

HIT it - targeting VOCs and SVOCs

Application experts from GERSTEL K.K. in Japan pondered how volatile compounds could be determined even more efficiently using Headspace techniques.
The answer was only a mouse-click away.

Headspace gas chromatography (HS-GC) is frequently used for the determination of flavor compounds in food. HS sampling techniques can be divided into the following broad categories:

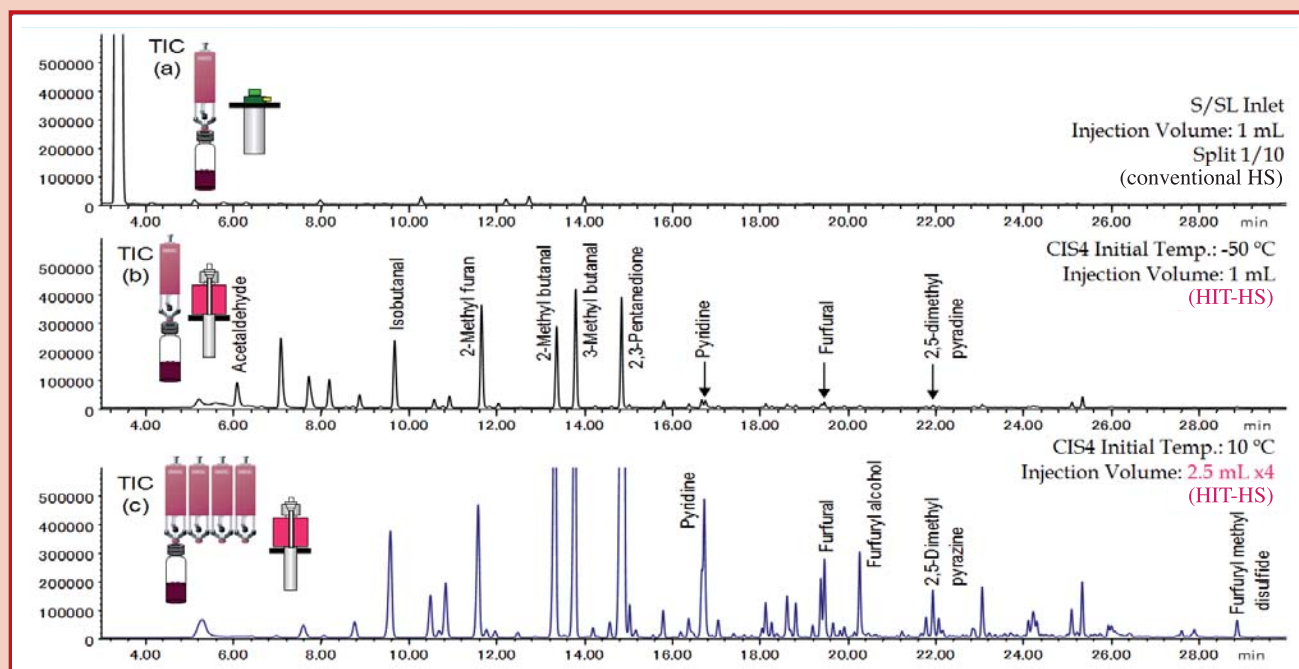
- Static headspace (SHS),
- Dynamic headspace (DHS),
- Headspace solid phase micro extraction (HS-SPME)

A further technique, headspace sorptive extraction (HSSE) using the GERSTEL Twister, is not addressed in this work. SHS is typically

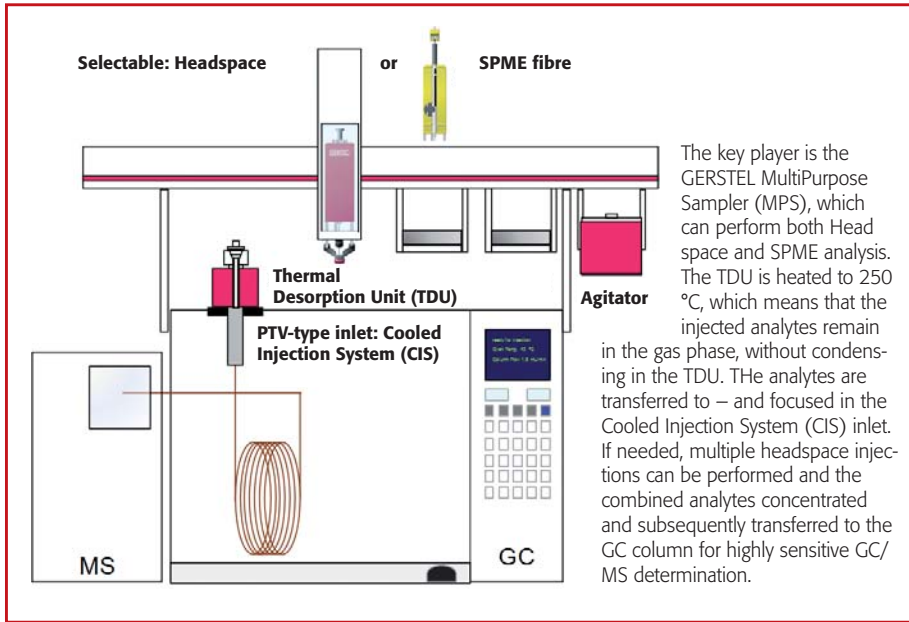
a one-step sampling technique: An aliquot of the gas phase in equilibrium with a solid or liquid sample inside a closed vial is taken and introduced to the GC inlet. Since only a fraction of the headspace can be injected, the technique may not achieve adequate sensitivity. For this reason, pre-concentration of the analytes found in the headspace has been studied. DHS and HS-SPME, on the other hand, are two-step sampling techniques that incorporate analyte concentration on an adsorbent trap or on an SPME fiber, respectively, followed by thermal desorption and

