MARKES international

TDTS

Thermal Desorption Technical Support

Note 78: Low ppt levels of geosmin, methyl-i-borneol and other odorants in drinking water using headspace – thermal desorption (HS-TD)

Key Words:

Environmental; Headspace; Odour; Headspace-trap; Water

Introduction

Drinking water sourced from natural rivers and streams is prone to contamination by naturally-occurring odorous compounds such as geosmin, methyl-*i*-borneol (MIB) and trihaloanisoles. These components produce a musty/"earthy" smell which concerns consumers and levels have to be monitored in both river- and drinking water.

The main challenge lies in the fact that the human nose can detect compounds like geosmin and methyl-*i*-borneol at very low levels. In both cases the olfactory limit is around 10 ng/L (~10 ppt) in drinking water.

Conventional analytical methods for monitoring low ppt levels of odorous compounds have included closed loop stripping of relatively large volumes (litre quantities) of water, with added salt, followed by GCMS – A messy, lengthy and relatively manual process. Purge-and-trap (P&T) methods have been developed for odorants in water, but also require the addition of salt. Over time salt tends to contaminate the purge and trap sample lines, plugging tubing/valving and causing high levels of analytical interference & downtime.

More recent methods involving solid phase extraction cartridges have been shown to offer the necessary sensitivity. However, here too, the method is relatively time consuming (typically 2-hour solid-phase extraction) and involves manual preparation steps such as drying each cartridge by hand and transferring the dried cartridge to a suitable thermal desorption apparatus.

Given the ever increasing demands on water supplies around the world (except here in S. Wales, UK where we have more water than we care to mention!) there is a growing need for fully-automated, cost-effective routine analytical methods for monitoring low ppt levels of odorants in water. A project was therefore initiated to investigate whether or not a fully-integrated and automated combination of dynamic headspace with analytical thermal desorption technology could meet the demands of this application *i.e.* to see if HS-TD could offer detection of geosmin, methyl-*i*-borneol and other odorants at levels down to 1 ppt using only 10 ml water volumes in regular (~20 ml) headspace vials and requiring, ideally, no additional sample preparation steps such as salting out.

Description of HS-TD-GCMS analytical system

The analytical system used was a 70-vial capacity G1888 Headspace (HS) Sampler from Agilent Technologies combined with a Markes International UNITY thermal desorber (TD), the relevant HS-TD interface kit and associated operating software. This combined sample-introduction system was connected to a 6890-5975 GCMS from Agilent-Technologies.

Using the combined HS-TD system, headspace vapours from thermostatted, pressurised vials were transferred to the electrically-cooled, sorbent-packed focusing trap of UNITY. After vapour transfer, the same sample vial was repressurised allowing the process of vapour transfer to the focusing trap to be repeated. In this application, 10 stages of pressurisation and vapour transfer were used. Focusing trap

Figure 1: The HS-TD analytical system

sorbents and trapping temperatures were selected to quantitatively retain the compounds of interest while water and other unwanted volatiles stayed in the vapour-phase and were purged to vent. Once the multi-stage process of transferring headspace vapours to the focusing trap was completed, the trap was purged with dry carrier gas in the sampling direction to remove residual water. The flow of carrier gas was then reversed and the trap heated at rates approaching 100°C/s. At this point, geosmin, MIB and other retained organics were desorbed into the carrier gas stream and transferred/injected into the GC analytical column.

Desorption of a UNITY focusing trap is so efficient, that splitless analysis is possible without significant peak broadening – i.e. all of the retained organics may be transferred to the analytical column in a narrow band of vapour ensuring optimum sensitivity. Splitless desorption was used throughout this project

The dynamic nature of HS-TD means that it is applicable to a wider analyte volatility range than conventional equilibrium HS. This improves the detection of higher boiling compounds. Repeated transfer of larger volumes of headspace vapour (compared to standard headspace) also offers a significant enhancement in sensitivity. Complete extraction of organic volatiles is possible in many cases, thus allowing similar detection limits to purge-and-trap but without issues such as foaming, mist-formation, *etc*. which can make routine P&T methods difficult.

Analytical conditions

The robustness of HS-TD for measuring trace odorants in drinking water was tested by repeating the application under 2 different sets of chromatographic conditions, first with a semi-polar DB-1701 column (see series 1 experiments below) and secondly with a non-polar DB-1MS column (see series 2 experiments below).
The same HS-TD and MS parameters were used both series of experiments.

