Chromatography Technical Note No AS174

Use of SPE and Twister (SBSE) to enrich Heptachlor and Heptachlor epoxide from water with a GC/QTOF in NCI

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Introduction

A previous application note (AS168) has been written which shows the determination of Organochlorine pesticides (OCPs) in water down to ppt (ng/l) levels using a GC/QTOF.

From the OCPs, Heptachlor and Heptachlor epoxide were chosen to develop an enrichment method using Solid Phase Extraction followed by Twister ™ to determine even lower detection limits down to ppt levels. Twister extraction is also known in literature as Stir Bar Sorptive Extraction (SBSE)

A Twister™ is a magnetic stir bar coated with polydimethylsiloxane (PDMS). Analytes partition from the sample matrix into the extraction phase and can then be directly thermally desorbed into the instrument.

Figure 1 shows how Twister instrument is set up with the GERSTEL MPS

Enrichment onto a twister bar is favored when an analyte is hydrophobic. Analytes with a partition coefficient Log K o/w of above 3 will show good recovery (above 90%) onto a PDMS Twister bar. Both Heptachlor and Heptachlor epoxide have Log K o/w which far exceed 3 (6.10 and 5.40 respectively). Therefore, in theory, these will show good recovery from an aqueous solution. Once the analytes are desorbed from the Twister they are cryo-focussed on the Cool Inlet System (CIS) and subsequently desorbed from the CIS onto the GC column.

Figure 2 shows the GERSTEL Dual Head with Thermal Desorption on Agilent GC/QTOF at Anatune

Instrumentation

Dual Head GERSTEL MPS *xt*
GERSTEL CIS4
GERSTEL TDU (Thermal Desorption Unit)
Maestro software integrated
Agilent 7890B GC with a 7200 QTOF mass spectrometer in NCI mode using Ammonia
PDMS twister

Method

Six different standards of Heptachlor and Heptachlor epoxide were prepared at 20 ng/l into 6 x 10 ml of 5% Methanol 95% Water (v/v). To each solution a twister was added and left to extract for 1 hour. After drying the twister with tissue, the twister was inserted in a TDU tube and placed within the TDU tray with a transport adaptor attached on the Multipurpose Sampler (MPS). Blank extracts were also prepared and extracted in the same way.

A blank SPE extract and a 1 pg/l SPE extract from ALS were supplied for analysis. Each extract was in Methanol. 0.5 ml of each was added to a 10 ml vial and 9.5 ml of deionised water was added. To each solution, a twister was added and left to extract for 1 hour. After drying the twister with tissue, the twister was inserted in a TDU tube and placed within the TDU tray with a transport adaptor attached on the Multipurpose Sampler (MPS).

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Results

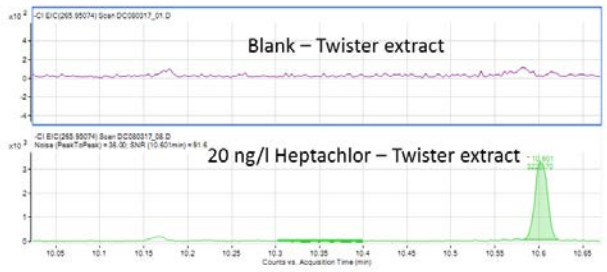

Figure 3 shows an extracted ion chromatogram for Heptachlor from a 20ng/l (Standard) twister extract compared to a blank extract. The retention time for Heptachlor was 10.6 minutes.

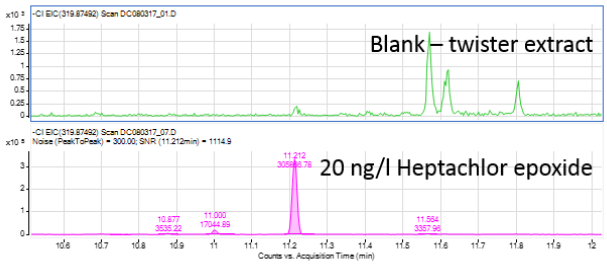

Figure 4 shows an extracted ion chromatogram for heptachlor epoxide from a 20 ng/l twister extract compared to a blank extract. The retention time for heptachlor epoxide was 11.2 minutes.

The signal to noise for the 20 ng/l heptachlor and heptachlor epoxide extract was calculated to be 91.6, and 1114.9 respectively.

Table 1 shows areas for six 20 ng/l twister extracts. This was produced from extracted ion chromatograms for both Heptachlor and Heptachlor epoxide. Percentage Relative Standard Deviation (% RSD) for Heptachlor and Heptachlor epoxide were calculated.