transfer to the GC system. For SPME, high selectivity can be achieved through choice of the optimal fiber coating, but the small volume of solid phase on the fiber may limit the sensitivity of the analysis.

In this study, we describe a new enrichment method for SHS and HS-SPME using the MultiPurpose Sampler (MPS) and a Thermal Desorption Unit (TDU) combined with a programmable temperature vaporizer (PTV) inlet, the Cooled Injection System (CIS) all from GERSTEL. The new enrichment method is called Hot Injection and



Total ion chromatograms of canned coffee by SHS analysis: (a) Conventional SHS with S/SL inlet (injection volume 1 mL, Split 1:1); (b) HIT-HS with CIS 4 Initial Temp. -50 °C (injection volume 1 mL, Split 1:1); (c) HIT-HS with CIS 4 Initial Temp. 10 °C, optimized for medium- to high boilers (injection volume 2.5 mL x4, Split 1:1).



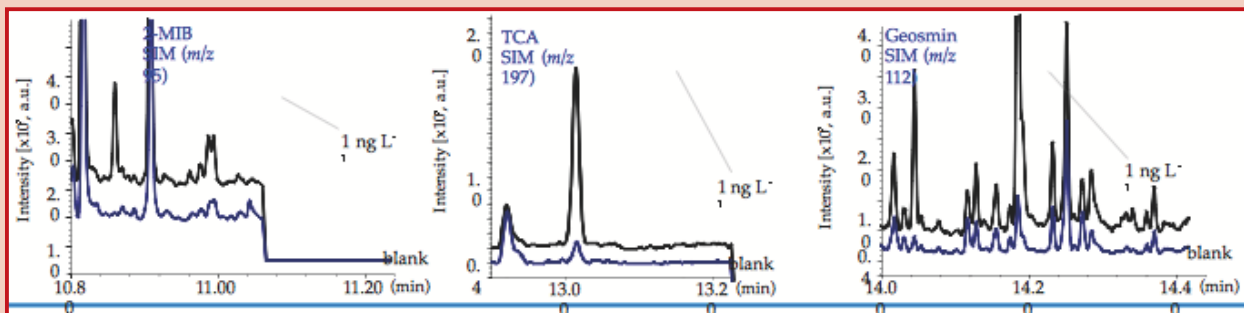
The GERSTEL MPS configured for HIT-SPME in combination with the TDU.

Trapping (HIT): A HS syringe or SPME fiber is inserted into the TDU, which is kept heated at 250 °C to prevent cold spots where analytes might be adsorbed. The desorbed analytes are trapped in the Tenax TA packed CIS liner at temperatures between -50 and 30 °C, enabling the use of multiple headspace injections for improved limits of detection (LODs). Trapped analytes can be introduced to the GC column in splitless mode for maximum sensitivity. The performance of the HIT technique in terms of LODs, linearity, and repeatability was demonstrated

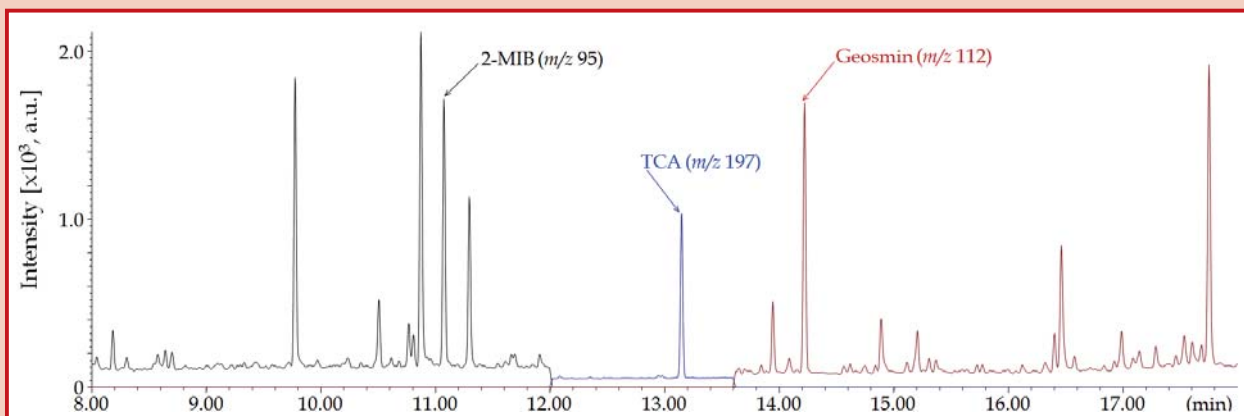
with aqueous samples such as drinking water and beverages.

