Chromatography Technical Note No AS115

Trace level enrichment of malodour analytes in water using Twister Technology

Dan Carrier, Anatune Ltd. Girton, Cambridgeshire, UK.
Yunyun Nei, Gerstel. Mülheim, Germany.

Introduction

Taste and odour in drinking water are two of the most widespread causes of customer complaints. Although there are no associated health effects, the extensive public relations difficulties resulting from taste and odour make it important to treat these problems. Many of the odour analytes can be detected with the human nose and palate at extremely low levels. Therefore, some form of enrichment is required to detect these analytes by GC/MS.

A Twister is a glass-encased magnetic stir bar coated with an extraction phase, typically polydimethylsiloxane (PDMS). When the Twister stirs an aqueous sample, analytes partition from the sample onto the PDMS phase. Just as in liquid-liquid extractions, analytes partition between the extraction phase, in this case PDMS, and the liquid sample phase (water). 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. Gerstel have a Twister calculator, whereby a CAS number can be entered for each analyte and an approximate recovery onto the Twister bar is calculated. For compounds with a low Log K_{ow}, two methods have been investigated to improve recovery and have been detailed within this application note.

Firstly, ethylene glycol silicon Twisters (EG Twisters) have recently been produced and these can give better recovery for more polar analytes compared to the PDMS Twisters. They also have a non-polar functionality to retain non-polar analytes. Secondly, derivatising the phenolic analytes with acetic anhydride can change the Log K_{ow} to recover more on the Twister bar.

After the Twisters have been stirred for a fixed amount of time, each Twister is then wash with deionized water, dried, placed in a TDU tube, fitted with a transport adaptor and placed into the Twister sample tray ready for analysis. Figure 1 shows a schematic of how the GC inlet is configured for Twister analysis.

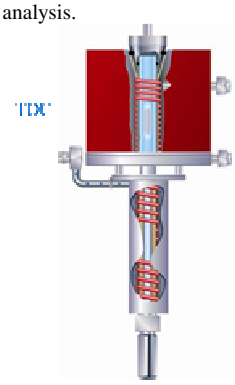

Figure 1 Schematic of GC Inlet for Twister analysis.

Each TDU tube with Twister is transferred into the thermal desorption unit (TDU) using the Multi Purpose 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 2 shows a photograph of the instrumentation which can be used.

Figure 2 Instrumentation for Twister analysis.

Anatune Ltd, Unit 4, Wellbrook Court, Girton Road, Cambridge, CB3 0NA, UK
Tel: +44 (0) 1223279210 Fax: +44 (0) 1223279253 Email: info@anatune.co.uk Internet: www.anatune.co.uk

Instrumentation

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

Method

Method 1

This analysis was carried out by Yunyun Nie at Gerstel in Germany. Thirty six analytes including 2,4,6-tribromophenol, 3-chloro-4-methylphenol, 4-chlorophenol, 4-chloro-2-methylphenol, 2,6-dibromophenol, 2,4,6-tribromoanisole, 2,6-dichlorophenol, 2-chloro-5-methylphenol, and 2-isopropyl-3-methoxypyrazine were prepared in 5/95 Methanol/Water pH3 (v/v) at varying concentrations from 0.02 ng/ml to 1.0 ng/ml. To every 10 ml of sample an EG Twister was added and stirred for 2 hours.

Method 2

Some initial work has also been carried out on malodourous analytes with PDMS Twisters using acetic anhydride to derivatise the phenolic analytes. Other malodourous analytes were left underivatised as they do not react with the acetic anhydride. The analytes were prepared in 5/5/90 acetic anhydride/methanol/basic water. To every 10 ml of sample, a PDMS Twister was added and stirred for 2 hours.

Figure 3 shows a photograph of some Twister extraction.

Figure 3 photograph of a typical Twister extraction.

GC/MS conditions

Column: 30 m x 0.25 mm id (Film thickness 0.5 µm Stabilwax (Restek)
Thermal gradient: 40°C (2 min); 10°C/min; 235°C (1.5 ml/min flow rate)
Single ion monitoring was performed. Two qualifier ions were used for each analyte.

TDU temperature program 40°C (0.5 minutes); 720°C/min;
220°C (2 min)
CIS 4: Glass wool deactivated liner,
CIS 4: Temperature Program -100°C; 16°C/s to 150°C; 12 °C/s to 220°C (5 min)

Results

Good precision and linearity was achieved for the majority of analytes using method 1. Table 1 shows typical linear regression for ten analytes from a seven point calibration between 0.02 ng/ml and 1 ng/ml without using an internal standard for Method 1 (EG Twisters). Unfortunately, phenol gave both poor precision and linearity and a deuterated internal standard may need to be used for phenol.

Analyte	Linear Regression (R^2)
2-methylphenol	0.989
2-isobutyl-3-methoxypyrazine	0.991
2-chloroanisole	0.991
2-chlorophenol	0.993
2,6 dimethylphenol	0.991
2-chloro-5-methylphenol	0.991
2-bromophenol	0.992
2,3,4-trichloroanisole	0.991
2,4,6-tribromophenol	0.997
2,5-dimethylphenol	0.993

Table 1 Linear regression for ten analytes using EG Twisters.

Figure 4 shows calibration plot for 2,5 dimethylphenol using EG Twisters.

