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Automated Dynamic Headspace Sampling of Aqueous Samples Using Replaceable Adsorbent Traps

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Abstract
Static (equilibrium) headspace sampling is commonly used for GC determination of volatiles in solid and liquid samples. Since this technique relies on the analyte partitioning between the sample and headspace and uses a fixed injection volume it may not provide adequate detection limits, particularly for higher molecular weight, higher boiling analytes, and for polar analytes in aqueous samples.

In this study we describe the use of an automated dynamic headspace sampler for determination of volatiles in high water content solids and aqueous samples. This sampler uses a two-needle design to flush the headspace of standard headspace vials onto replaceable adsorbent traps that can be thermostatted to control interference from water vapor. After sample collection, the adsorbent traps can be automatically dry purged to further eliminate trace water before introduction into the integrated thermal desorber. This design enables automated optimization of trapping conditions including choice of adsorbent, and has the potential for automated internal standard addition and automated calibration.

Performance of the new system was compared to traditional

static headspace analysis using high water content solid samples like fruits and vegetables, and also beverages. To illustrate the versatility of the new design, several sample types with high water content were tested with a series of adsorbent traps to determine optimal trapping conditions. Better detection limits were obtained with dynamic headspace for all sample types.

Introduction

The GERSTEL Dynamic Headspace System (DHS) (Figure 1) is an accessory for the MultiPurpose Sampler (MPS 2) which enables dynamic purging of the headspace above a sample. Analytes in the purged headspace are trapped onto a 2 cm adsorbent bed in a compact glass tube. The tube is then placed into the Thermal Desorption Unit (TDU) and the analytes thermally desorbed and introduced to the gas chromatograph. The analytes are cryofocused in the Cooled Injection System (CIS 4) inlet to improve peak shape and increase sensitivity.

Figure 1. GERSTEL MPS 2 with DHS option on an Agilent Technologies 7890 GC / 5975 MSD.

Figure 2 shows a schematic of the trapping and desorption process.