HS parameters

Oven:	45°C
Sample valve:	70°C
Transfer line:	85°C
GC cycle time:	60 min
Vial equilibration:	2.0 min
Inject time	35 min
Septa:	Blue silicone PTFE

HS-TD parameters

HS-TD line purge:	1.0 min
Pressurisation time:	0.5 min
Sampling time:	1.5 min
Equilibration time:	0.0 min
Sample cycles:	10
Post sample flush:	2.0 min

TD parameters

Cold Trap:	General purpose (U-T2GPH)
Cold trap low temp:	50°C
Trap purge time:	2.0 min
Cold trap high temp:	300°C for 5 min
TD flow path:	160°C

GC parameters - Series 1 experiments

Carrier gas:	He
Column:	60 m x 0.25 mm x 0.25 mm DB-1701
Constant pressure mode:	22.5 psi
Temp programme:	50°C (2 min), 5°C/min to 175°C, 20°C/min to 260°C (2 min)

GC parameters - Series 2 experiments

Carrier gas:	He
Column:	60 m x 0.25 mm x

	0.25 mm DB-1MS
Constant pressure mode:	22.5 psi
Temp programme:	50°C (2 min), 5°C/min to 170°C, 2°C/min to 175°C, 30°C/min to 300°C (1 min)

MS conditions

MS Source temperature: 230°C
MS Quadrupole temperature: 150°C
MSD transfer line temperature: 280°C
EM volts: 1200
SIM scan settings:

Group 1- 95, 108, 135
Group 2- 195, 197, 210, 212
Group 3- 112, 182

Sample preparation

Standard solutions were tested over a concentration range of 1 ppt to 50 ppt. Spiked water samples were prepared by injecting varying quantities of a 10 ppb stock standard solution containing geosmin, 2-methyl-*i*-borneol (MIB), 2,4,6-trichloranisole (TCA 1), and 2,3,4-trichloroanisole (TCA 2) into 10 ml of HPLC grade water. Samples were then poured into 20 ml headspace vials and sealed prior to analysis. No salt was added.

Headspace samples were analysed using the conditions described above.

Results from series 1 experiments (DB-1701 column)

Figure 2 shows a selected ion (SIM) chromatogram of the compounds of interest at concentrations of 50 ppt and 5 ppt run on the DB-1701 column.

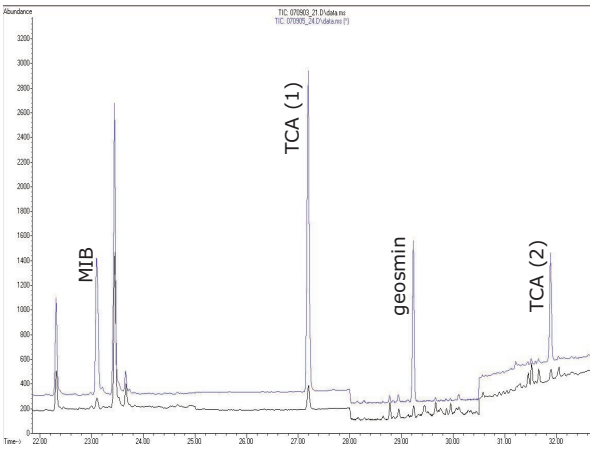

Figure 2: Selected ion chromatogram at 50 ppt (top) and 5 ppt (bottom)

Figures 3 and 4 show close ups of the 5 ppt standard solution.