Canned Coffee by HS and HIT-HS

The figure on page 14 shows total ion chromatograms (TICs) of canned coffee obtained by conventional HS using S/SL inlet (TIC a) and that of HIT-HS (TIC b, c). In TIC b, as injection was done with CIS 4 initial temp. at -50 °C, very volatile compounds (e.g. acetaldehyde) were detected. In TIC c,



SIM chromatograms showing 3 off-flavor compounds in water (1 ng/L and blank).



SIM chromatogram of water spiked with 10 ng/L of 2-MIB, TCA and geosmin. Concentrating the analytes through multiple injections for each GC/MS run enables clear and unambiguous determination.

2.5 mL x4 was introduced into the TDU-CIS 4 system for further concentration. The CIS 4 initial temperature was set to 10 °C, enabling proper water management. Using four 2.5 mL HS injections resulted in enhanced sensitivity. Furthermore, lower vapor pressure compounds (e.g. furfuryl methyl disulfide) could be determined.

Off-flavors in Water by HIT-HS

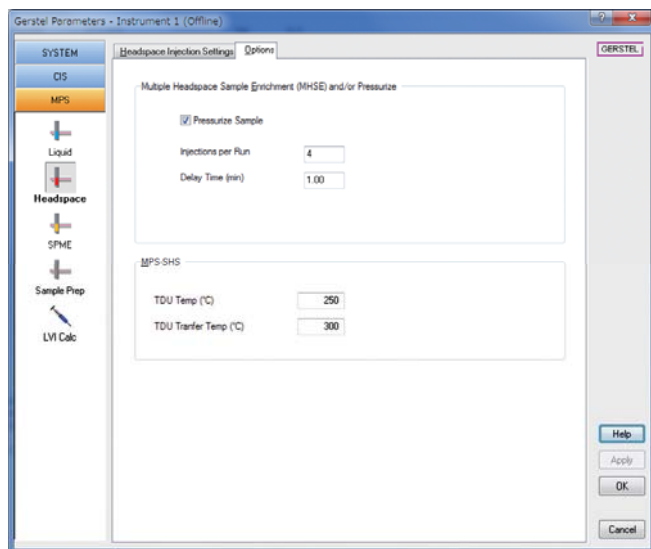
To maximize the sensitivity, we chose four 2.5 mL injections as optimum for the deter-

mination of 2-MIB, TCA, and geosmin in water. The method resulted in good linearity with a correlation coefficient (R^2) above 0.9950 for 7-level calibration curves between 1 and 200 ng/L. SIM chromatograms of fortified natural water spiked at 1 ng/L are shown on page 15. The repeatability of this method was determined by analysis of natural water spiked at 1 ng/L. The relative standard deviation (RSD) for each compound was in the range from 4.2 to 8.6 % (n=7). The limits of detection (LODs) were calculated as 3 times the standard deviation estimated from replicate determinations

(n=7) at the lowest concentration determined for each compound. LODs were 0.12 ng/L for 2-MIB, 0.36 ng/L for TCA and 0.30 ng/L for geosmin, respectively.

Conclusion

The HIT technique provides significantly enhanced sensitivity for HS analysis of flavor and off-flavor compounds. Also, HIT resulted in good linearity and repeat-ability for the determination of off-flavor compounds in water, achieving very low LODs at sub-ng/L levels.



MAESTRO and HIT-HS: To improve the sensitivity and lower the limits of detection significantly for your Headspace analysis, simply increase the number of injections per GC/MS run: On the MAESTRO method page, just type in the number of injections (concentration steps) and off you go. This is the most convenient way by far to automate analyte concentration and sample introduction for HS-GC/MS.

Source

Jun Tsunokawa, Kikuo Sasamoto and Nobuo Ochiai, GERSTEL K.K., Tokyo: "Hot Injection and Trapping Using SHS/SPME and a Thermal Desorption System for GC/MS-Analysis". Poster presentation at PITTCON 2012.

HIT-HS-GC/MS System based on the GERSTEL MPS.