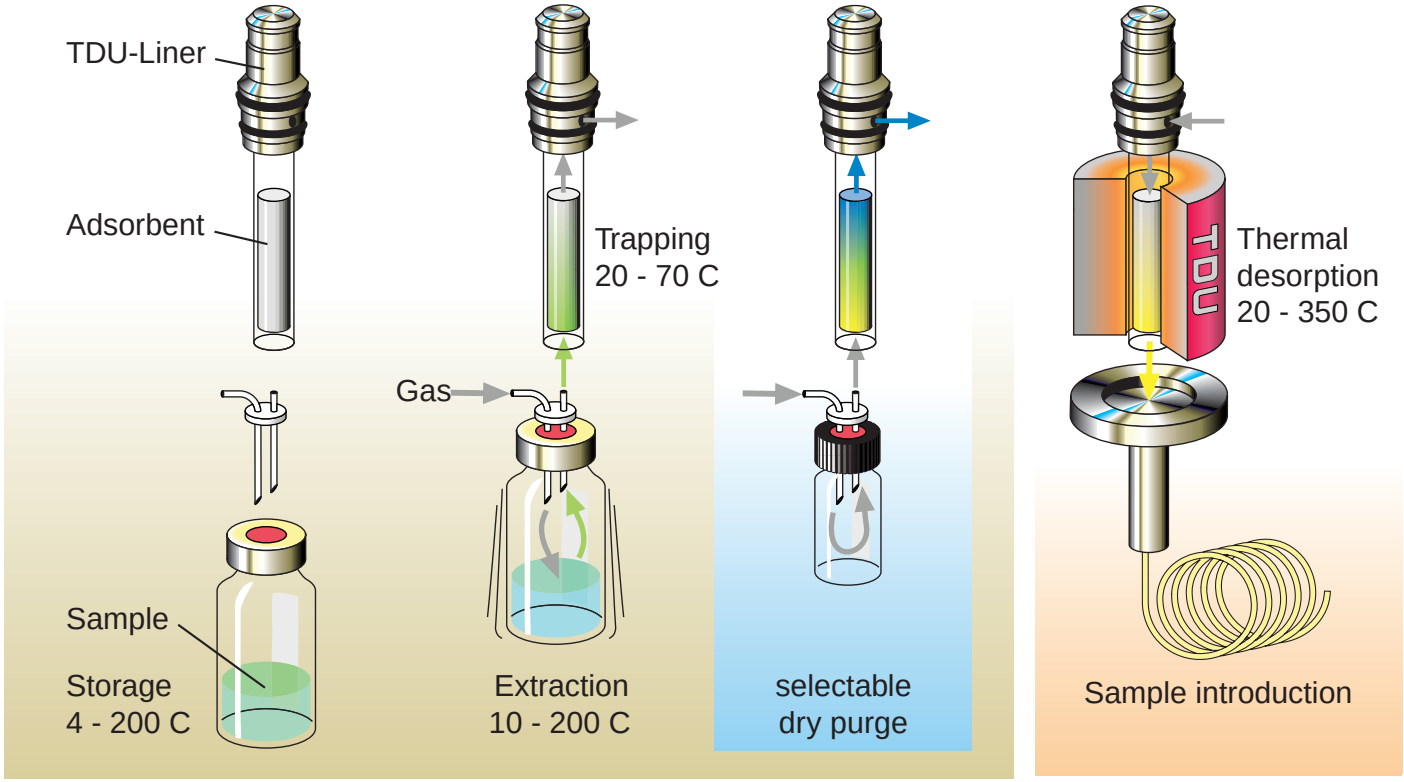

Figure 2. Schematic view of DHS process.

Aqueous and high water content samples can often be problematic for headpsace analysis. The presence of water vapor in the headspace above the sample can lead to poor precision. The increased sensitivity from agitation and dynamic purging of the sample offered by the GERSTEL DHS allows analysis to be carried out at lower temperatures, thereby reducing the amount of water in the headspace. Water can also be managed using a dry purge function in the DHS or the solvent vent function in the TDU.

This study examines optimization of parameters required for dynamic headspace analysis of aqueous samples. Several sample types are shown as examples.

Experimental

Optimized analysis conditions.

Trap:	Carbopack X/Carboxen 569
DHS:	50°C trap temperature
	30°C incubation temperature
	150 mL purge volume
	25 mL/min purge flow
TDU:	solvent venting
	50°C (3 min); 720°C/min;
	250°C or 330°C (3 min)
PTV:	0.2 min solvent vent (50 mL/min)
	split 20:1
	-150°C; 12°C/s; 250°C (3 min)
Column:	20 m Rtx-624 (Restek)
	d_i = 0.18 mm d_f = 1.0 µm
Pneumatics:	He, ramped pressure mode
	19.6 psi (2 min); 1.36 psi/min;
	38.6 psi (5 min)
Oven:	40°C (2 min); 15°C/min;
	250°C (5 min)
MSD:	Scan, 15 - 350 amu

Sample Preparation. Two grams of solid or 5.0 mL of liquid were added to a 20 mL screw cap headspace vial. The final concentration of the BTEX standard was 80 ppb in 5 mL water.

Results and Discussion

The first parameters investigated were the effect of DHS purge flow and purge volume. The BTEX standard was used for these tests. Figure 3 shows the results of varying these two parameters for this sample type. The purge flow was varied from 10-100 mL/min at a constant volume of 150 mL. The area of the toluene peak (m/z=91) was used as a recovery indicator. The results show the area reaching a maximum quickly at 25 mL/min. The purge volume was then varied from 50-300 mL with a constant purge flow of 25 mL/min. The results show a maximum around 150 mL with a sharp drop off at higher volumes, most likely due to breakthrough on the TDU adsorbent tube.

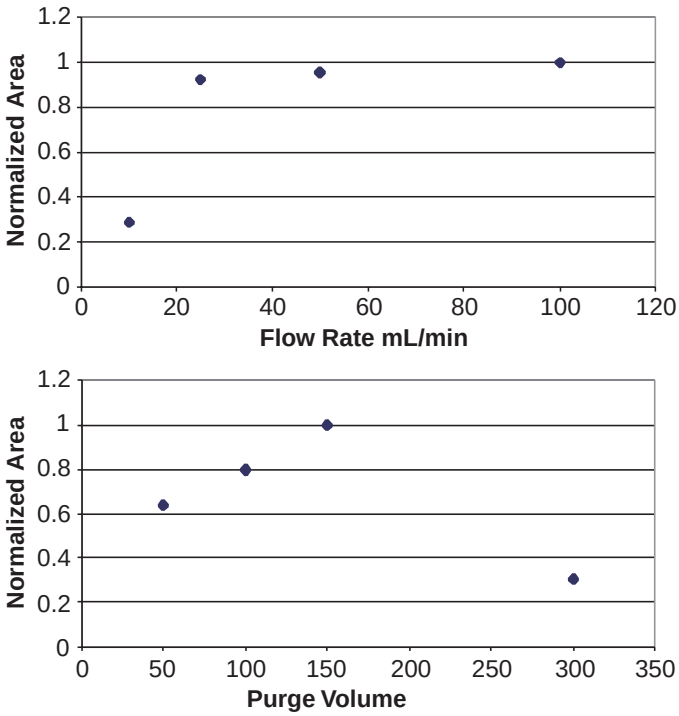

Figure 3. Optimization of purge volume and flow.

