Chromatography Technical Note No AS152

Optimisation and validation of an ITSP method for the determination of Taste and Odour compounds in water

Camilla Liscio, Anatune Ltd. Girton, Cambridgeshire (UK).
Richard Davis, Anatune Ltd. Girton, Cambridgeshire (UK).

Introduction

Preliminary work in the Anatune Applications team (Application note AS145) showed the potential of SPE automation using ITSP (Instrument Top Sample Preparation) cartridges for the enrichment of taste and odour compounds (TOCs) in water.

In fact, TOCs are regularly monitored by water companies due to their very low odour detection threshold (ng/L), affecting the public perception of the drinking water quality. Hence, the need for sensitive and robust measurement procedure which can deliver high throughput sample preparation and trace levels detection is critical.

This application note describes further optimisation of the fully automated solution previously developed in our laboratory.

The initial developed method used dichloromethane as elution and injection solvent for large volume injection (LVI). In fact, dichloromethane is a very good extracting solvent and highly volatile, therefore a common choice for GC-MS applications. Nevertheless, chlorinated solvents usually require more expensive disposal costs and are less desirable for health and safety in the work environment. The use of acetone as an alternative solvent was therefore investigated during the method optimisation.

The finalised method was then used to perform a validation batch based on the WRc publication NS30 by Gardner and Wilson **[1]**.

The validation batch included a full six point calibration (1-25 ng/L range) and five different water matrices (reverse osmosis water as analytical quality control (AQC), soft water, medium water, hard water and surface water). Blanks samples were run for each matrix type. Matrices were analysed at four spiked concentration levels (1 ng/L, 5 ng/L, 10 ng/L and 20 ng/L). All samples were analysed in duplicate over several days.

Figure 1: Gerstel Dual Head MPS with Agilent GC 7890B coupled to MS QQQ 7010

Instrumentation

Gerstel Multipurpose Sampler (MPS) 2 XL Dual head
Gerstel Cooled Injection System (CIS) 4

Instrument Top Sample Preparation (ITSP), ITSP Solutions

Agilent GC 7890B
Agilent MS 7010 Triple Quadrupole

Methods

Optimized Automated Sample Preparation

35 mL of water sample was transferred to 40 mL amber vial and 1 g of NaCl and 5 mL MeOH were added, respectively.

Calibration standards and samples were prepared by spiking with a methanolic mixed standard solution of the target analytes and a methanolic standard solution of the two internal standards (2,4-dichlorophenol D3 for Phenols and 2,4,6-trichloroanisole D5 for Taste and Odour compounds).

The ITSP procedure was carried out using the left MPS fitted with 2.5 ml headspace syringe (SPE needle).

The right MPS head fitted with a 10 µl syringe was used to inject 10 µl of the extract into the Cooled Injection System (CIS 4) for GC-MS analysis

GC/MS conditions:

CIS4 inlet:

- Injection volume: 10 µL large volume injection (LVI)
- Injection mode: Solvent Vent

GC:

- Column: Agilent DB-5MS Ultra Inert 30 m x 0.25 mm x 0.25 µm
- He carrier gas 1mL/min

MS:

- High-Efficiency EI source
- Collision cell: Nitrogen as collision gas 1.5 mL/min
- MS Mode: Selected Reaction monitoring (SRM)

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

Compound ID	*RT (min)*	*SRM Quantifier*	*SRM Qualifier*
2-Isopropyl-3-methoxypyrazine (IPMP)	10.72	137.0 > 109.1	137.0 > 105.0
2-Isobutyl-3-methoxypyrazine (IBMP)	12.36	124.0 > 94.0	124.0 >81.0
MIB	12.44	108.0 > 93.0	107.0 >91.1
Geosmin	16.34	112.1 > 97.1	112.1 >83.0
2-chloroanisole	10.97	142.0 > 99.0	142.0 >127.0
3-chloroanisole	10.77	142.0 > 112.0	142.0 >77.0
4-chloroanisole	11.28	142.0 > 99.0	142.0 >127.0
2,4,6-trichloroanisole	15.04	210.0 >194.9	210.0 > 166.9
2,4,6-tribromoanisole	19.56	344.0 > 329.0	346.0 > 303.0
IS 2: 2,4,6-trichloroanisole D5	14.99	214.9 > 196.8	214.9 > 168.9

Table 2: Compounds IDs, retention times (RT), Quantifier and Qualifier SRM transitions for the target TOCs

Results and Discussion

ITSP optimization

Sample loading and elution volume were optimised to achieve sensitivity maximum. Recovery and LVI optimisation experiments were performed to compare acetone and dichloromethane performances. Similar recoveries were obtained for the two solvents. However, acetone showed better reproducibility, especially at low concentrations (DCM RSD 16-22% versus Acetone RSD 5-13%, respectively). Acetone was therefore chosen as elution and injection solvent for the finalised method.

