validation criteria unless otherwise stated in specific methods. For example EPA 8270 requires a minimum r^2 >0.99.

System precision values of all compounds demonstrate good repeatability with all results <4%. It is common industry practice to include RSD's below <10% when not stipulated in the reference method.

Table 2 Correlation coefficient and system precision results for all PAHs

PAH	Correlation coefficient (r^2)	RSD(%)	SIM Ions (Quantifier and qualifier)
Naphthalene	0.9982	0.21	128, 127, 102
Acenaphthylene	0.9935	2.59	152, 151, 150
2-Bromonaphthalene	0.9967	1.52	127, 206, 208
Acenaphthene	0.9984	0.69	153, 154, 152
Fluorene	0.9982	1.09	165, 166, 163
Phenanthrene	0.9991	0.50	178, 176, 76
Anthracene	0.9960	0.75	178, 176, 179
Fluoranthene	0.9984	1.81	202, 200, 201
Pyrene	0.9984	1.75	202, 200, 101
Benz(a)anthracene	0.9995	1.79	228, 226, 229
Chrysene	0.9994	1.08	228, 226, 113
Benzo(b)fluoranthene	0.9995	3.72	252, 250, 253
Benzo(a)pyrene	0.9995	2.69	252, 250, 253
Indeno(1,2,3-cd)pyrene	0.9994	1.49	276, 274, 138
Dibenz(ah)anthracene	0.9955	1.86	278, 276, 139
Benzo(ghi)perylene	0.9994	1.26	276, 138, 137

Table 3 shows some example recovery and precision values for the spiked LOQ samples. With recovery between 40 – 108% for all compounds and precision <7% at the LOQ level.

Table 3 Example recovery and precision results taken from spiked LOQ sample

PAH	Recovery (%)	RSD(%)
Naphthalene	107.95	2.70
Acenaphthene	88.11	1.92
Pyrene	105.90	1.25
Benzo(b)fluoranthene	99.32	1.80
Benzo(ghi)perylene	104.40	2.58

The extracted blank was shown to have no PAHs present as expected. An overlay spectra showing 2-bromonaphthalene from a spiked LOQ sample (red) and a water sample (green) can be seen in Figure 2.

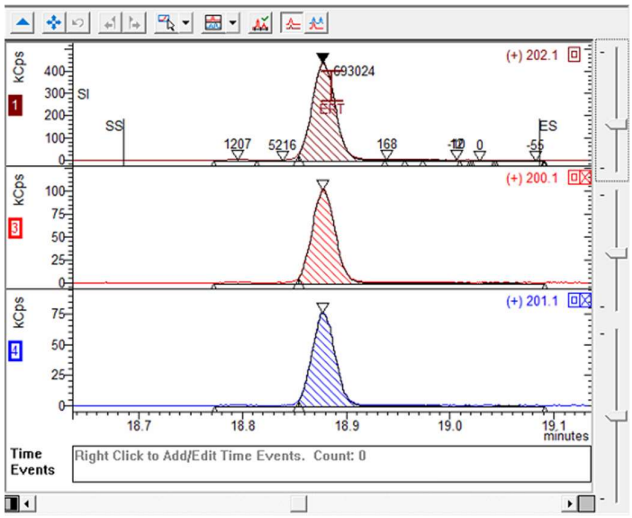

Figure 1 Example mass spectra of Fluoranthene from a linearity sample (L3) showing quantifier (top) and qualifier plots (middle and bottom)

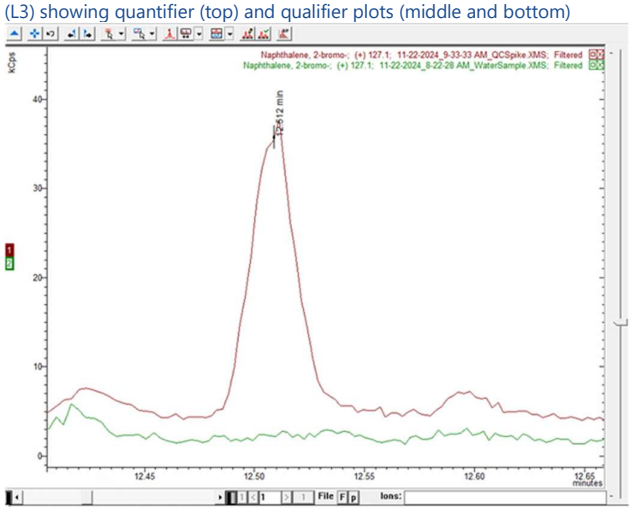

Figure 2 Overlaid spectra of 2-bromonaphthalene from an LOQ sample (red) and a water sample (green)