The DHS accessory is capable of performing a dry purge step. A set of experiments was conducted to investigate possibilities to remove remaining water from the Carbopack X/Carboxen 569 packed TDU tube. The BTEX sample was equilibrated for 5 minutes at 30°C, then extracted with a purge flow of 25 mL/min and a purge volume of 150 mL. The dry purge flow was varied from 10-50 mL/min while keeping the volume constant at 150 mL. The trap was kept at 30°C. No reduction in the water peak was noted. The experiments were repeated with a trap temperature of 50°C, again no reduction in the water was seen.

Therefore, in this case, an alternative way to manage water was tried: Solvent vent in the TDU. In the solvent vent mode, the flow through the adsorbent tube goes to vent for a preset period of time. The TDU is maintained at a low temperature. After the initial solvent venting, the vent valve is closed, the TDU is heated and the effluent/analytes are refocused in the CIS 4. The difference of solvent venting compared to the DHS purge is that the flow across the tube runs counter to the sampling direction. This feature offers a second mechanism of reducing the water content.

In the first set of experiments, the TDU temperature was varied (40, 50 or 60°C) while keeping the flow constant at 50 mL/min with a vent time of 3 minutes. The water level was highest at 40°C, and very little difference was seen between 50 and 60°C. The analyte (BTEX) peaks were highest for the 50°C setting. The vent time was varied from 3 to 5 minutes with a constant flow of 50 mL/min and a TDU temperature of 50°C. The results showed similar levels of water, but lower analyte peaks for the 5 minute vent time. The vent flow was increased above 50 mL/min with no further benefit in water reduction and analyte retention.

Lastly, the DHS extraction temperature was optimized. Values of 30, 40 and 50°C were tried. The purge volume was set to 150 mL, purge flow to 25 mL/min. The TDU was operated in solvent vent mode with a vent flow of 50 mL/min, vent time 3 minutes and a TDU temperature of 50°C. Figure 4 shows an overlay of the three runs. The analyte peak heights are similar for the three runs, but the water on the adsorbent tube is greatly reduced at the lower incubation/extraction temperature.

The optimized conditions are listed in the experimental section and were used for all subsequent analyses, except where noted.

