Chromatography Technical Note No AS156

Use of SBSE for clean-up of QuEChERS extracts from complex matrices

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Introduction

Due to its non-selective nature, the use of QuEChERS (quick, easy, cheap, effective, rugged and safe) as an extraction technique has been widely adopted for many multi-residue methods. However, due to matrix interferences in many cases a more specific and often multi-step clean-up is required in order to attain the required limits of detection for some analytes.

GERSTEL application notes [1, 2] have detailed the use of stir bar sorptive extraction (SBSE) as an alternative to SPE procedures following QuEChERS extraction for analysis of polycyclic aromatic hydrocarbons (PAHs) in seafood. A previous Anatune application note [3] has also demonstrated the suitability of SBSE for determination of PAHs in water.

Within this application note, we show how SBSE can be utilised for clean-up and enrichment of PAHs from QuEChERS extracts of complex matrices.

QuEChERS extracts were provided by Gareth Proctor at EA Leeds in order to evaluate this approach. The procedure uses SBSE as a combined clean-up and enrichment step following the initial QuEChERS extraction into acetonitrile.

A TwisterÊ is a magnetic stir bar coated with an extraction phase. Analytes partition from the sample matrix into the extraction phase and can then be directly thermally desorbed into the instrument. As polar and high molecular weight matrix components are not extracted, matrix interferences are reduced and high enrichment of analytes can be achieved.

This work was performed on an Agilent Triple Quadrupole 7000 with Multiple Reaction Monitoring detection (MRM) providing a highly selective and sensitive method for these compounds. Figure 1 shows the Twister set up with the GERSTEL MultiPurpose sampler (MPS).

Figure 1: Twister instrument set up with GERSTEL MPS

Instrumentation

GERSTEL MultiPurpose Sampler (MPS) 2 XL Dual head
GERSTEL Cooled Injection System (CIS) 4
Agilent GC 7890B
Agilent 7000 Triple Quadrupole

Method

Sample extraction:
An aliquot (1ml) of the QuEChERS extract (in MECN) was taken and 4ml of aqueous 0.1M sodium hydrogen carbonate added. Samples were extracted for 90 minutes using a Gerstel PDMS twister stir bar (10mm x 0.5mm) at 1200rpm. After the twisters had been stirred, each twister was then rinsed with water, dried and 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 (TDU) 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 then heated to transfer the analytes onto the GC column.

QuEChERS extracts (in MECN) were provided of calibration standards, blanks and samples.

GC/MS conditions:

TDU temperature program: 40°C, ramped to 300°C (hold 5 min) Splitless desorption.
CIS 4 temperature Program -120°C; ramped to 300°C (hold 3 min)

GC-MS conditions were provided by the customer, and included two MRM transitions for each analyte.

Results

Good correlation was achieved for the extracted calibration standards, as shown in Table 1, alongside recovery data for an AQC sample at 250 µg/L. Example calibration curves are given in Figures 2 and 3.

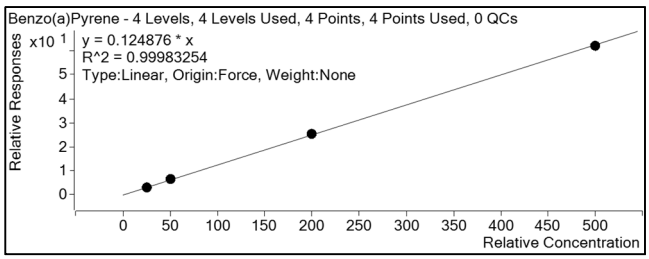

Figure 2: Calibration for Benzo(a)Pyrene (25-500 µg/L)

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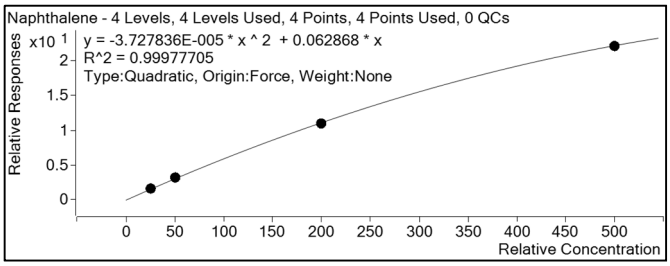

Figure 3: Calibration for Napthalene (25 to 500 µg/L)

Table 1: Recoveries - calculated accuracy of AQC sample (250 µg/ml) and calibration data