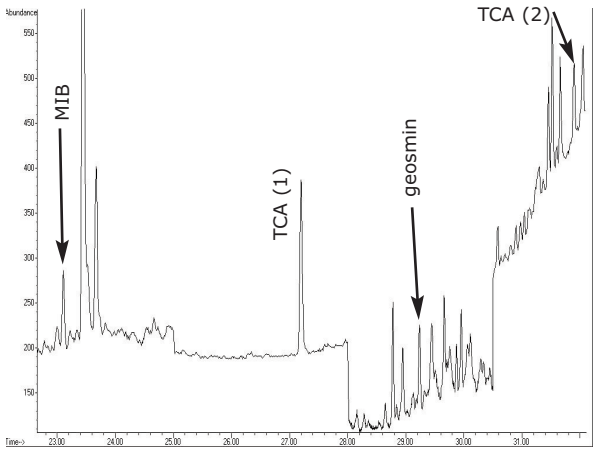

Figure 3: Close up of of the 5 ppt level standard

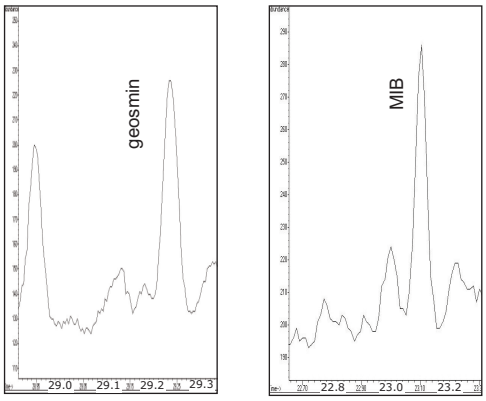

Figure 4: Close-up of geosmin and MIB at the 5 ppt level. Note narrow gaussian peak shapes

Figure 5 shows a close-up of geosmin, MIB and TCA at the 1 ppt level.

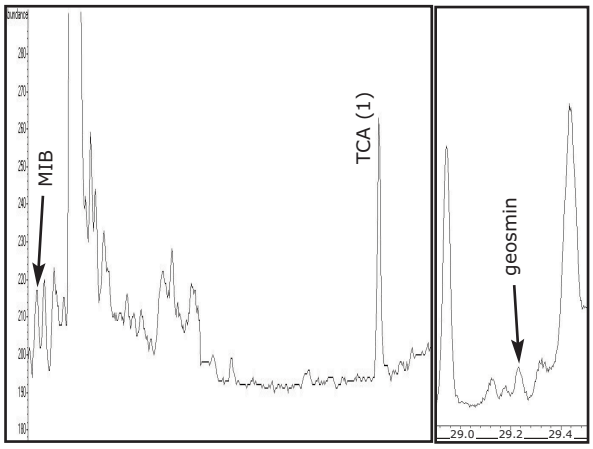

Figure 5 close-up of geosmin, MIB and a trichloroanisole at the 1 ppt level

Figures 6 and 7 display good system linearity with R^2 values of 0.9973 for TCA(1), 0.9965 for TCA (2), 0.9976 for geosmin and 0.9976 for MIB.

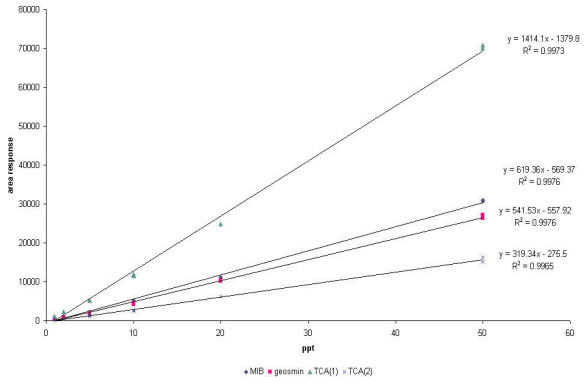

Figure 6: Linearity of standard analysis from 1 ppt to 50 ppt

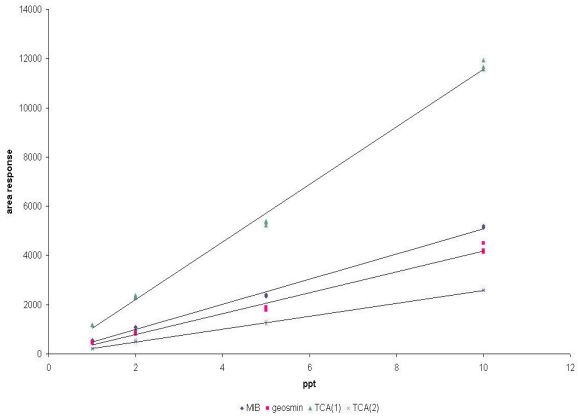

Figure 7: Close up of linearity from 1 ppt to 10 ppt

Table 1 displays the area response values for each of the triplicate measurements of the target compounds. Results show good reproducibility even at these ultra-trace levels. Note the average background levels for each target compound were subtracted in each case.

A chromatogram of real tap water is shown in Figure 8. This demonstrates that Welsh drinking water is as pure as it is plentiful, as neither MIB nor geosmin were detected.