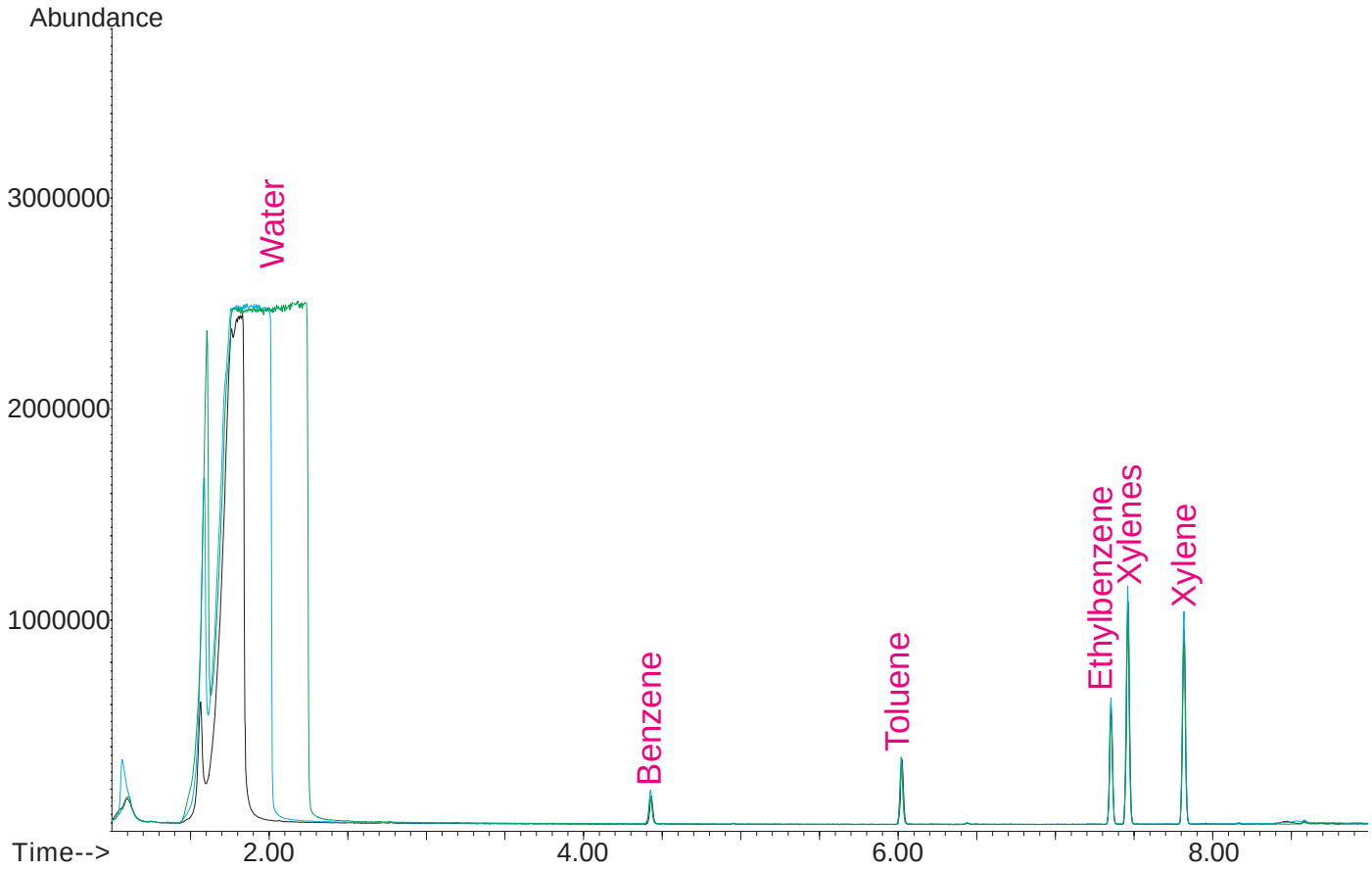

Figure 4. Overlay of Varying Incubation/Extraction Temperature.

In the GERSTEL MAESTRO software, the user can select whether to use a single TDU tube for all samples or a separate TDU tube for each sample. The selection is made in the DHS method page. The latter enables easy optimization of trap sorbent materials. Figure 5 shows a stacked view of Total Ion Chromatograms for a DHS extract of coffee using 4 different trap materials. The Carbopack X and mixed Carbopack X/Carboxen 569 show the best recovery for analytes from the coffee sample. The mixed bed shows better retention of some lower boiling components, such as furan.