Figure 3 shows an example screenshot from SCION MSWS showing quantifier ion for fluorene spiked LOQ sample, linearity result for fluorene and QC accuracy (verification deviation).

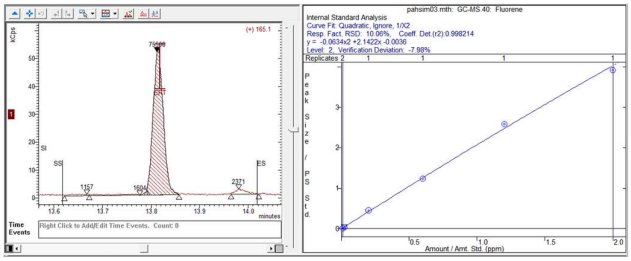

Figure 3 Example data review tab for fluorene LOQ sample 1 showing quantifier plot, linearity, and QC recovery

Conclusion

A method has been successfully developed and validated for the determination of polycyclic aromatic hydrocarbons (PAHs) as an example of semi volatile organic compounds (SVOCs) in water.

Samples were extracted by liquid-liquid extraction (LLE), check out the SCION knowledge centre on our website where we have multiple technical notes on sample preparation including LLE.

Spiked samples were employed at the required LOQ level to confirm the good working of both the instrument method and LLE extraction process of samples. Confirmation of the LOQ level in this way, although more time consuming is the best way to assure a good method rather than relying on theoretical LOQ's.

It is recommended to use quality control samples, for example spiked samples at L3 level throughout the analytical run to monitor the status of the instrument over lengthy run times (i.e. bracket every 20 samples).

SCION instruments recommends checking with local regulatory authorities to ensure all testing and reporting requirements are met, or contact the SCION applications team for assistance.

For more information, please contact:

E: sales-eu@scioninstruments.com

W: www.scioninstruments.com

Ordering Information

Ordering Information for the 8300 GC	
Part	**Part Number**
SCION SQ SELECT, w/8300, SSL-T21; 120V	SCIONSQ83SEL311
SCION SQ SELECT, w/8300, SSL-T21; 230V	SCIONSQ83SEL312
8400 PRO Autosampler for 8300 and 8500 GC	840000001
Suggested Consumables	
Part	**Part Number**
SCION-5MS 30m x 0.25mm x 0.25µm	SC32223
Liner TAPER QW ULTRA PK/5	41312117
15% Graphite/85% Vespel Ferrule 1/16" with 0.4 mm hole pk/10	41312148
BTO Septa 9 mm, pk/50	CR298713
10 µL fixed needle syringe, 5 cm, 0.47 mm OD, 26 g conical needle	41312133
Vial, 9-425 Screw Thread, 2 mL Clear Glass 12 x 32 mm Flat Base with Label, pk/100	41311000
Cap, Screw, Blue 9-425 Open Top Ribbed with 9mm Red PTFE/Sil Septa 1mm Thick. 100pcs/pk.	41311002

For ordering info on the SCION 8500 GC, which offers greater functionality with the option of up to 4 detectors (including MS), please contact your local SCION sales representative.

References

[1] United States Environmental Protection Agency, https://www.epa.gov/sites/default/files/2014-03/documents/pahs_factsheet_cdc_2013.pdf, (accessed Feb 2025)

[2] United Sates Environmental Protection Agency, https://www.epa.gov/east-palestine-oh-train-derailment/what-are-svocs-and-vocs, (accessed January 2025)

[3] Public Health England, https://www.gov.uk/government/publications/benzoapyrene-properties-incident-management-and-toxicology/polycyclic-aromatic-hydrocarbons-benzoapyrene-general-information, (accessed January 2025)