Thermal Desorption Technical Support

Note 78b: Supplement to TDTS 78 - Low ppt levels of odorants in drinking water using headspace – thermal desorption (HS-TD)

Key Words:

Environmental; Headspace; Odour; Headspace-trap; Water; HS40

Introduction

Please read this application note supplement in conjunction with TDTS No 78.

HS-TD-GCMS analytical system

The robustness of HS-TD for measuring trace odorants in drinking water, as shown in TDTS 78, was further tested by repeating the application using an alternative commercial HS unit. In this case, the analytical system comprised a 40-vial capacity HS40 Headspace (HS) Sampler from Perkin Elmer Ltd combined with a Markes International UNITY thermal desorber (TD), the relevant Markes 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 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

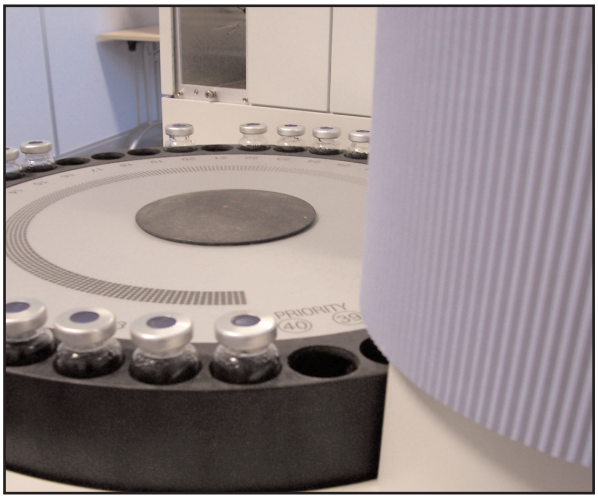

Figure 1: The HS-40 headspace sampler

Analytical conditions

HS parameters

Sample	45°C
Needle:	75°C
Transfer line:	90°C
GC cycle time:	40 min
Vial equilibration:	3.0 min
Pressurisation:	30 min
Inject time	9.99 min
Withdrawal:	1 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

Carrier gas:	He
Column:	60 m x 0.25 mm x 0.25 mm DB1-MS
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 5 ppt. Spiked water samples were prepared by injecting varying quantities of a 10 ppb stock standard solution containing geosmin, 2-Methyl-*i*-borneol (MIB), and 2,4,6-trichloranisole (TCA 1) 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

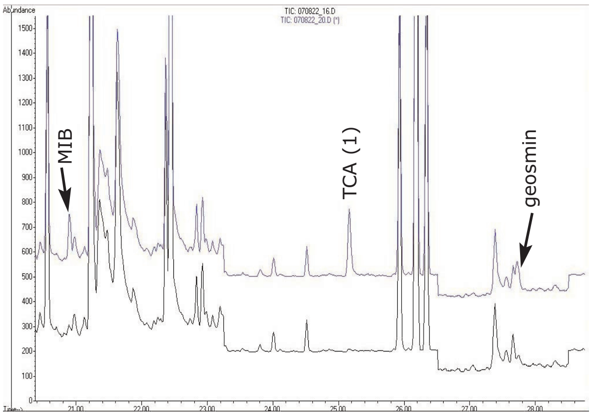

Figure 2: Selected ion chromatogram of water blank (bottom) and 5 ppt level standard (top)

Figure 2 shows a representative chromatogram of the blank HPLC grade water overlaid with a 5 ppt standard solution. This clearly demonstrates that the HPLC grade water contains minimal levels of the compounds of interest compared to the spiked sample. Figure 3 shows a close-up of geosmin and MIB at the 1 ppt level chromatogram.

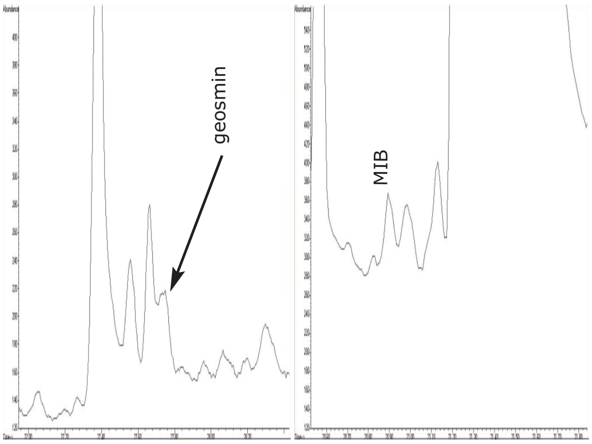

Figure 3: Close-up of geosmin and MIB at the 1 ppt level

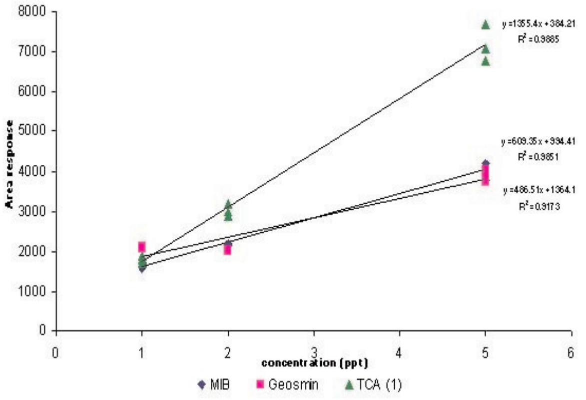

Figure 4: Linearity of standards from 1ppt to 5 ppt

Figure 4 shows system linearity plot from 1 to 5 ppt with R^2 values of 0.9885 for TCA, 0.9173 for geosmin and 0.9851 for MIB.

	Area response	
Conc. (ppt)	**MIB**	**Geosmin**
1	663	637
1	576	542
1	520	589
2	1329	881
2	1391	867
2	1348	829
5	3518	2840
5	3504	2527
5	3078	2660

Table 1: Area response values for 1 to 5 ppt level standards with corresponding background water levels subtracted.

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 that average background levels for each target compound were subtracted from the respective values.

Conclusions

These results clearly demonstrate the fundamental sensitivity and robustness HS-TD-GC/MS system for this application. 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.

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

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