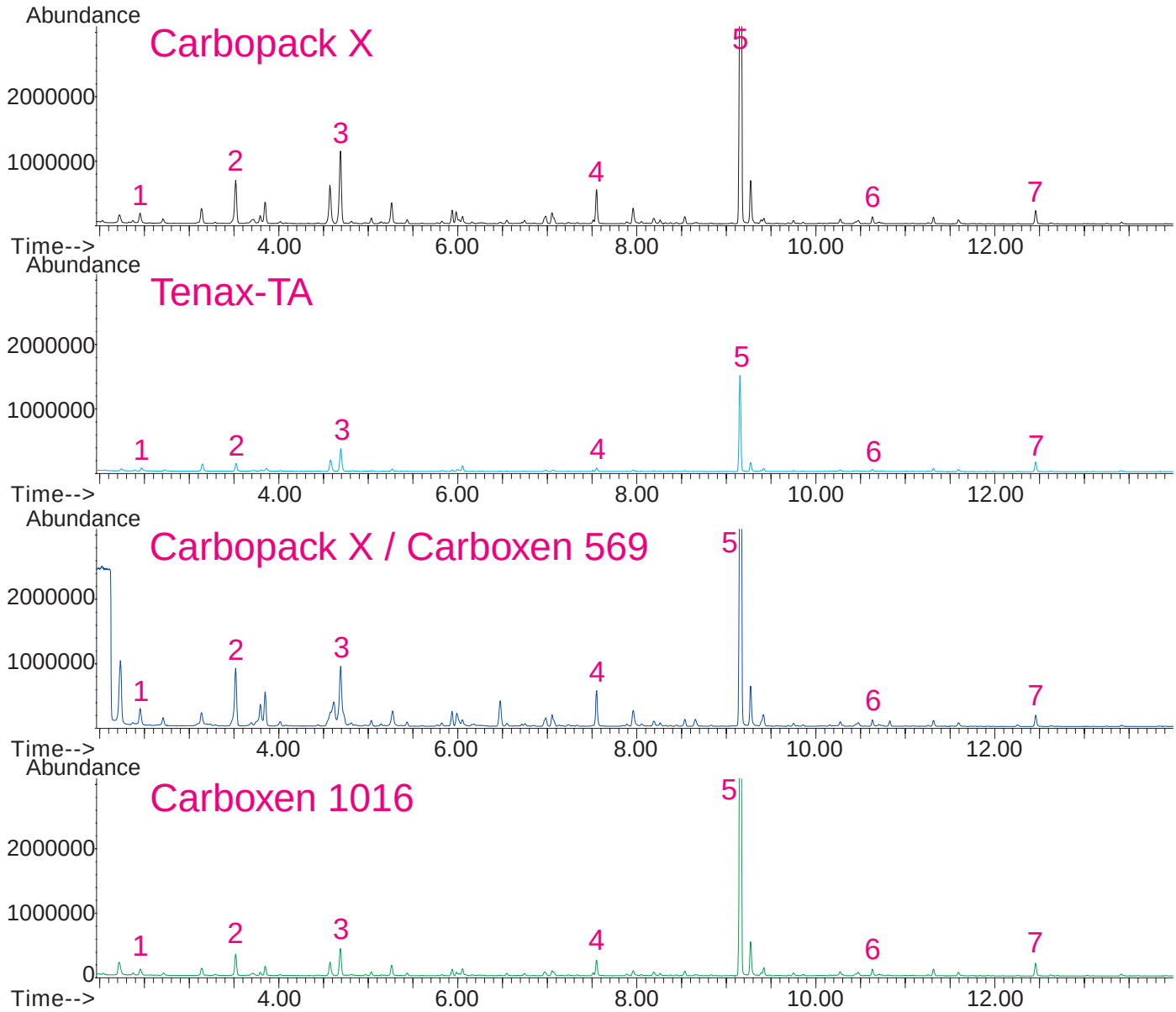

Figure 5. Sorbent trap optimization for coffee sample. 1: Furan, 2: 3-Methylfuran, 3: 2-Methylbutanal, 4: Furancarboxaldehyde, 5: Benzaldehyde, 6: 4-Methylbenzaldehyde, 7: 4-Methyl-2-phenyl-1,3-dioxolane.

Figure 6 shows an overlay of three separate extracts of a beer sample trapped on Tenax TA. The overlay illustrates the good repeatability for this type of analysis.