Compound	Cal fit	R^2	Accuracy (%)
Naphthalene	Quadratic	0.9997	92.8
1-methyl napthalene	Quadratic	0.9995	110.1
2-methyl naphthalene	Quadratic	0.9993	112.0
acenaphthylene	Quadratic	0.9999	95.9
acenaphthene	Quadratic	0.9999	94.9
Fluorene	Quadratic	0.9999	87.3
Dibenzothiophene	Quadratic	0.9999	99.0
Anthracene	Quadratic	0.9996	91.6
Phenanthrene	Quadratic	0.9992	98.1
Fluoranthene	Quadratic	0.9997	78.4
Pyrene	Quadratic	1.0	93.7
Benzo[a]anthracene	Quadratic	1.0	111.8
Triphenylene	Linear	0.9997	110.8
Chrysene	Quadratic	1.0	105.1
Benzo(e) Pyrene	Quadratic	1.0	83.7
Benzo[k]Fluoranthene	Quadratic	0.9997	90.5
Benzo(a)Pyrene	Linear	0.9998	112.6
Benzo[b]Fluoranthene	Quadratic	0.9999	91.8
Benzo[j]Fluoranthene	Quadratic	0.9998	84.2
Perylene	Linear	0.9995	101.8
Dibenzo[ah]anthracene	Quadratic	0.9995	93.4
Benzo[ghi]perylene	Linear	0.9999	90.1
indeno[1,23-cd]pyrene	Linear	0.9999	87.9

Example chromatograms are shown in Figures 4 and 5.
Figure 4 shows duplicate AQC samples to demonstrate the repeatability of the method. Figure 5 shows the low LOD standard at 2.5 µg/L and matrix blank for selected MRM transitions. Based on the signal to noise for this extracted standard, an estimated limit of detection of approximately 96 ng/L should be achievable.

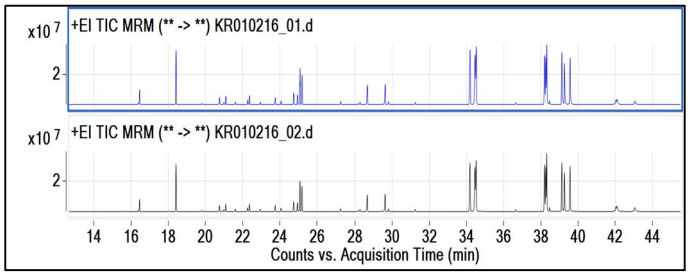

Figure 4: AQC @250 µg/L following SBSE clean up (all MRMs)

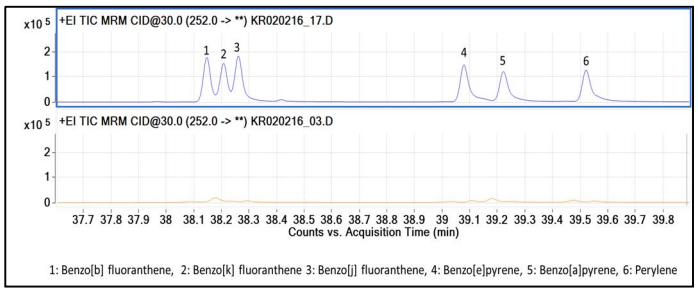

Figure 5: LOD standard @2.5µg/L (top trace in blue) and matrix blank (bottom trace) following SBSE clean up (MRM 252>)

Discussion

This application note demonstrates the potential for SBSE to be used as an additional clean up and enrichment following QuEChERS extraction of complex matrices.

The Twister enables extraction and enrichment of analytes from the sample extract without matrix interferences and alongside the selectivity and sensitivity of targeted MRM acquisition, low limits of detection are achievable.

The method could be further optimized if lower limits of detection are required, such as utilizing the increased sensitivity of the Agilent 7010 Triple Quadrupole GC-MS.

If you would like to discuss this further, please do not hesitate to contact us, either by emailing enquiries@anatune.co.uk, or call us now on +44 (0)1223 279210.

References

[1] GERSTEL AppNote 6/2010 part a: Alternative Procedure for extraction and Analysis of PAHs in Seafood by QuEChERS-SBSE-GC-MS.

[2] GERSTEL AppNote 6/2010 part b: High Throughput Method for the Determination of PAHs in Seafood by QuEChERS-SBSE-GC-MS.

[3] Anatune Technical Note No AS127: Trace analysis of Polycyclic Aromatic Hydrocarbons (PAHs) in water using Twister SBSE Technology

Acknowledgement

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