	Area response	
Conc. (ppt)	MIB	Geosmin
1	564	462
1	496	468
1	527	437
2	1086	800
2	1081	848
2	971	824
5	2407	1777
5	2389	1902
5	2337	1864
10	5135	4137
10	5125	4193
10	5194	4499

Table 1: Area response values of 1 to 10 ppt standards with corresponding background water levels subtracted

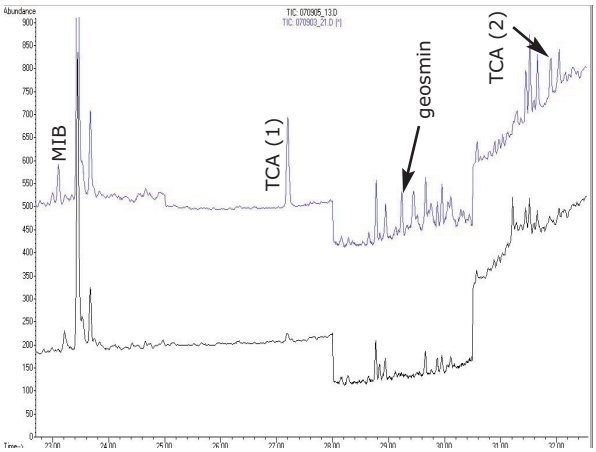

Figure 8: Comparison of real drinking water sample (bottom) against 5 ppt odour standard (top)

Results from series 2 experiments (DB-1MS column)

Figure 9 shows a selected ion (SIM) chromatogram of the compounds of interest at concentrations of 50 ppt and 5 ppt run on the DB-1MS column.

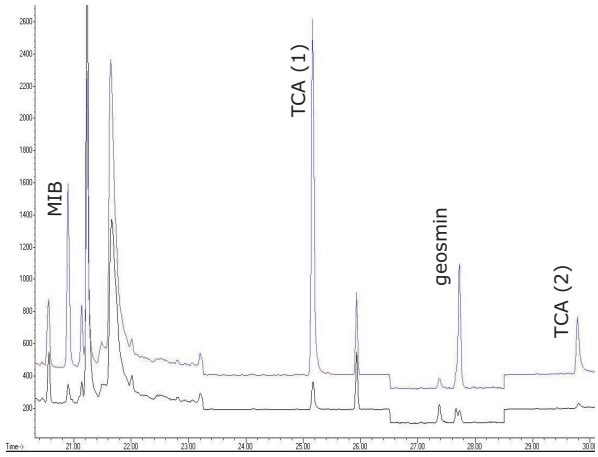

Figure 9: Selected ion chromatogram at 50 ppt (top) and 5 ppt (bottom)

Figure 10 shows a representative chromatogram of the blank HPLC-grade water overlaid with a 5 ppt level standard. This clearly demonstrates that the HPLC grade water contains minimal levels of the compounds of interest compared to the spiked sample.

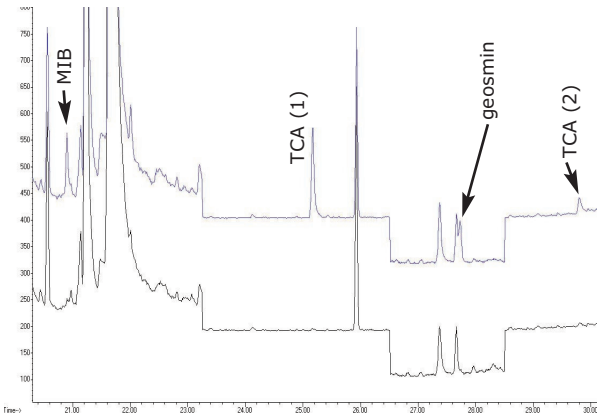

Figure 10: Selected ion chromatogram of water blank (bottom) and 5 ppt standard (top)

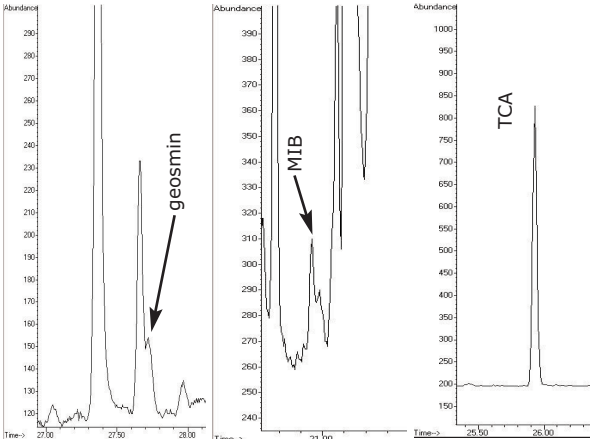

Figure 11: Close-up of geosmin, MIB and a trichloroanisole at the 1 ppt level

Figure 11 shows close-up examples of odorants at the 1 ppt level.