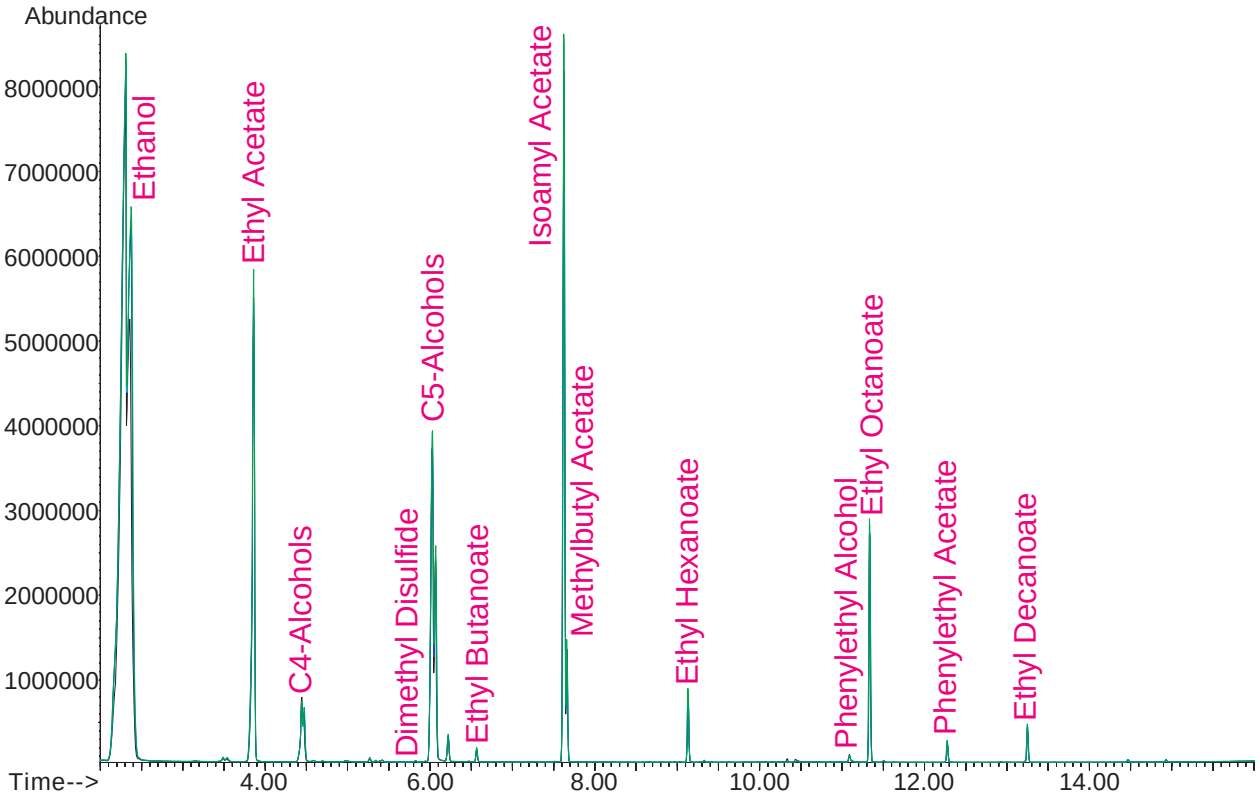

Figure 6. Overlay of beer replicates.

Several other sample types were examined using the optimized parameters. Figures 7 and 8 show the results for a 2 g fresh strawberry sample and a 5 g cola sample, respectively.

