

Chromatography Technical Note No AS 127

Trace analysis of Polycyclic Aromatic Hydrocarbons (PAHs) in water using Twister SBSE Technology

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Introduction

Polycyclic Aromatic Hydrocarbons, PAHs, are found naturally in the environment but they can also be man-made. They are created from incomplete burning of carbon-containing materials like coal, oil, gas, and garbage. The toxicity of PAHs is structure-dependent.

Current methods for PAHs usually involve a liquid / liquid extraction with dichloromethane, based upon the EPA Method 610. The extraction takes up a significant time and can increase contamination possibilities.

Within this application note, we show how PAHs can be extracted from water samples using Twister SBSE (Stir Bar Sorptive Extraction) technology, to achieve a fully automated method on a GC-Single Quadrupole instrument.

A Twister is a glass-encased magnetic stir bar coated with an extraction phase. When the twister stirs an aqueous sample, analytes partition between the extraction phase, in this case PDMS, and the liquid sample phase (water), just as in liquid-liquid extractions. The percentage recovery onto the twister bar will depend on the Log K_{ow} for each analyte. Log K_{ow} is the octanol-water partition coefficient. A high Log K_{ow} would suggest the analyte is lipophilic and this would likely be adsorbed onto the twister bar. Here, PAHs have a Log K_{ow} greater than 3, which enables a high recovery using Twisters.

Figure 1 shows a photograph of the instrumentation which can be used.



Figure 1: Instrumentation for Twister analysis.

Figure 2 shows a schematic of how the GC inlet is configured for twister analysis.

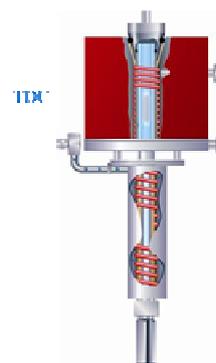


Figure 2: Schematic of GC Inlet for Twister analysis: Gerstel Thermal Desorption Unit (TDU) and Cooled Injection System (CIS) 4.

Instrumentation

Gerstel MultiPurpose Sampler MPS 2 XL
Gerstel Thermal Desorption Unit (TDU)
Gerstel Cooled Injection System (CIS) 4
Agilent GC 7890A
Agilent 5975 C inert XL MSD
Maestro Version 1.4.8.14/3.5

Method

Extraction procedure:

A mix of sixteen PAHs was prepared in LC-MS grade water at varying concentrations from 0.01 $\mu\text{g/l}$ to 1.0 $\mu\text{g/l}$. To every 100 ml of sample, containing 5% of methanol, a PDMS twister was added and stirred for 2 hours.

After the twisters have been stirred for this fixed amount of time, each twister is then dried, placed in a TDU tube, fitted with a transport adaptor and placed into the twister sample tray ready for analysis. Each TDU tube with twister is transferred into the thermal desorption unit using the MultiPurpose Sampler (MPS). A fast temperature ramp is used to desorb the extracted analytes from the twister onto the Cooled Injection System (CIS) which is set at a cold temperature to focus the analytes of interest. Once the analytes have been focused into a tight band on the CIS, another fast temperature ramp is used to desorb the analytes onto the GC column.

Figure 3 shows a photograph of some twister extraction.



Figure 3: Photograph of a typical twister extraction.

GC/MS conditions:

Column: HP-5 30 m x 0.25 mm x 0.5 µm (J&W Agilent)
 Carrier gas: Helium at 1.5 ml/min flow rate
 Thermal gradient: 50°C (1 min); 40°C/min to 110°C; 15°C/min to 310°C (hold 10 min)
 Single ion monitoring was performed, using one ion for each analyte.

TDU temperature program: 50°C (0.5 minutes); 450°C/min to 280°C (hold 5 min)
 CIS 4 temperature Program -100°C; 12°C/s to 280°C (hold 5 min)
 The CIS 4 was fitted with a Glass wool deactivated liner.

Results

Good linearity was achieved for the majority of analytes ($R^2 > 0.99$). Table 1 shows the correlation coefficient from a five point calibration between 0.01 µg/l and 1.0 µg/l.

Analyte	Correlation coefficient (R^2)
Naphthalene	0.9998 (linear fit)
Acenaphthylene	0.9996 (linear fit)
Acenaphthene	0.9999 (linear fit)
Fluorene	0.9995 (linear fit)
Phenanthrene	0.9988 (linear fit)
Anthracene	0.9969 (linear fit)
Fluoranthene	0.9964 (linear fit)
Pyrene	0.9966 (linear fit)
Benzo(a)anthracene	0.9981 (linear fit)
Chrysene	0.9994 (linear fit)
Benzo(b)fluoranthene	0.9996 (linear fit)
Benzo(k)fluoranthene	0.9986 (linear fit)
Benzo(a)pyrene	0.9993 (linear fit)
Indeno(123cd)pyrene	0.9980 (linear fit)

Table 1: Correlation coefficient for PAHs

A quadratic model has been used for Dibenz(ah)anthracene and Benzo(ghi)perylene. Further method development is required for these two high mass PAHs, such as improving the Twister desorption conditions.