Linearity and LODs

SRM extracted chromatograms of all target compounds for the 1ng/L spike in reverse osmosis water are shown in Figure 2.

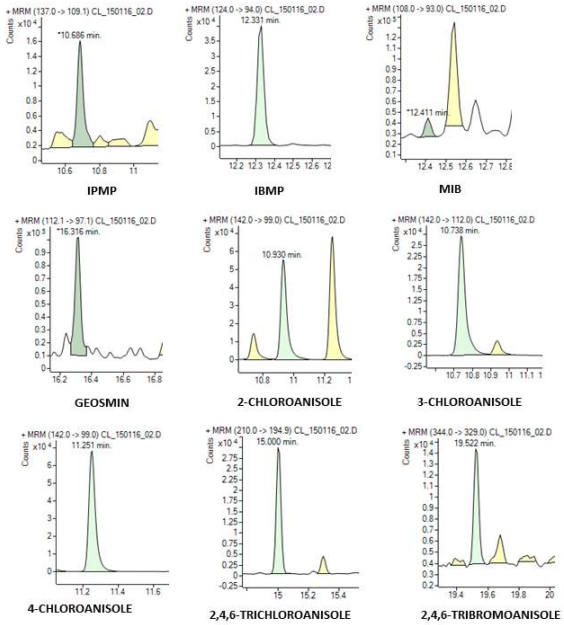

Figure 2: SRM extracted chromatograms at 1 ng/L for all target TOCs

Good linearity was obtained for all TOCs. LODs were calculated as 3 SD of the blank. Table 2 summarizes R^2 and LODs for all the target compounds and Figure 3a and b show an example of calibration curve plots obtained for MIB and Geosmin.

Compound ID	*LOD (ng/L)*	*R^2*
2-Isopropyl-3-methoxypyrazine (IPMP)	0.7	0.9898
2-Isobutyl-3-methoxypyrazine (IBMP)	0.6	0.9949
MIB	1.0	0.9947
Geosmin	0.6	0.9975
2-chloroanisole	0.6	0.9952
3-chloroanisole	0.8	0.9952
4-chloroanisole	0.7	0.9966
2,4,6-trichloroanisole	0.9	0.9964
2,4,6-tribromoanisole	1.1	0.9958

Table 2: LOD and R2 linearity coefficients for the target TOCs

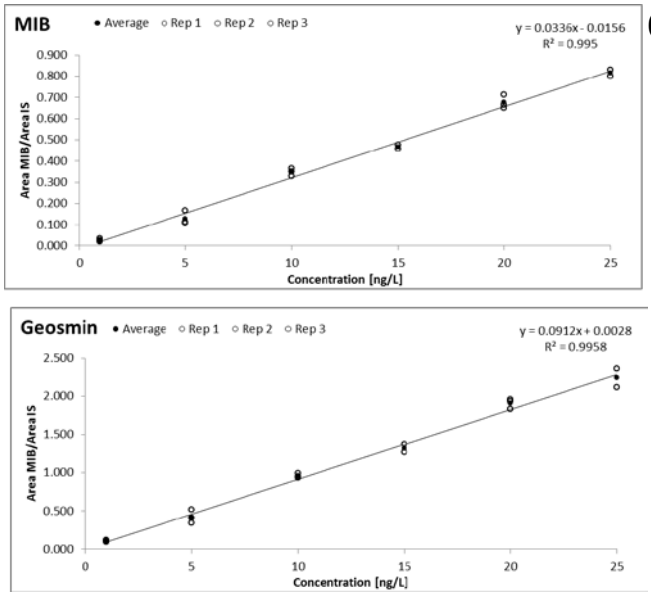

Figure 3: Calibration curve plots for MIB (a) and Geosmin (b)

Spiked water matrices

Reproducible results (average RSD% between 6 and 10%) were achieved for the five different matrices over the tested analytical range (1-20 ng/L) for TOCs. Figure 4 shows the recoveries obtained at the four spiked levels for MIB, Geosmin, isobutylmethoxypyrazine (IBMP) and trichloroanisole. Similar results were obtained for the other target TOCs.