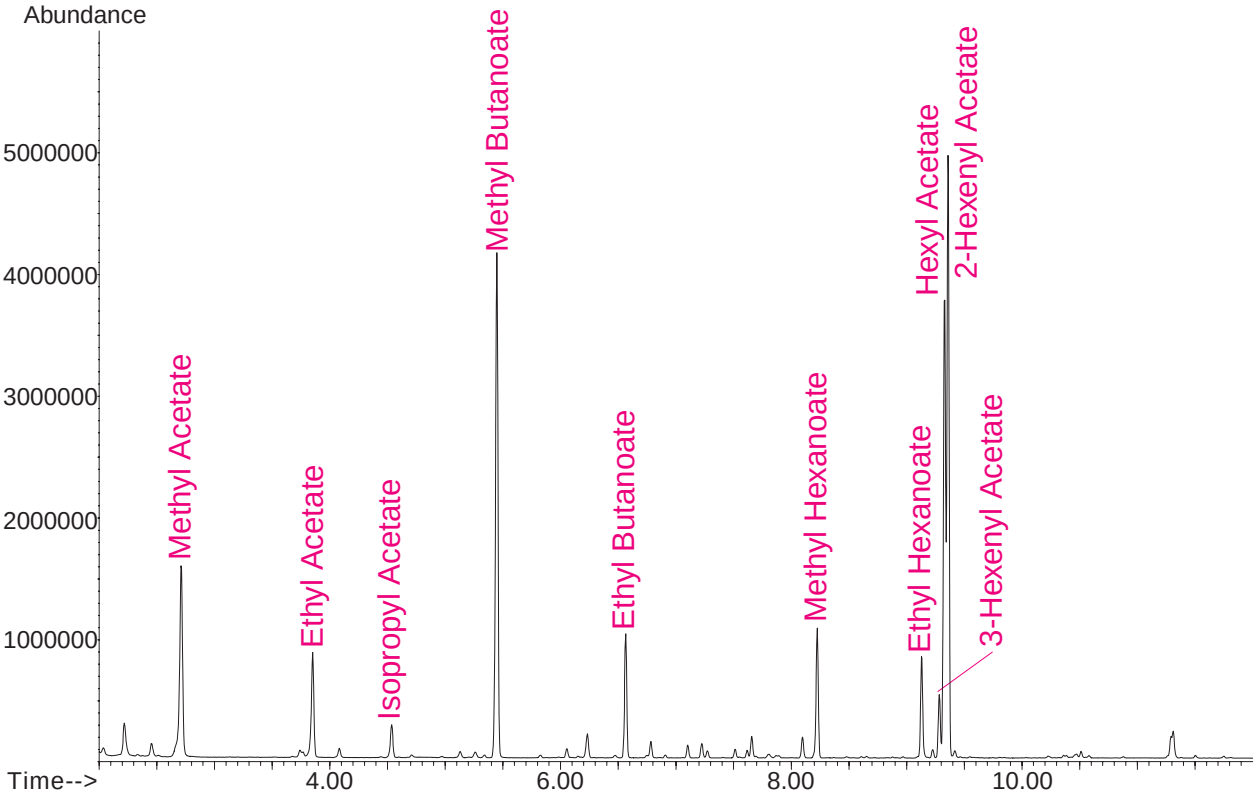

Figure 7. Total ion chromatogram for a 2 g fresh strawberry sample.

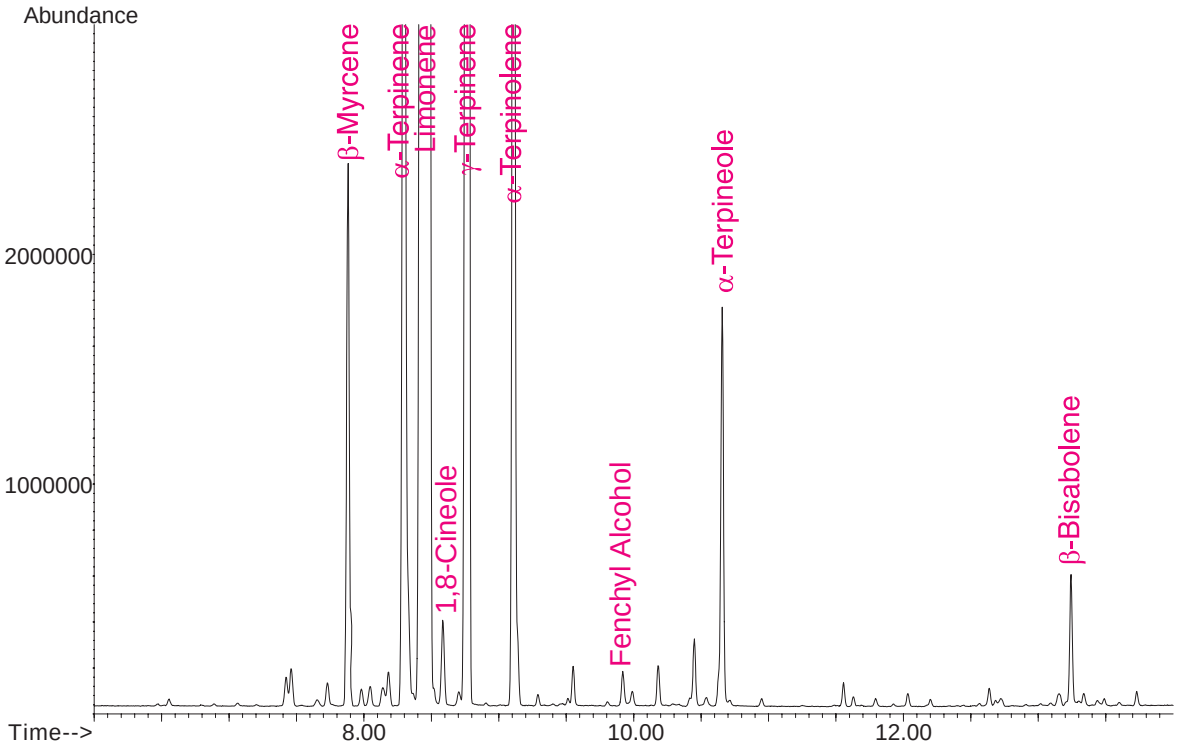

Figure 8. Total ion chromatogram for a 5 g Cola sample.

Figure 9 shows a comparison of static and dynamic headspace analysis of a cola sample. In the static headspace extractions the sample was equilibrated at 50°C for 15 minutes. The dynamic headspace extraction (150 mL purge volume) shows 18-132 times greater (see figure) response than the 1.0 mL injection following static headspace extraction.