Figures 12 and 13 show good system linearity with R^2 values of 0.9980 for TCA(1), 0.9978 for TCA (2), 0.9979 for geosmin and 0.9961 for MIB.

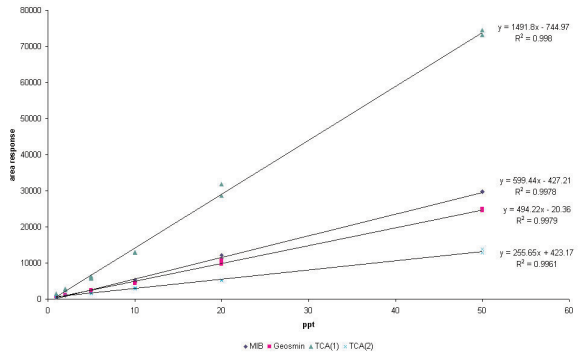

Figure 12: Linearity of standards from 1 ppt to 50 ppt

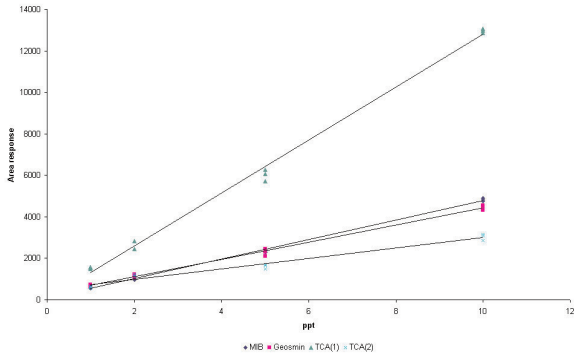

Figure 13: Close up of linearity from 1 ppt to 10 ppt

	Area response	
Conc. (ppt)	MIB	Geosmin
1	363	428
1	289	328
1	235	356
2	788	900
2	746	778
2	646	808
5	1998	1774
5	1974	1996
5	2062	2036
10	4431	4189
10	4603	4007
10	4492	4228

Table 2: Area response values of 1 to 10 ppt standards with corresponding background water levels subtracted

Table 2 displays the area response values for each of the triplicate measurements of the target compounds. Results show good reproducibility even at these ultra-trace levels. Note that average background levels for each target compound were subtracted in each case.

A chromatogram of real tap water is shown in Figure 14 overlaid with that of a 5 ppt standard.

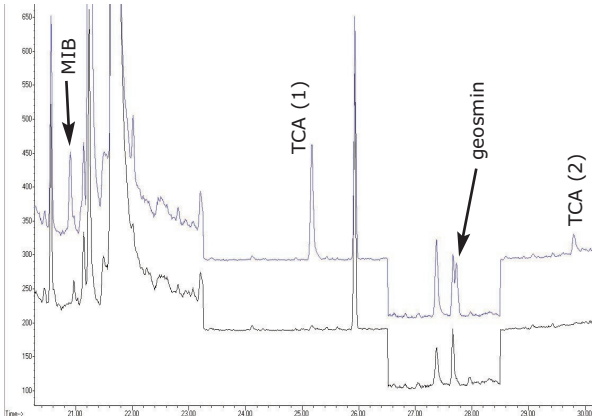

Figure 14: Comparison of real tapwater sample (bottom) against 5 ppt odour standard (top)

Conclusions

These results clearly demonstrate the fundamental sensitivity of the combined HS-TD-GCMS system used in this work. Quantitative detection of key odorous compounds such as geosmin and methyl-*i*-borneol has been demonstrated at levels down to 1 ppt in drinking water, with only 10 ml volume of water samples in standard headspace vials and with no salt added.

The fact that this was acheived under two different sets of chromatographic conditions also indicates the robustness of this approach for routine operation.

If even lower limits of detection were required, the addition of salt to each HS sample vial prior to analysis and the use of aluminium coated HS vial septa to reduce system background should facilitate this.

Trademarks

UNITY™ is a trademark of Markes Int. Ltd.

Acknowledgements

Markes International would like to thank Chris Sandy of Agilent Technologies, UK for the loan of the G1888 automated HS sampler and his technical help during this project.

Applications were performed using the stated analytical conditions. Operation under different conditions, or with incompatible sample matrices, may impact the performance shown.