Description	Heptachlor	Heptachlor epoxide
Blank	0	0
Twister extract 1	10202.88	358306.80
Twister extract 2	8511.26	292092.70
Twister extract 3	9794.07	349707.02
Twister extract 4	9305.69	355425.21
Twister extract 5	9707.83	319232.13
Twister extract 6	7906.07	302097.69
Mean	9237.97	329476.93
SD	868.1	28864.82
%RSD	9.40	8.76

Table 1 shows areas from extracted ion chromatograms (six different 20 ng/l twister extracts).

An internal standard was not used for this work. However, if you take Heptachlor being an internal standard for Heptachlor epoxide and vice versa; precision can be improved further to 6 % RSD.

Figure 5 show a selected part of the MS spectra for Heptachlor epoxide (20ng/l extract) which shows its characteristic ions. This shows expected isotope ratio pattern for $C_{10}H_6Cl_5O$ and accurate mass was calculated to be less than 3 ppm.

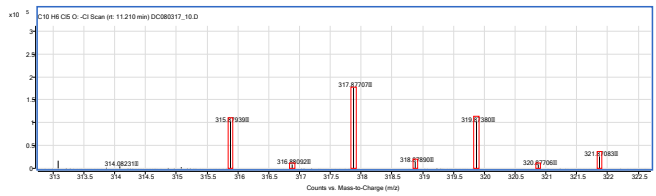

Figure 5 MS Spectra for Heptachlor epoxide with predictive isotope highlighted in red.

The SPE extracts (from ALS) as detailed in the method were then analysed. Figure 6 shows a blank, an extracted blank and 1.0 pg/l twister extracts comparison for Heptachlor.

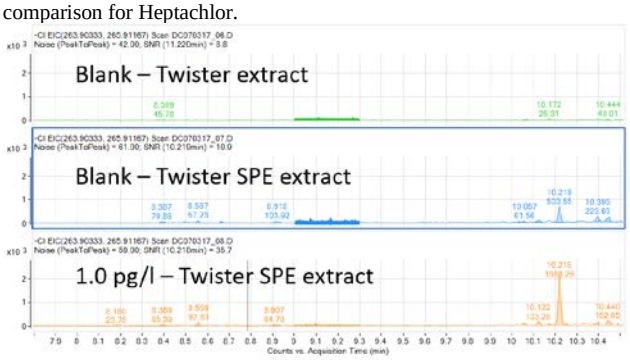

Figure 6 Extracted ion chromatogram comparison of SPE extracts with blank twister (Heptachlor)

Trace Heptachlor was detected in the Blank twister SPE extract. The signal to noise for 1.0 pg/l extract was calculated to be 35.7 for Heptachlor.

Figure 7 shows a blank, an extracted blank and 1.0 pg/l twister extracts comparison for Heptachlor epoxide.

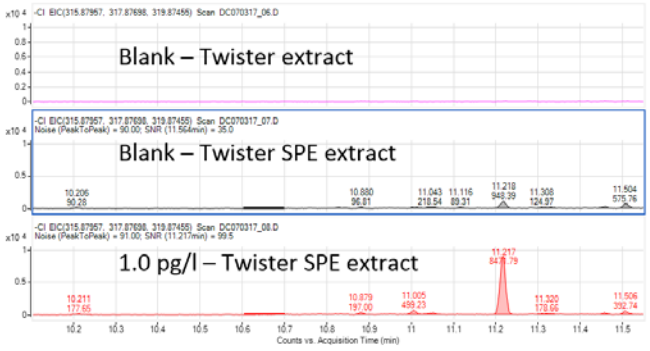

Figure 7 Extracted ion chromatogram comparison of SPE extracts with blank twister (Heptachlor epoxide).

Trace Heptachlor epoxide was detected in the Blank twister SPE extract. The signal to noise for 1.0 pg/l extract was calculated to be 99.5 for Heptachlor epoxide.

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Summary

Further work will be performed to improve on reducing background levels of Heptachlor and Heptachlor epoxide in blank SPE extracts. Work will also be performed to enhance detection for heptachlor. This work will be extended for other OCPs.

With the use of an advanced automated enrichment using twister and use of NCI soft ionisation with the GC/TOF, we can achieve a selective, sensitive and highly robust method for heptachlor and heptachlor epoxide in water,

We have enclosed a video of how twister can be performed to show how easy the technique can be performed.

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