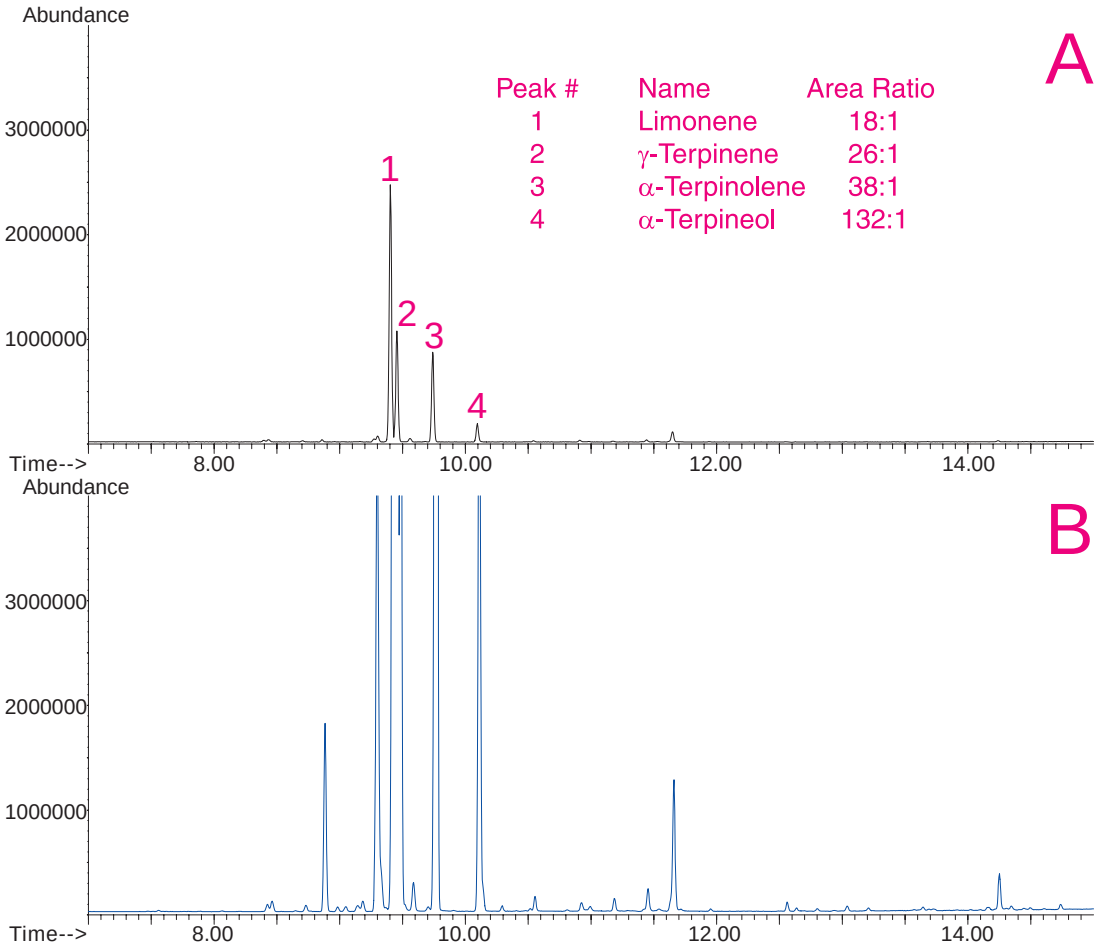

Figure 9. Comparison of static and dynamic headspace analysis of a cola sample.

Conclusions

The GERSTEL Dynamic Headspace (DHS) accessory for the MultiPurpose Sampler (MPS 2) adds a high-performance tool to the analyst's toolbox for trace analysis of aqueous and high water content samples. Dynamic Headspace is a concentration technique that provides better sensitivity and lower detection limits than SPME or static headspace. The ability to automatically change traps facilitates method optimization as shown in this paper. A wide range of adsorbent materials can be packed into the TDU tubes including customized trapping material or combinations for specific analytes or for best possible water management. Successful method optimization examples were provided, involving selection of optimal adsorbent(s), flows and temperatures as well as water management. The DHS sample incubation/ extraction temperature can be varied from 20-200°C and the trapping temperature from 20-70°C for method optimization. Several options have been presented for effective water management: The sample temperature can be reduced to reduce water transfer into the trap; the trap temperature can be increased to eliminate condensation; the DHS dry purge can be selected in the method to remove water from the trap following the extraction step; or the solvent vent mode in the TDU can be selected to purge water from the trap prior to thermal desorption. Based on the optimized methods, successful examples of the determination of flavor compounds in fruit and beverages were presented.

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