Figure 4 shows calibration plot, corrected by Internal Standard, for Naphthalene, Phenanthrene and Chrysene.

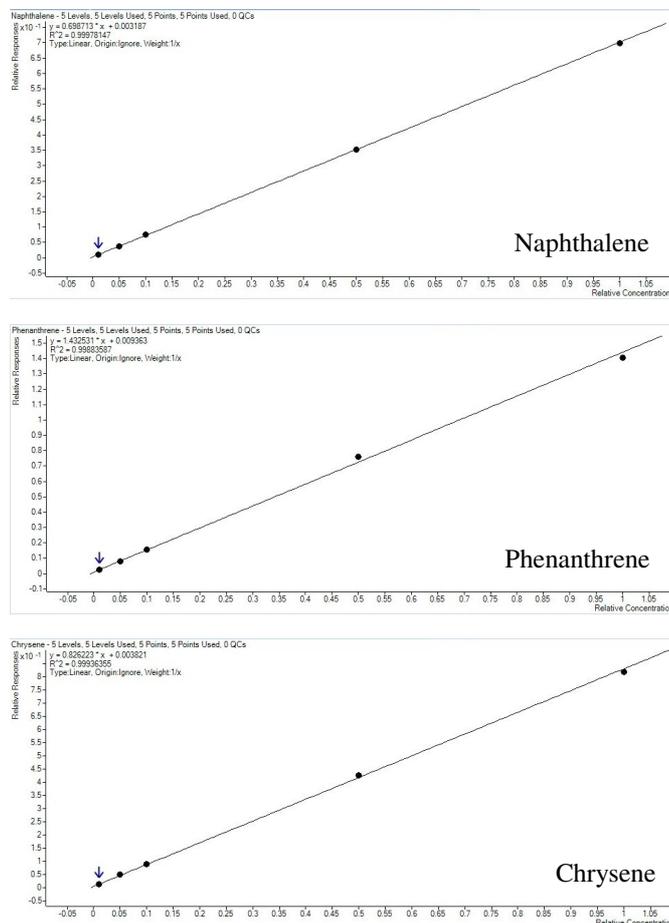


Figure 4: Calibration plot for Naphthalene, Phenanthrene and Chrysene.

Good precision was also achieved for the majority of analytes (RSD < 10%). Table 2 shows precisions obtained for five replicate twister extractions at 0.5 µg/l, using internal standard.

Analyte	% RSD
Naphthalene	2.58
Acenaphthylene	2.96
Acenaphthene	1.55
Fluorene	3.44
Phenanthrene	5.44
Anthracene	5.03
Fluoranthene	6.64
Pyrene	6.64
Benzo(a)anthracene	5.69
Chrysene	6.08
Benzo(b)fluoranthene	10.74
Benzo(k)fluoranthene	5.10
Benzo(a)pyrene	8.49
Indeno(123cd)pyrene	8.12

Table 2: Precision achieved at 0.5 µg/l.

Benzo(b)fluoranthene will require some further method development to get an RSD lower than 10%.

Figure 5 shows an example of extracted chromatogram (SIM ion 252) of three PAHs at the lowest calibration standard 0.01 $\mu\text{g/l}$: benzo(k)fluoranthene, benzo(b)fluoranthene and benzo(a)pyrene compared to an extracted blank.

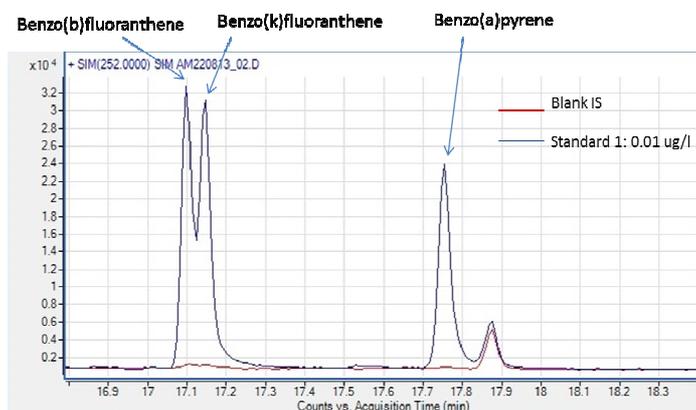


Figure 5: SIM chromatogram (ion 252) comparison of benzo(k)fluoranthene, benzo(b)fluoranthene and benzo(a)pyrene at 0.01 $\mu\text{g/l}$ vs an extracted blank.

Discussion

Good precision and linearity could be achieved with this enrichment twister method for 13 PAHs. Further method development is required for Dibenz(ah)anthracene, Benzo(ghi)perylene and Benzo(b)fluoranthene. The technique is simple and avoids the use of liquid-liquid extractions.

Future work will be carried out and presented in another application note: such as precision at the top and bottom range and recoveries in real water samples to calculate theoretical Limits of Detection. This could be done by NS30 water industry performance testing.

If you are interested in Twister applications, please contact Anatune on enquiries@anatune.co.uk.