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

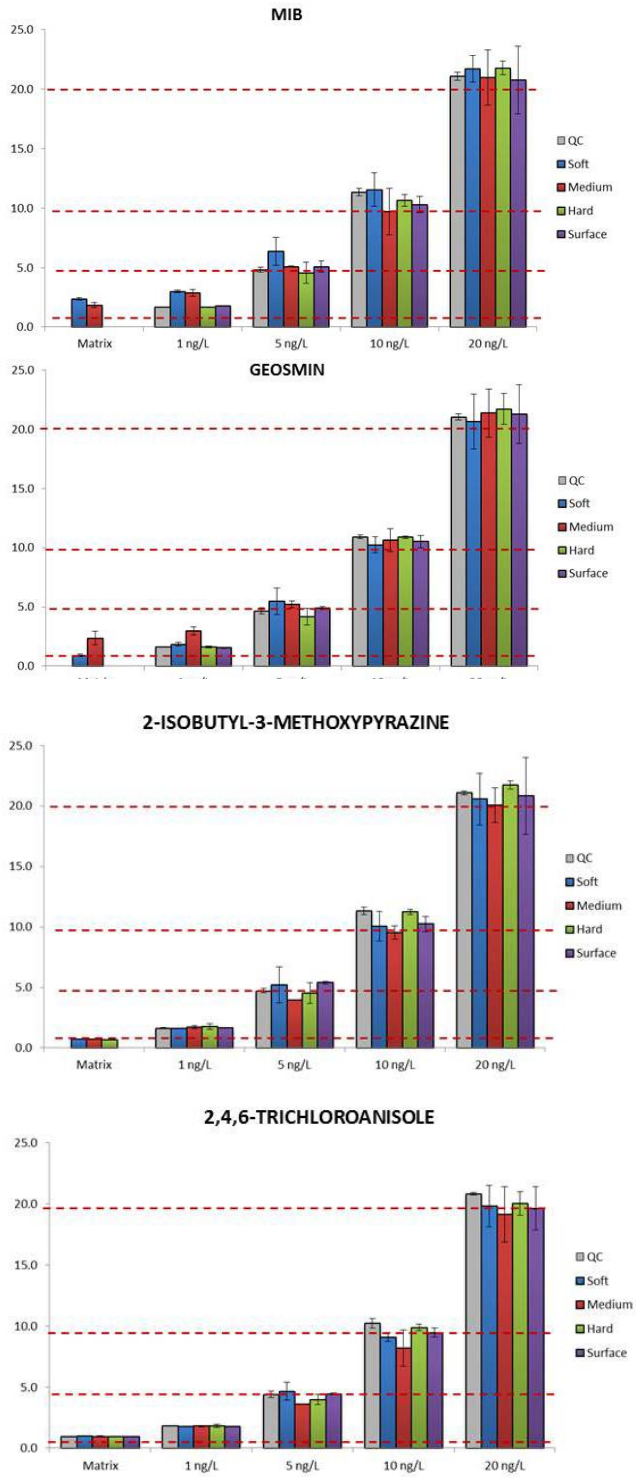

Figure 4: Calculated concentrations for MIB, Geosmin, Isobutylmethoxypyrazine (IBMP) and Trichloroanisole in the five spiked matrices: reverse osmosis water (QC), soft, medium, hard and surface water.

Conclusions

The fully automated solution developed and optimized for the determination of trace levels of TOCs in water proved to be robust and reproducible. Acetone was demonstrated a very good alternative to DCM giving comparable recoveries and better reproducibility. Good linearity and limit of detections were obtained for all TOCs. Five different water matrices were tested at 4 concentration levels and data showed very good consistency, proving the capability of the method to deal with matrix effects.

Acknowledgements

Phine Banks, Account manager West of England and Wales, Anatune, Cambridge (UK)

Jeff Stubbs, Water & Environmental Market Specialist, Anatune, Cambridge (UK)

Steve Jones, Welsh Water

Anaïs Maury, Synthomer, Harlow, UK

References

1. *Gardner M. and Wilson A., Manual on analytical quality control for the water industry, NS30, WRC, 1989.*

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