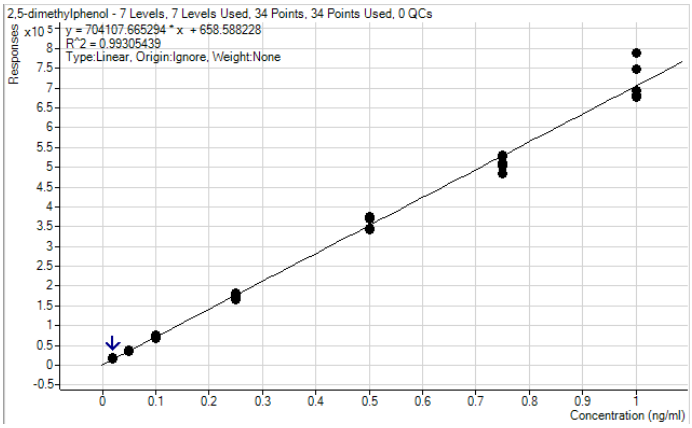

Figure 4 Calibration line for 2,5 dimethylphenol using EG Twisters.

As you can see from Figure 4, each calibration line contains five replicates at each calibration level. Table 2 shows precision obtained for five replicate Twister extractions at 0.05 ng/ml (EG Twister method).

Analyte	% RSD
2-methylphenol	8.7
2-isobutyl-3-methoxypyrazine	5.7
2-chloroanisole	2.7
2-chlorophenol	3.6
2,6 dimethylphenol	5.2
2-chloro-5-methylphenol	4.0
2-bromophenol	6.1
2,3,4-trichloroanisole	1.7
2,4,6-tribromophenol	2.3
2,5-dimethylphenol	3.1

Table 2 Precision achieved for five replicate Twister extractions at 0.02 ng/ml.

Anatune Ltd, Unit 4, Wellbrook Court, Girton Road, Cambridge, CB3 0NA, UK
Tel: +44 (0) 1223279210 Fax: +44 (0) 1223279253 Email: info@anatune.co.uk Internet: www.anatune.co.uk

Figure 5 shows an example chromatogram (Single Ion Monitoring) of 2-chloro-5-methyl phenol, 2-chloro-4-methyl phenol, and 2,6-dimethyl phenol at 0.02 ng/ml using EG Twisters.

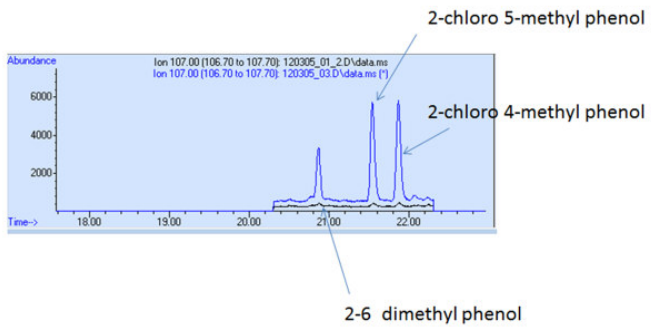

Figure 5 example chromatogram (Single Ion monitoring) of 2-chloro-5-methyl phenol, 2-chloro-4-methyl phenol.

For Method 2 using the PDMS Twisters, good precision and linearity was achieved for the malodourous analytes tested. Table 3 shows linear regression for these analytes (calibration between 0.02 ng/ml and 1 ng/ml without using an internal standard).

Analyte	Linear Regression (R^2)
3-chloroanisole	0.998
2-methylisoborneol	0.998
2,6-dimethylphenylacetate	0.998
2,4,6-tribromophenylacetate	0.993

Table 3 Linear regression for malodorous analytes using PDMS Twisters.

Figure 5 shows calibration plot for 2,4,6-tribromophenylacetate using PDMS Twisters.

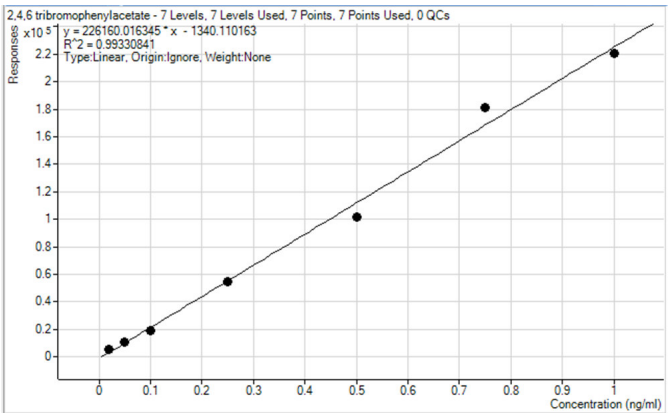

Figure 5 Calibration plot for 2,4,6-tribromophenylacetate using PDMS Twisters.

Table 4 shows precision obtained for six replicate Twister extractions at 0.25 ng/ml (PDMS Twister method).

Analyte	% RSD
3-chloroanisole	5.1
2-methylisoborneol	8.0
2,6-dimethylphenylacetate	4.2
2,4,6-tribromophenylacetate	8.6

Table 4 Precision achieved for six replicate Twister extractions at 0.25 ng/ml.

Discussion

Good precision and linearity could be achieved with both enrichment Twister methods. The technique is simple and avoids the use of liquid-liquid extractions.

David Benanou, who is a pioneer and huge advocate of Twister stir bar technology, is leading a workshop for extracting malodour contaminants from drinking water in October 2012 at Anatune. Therefore, we hope to progress the application work in this area.

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