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Automated Dynamic Headspace Sampling using Replaceable Sorbent Traps

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Abstract
Static (equilibrium) headspace injection 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.

In this study, we describe a new automated dynamic headspace analyzer that uses a two-needle design to flush the headspace of vessels ranging from 10 mL to 1.0 L onto replaceable adsorbent traps. The clean adsorbent traps are stored in a sealed tray on the x-y-z robotic sampler which transports them to the sample vessel, then directly to the integrated thermal desorber. This design enables automated optimization of trapping conditions including choice of adsorbent.

Performance of the new system was assessed using standard sample types and compared to traditional static headspace (HS) analysis and optimized SPME sampling. In general, better detection limits were obtained with dynamic headspace while maintaining reproducibility comparable to the other techniques.

To illustrate the new design, several sample types were tested with a series of adsorbent traps to choose optimal trapping conditions. A prototype DHS design was constructed for larger vessels. It was used to contain large and bulky samples for dynamic headspace analysis.

Introduction

The principles of static headspace gas chromatography are well established [1]. It is used in a variety of industries for detection of volatile and semi-volatile materials in both liquid and solid samples. It is simple, reliable and easily automated. It does not, however, provide as low detection limits as other headspace techniques such as solid phase microextraction (SPME), In-Tube Extraction (ITEX), or Dynamic Headspace (DHS).

This note demonstrates the versatility of a new DHS design for the GERSTEL MPS 2 autosampler. The results are compared to other headspace techniques, static, SPME, and ITEX. Results for a prototype DHS unit for larger items are also shown.

Experimental

Instrumentation. All analyses were conducted using an Agilent 6890 gas chromatograph with 5975 mass spectrometer. Sample extraction and introduction were fully automated using a GERSTEL MPS 2 autosampler configured for DHS, ITEX, SPME injection, or Static Headspace injection. A GERSTEL Twister Desorption Unit (TDU) was used for thermal desorption of the adsorbent-filled traps in conjunction with the DHS module and with the off-line large sample DHS unit.

Sample Preparation. For SPME, SHS, ITEX, and DHS, the samples were placed in 20 mL screw cap vials. The sample amounts were 100 mg for coffee powder and shower gel, and 300 mg for the cheese. The cheese was stored in a freezer and ground prior to weighing. For the large sample prototype DHS, 50 mL of herbal liqueur, a fabric dryer sheet, or a whole carnation were placed in a 500 mL jar. The carnation was heated to 60°C using a 2‘ x 1“ heated tape (Cat.no. K-36001-52, Cole-Parmer, USA) attached to the outside of the jar.

Sample Introduction. All extraction methods were automatically executed using the MPS 2 autosampler, with the exception of the large sample DHS extractions.

Analysis conditions (except DHS Large Sample).

Column:	30 m SolGel Wax (SGE)
	d_i = 0.25 mm d_f = 0.25 µm
Pneumatics:	He, constant flow = 1.2 mL/min
Oven:	40°C (2 min); 15°C/min;
	250°C (2 min)
MSD:	scan mode; 28-280 amu

In the automated DHS mode, samples are heated and extracted in the GERSTEL DHS module. Analytes are trapped on Tenax TA packed TDU tubes. After extraction, the TDU tubes are transported to, and subsequently desorbed in the GERSTEL Twister Desorption Unit. The analytes are cryofocused in the GERSTEL CIS 4 programmable temperature vaporizer inlet. The inlet is then heated to release the analytes onto the column.

DHS conditions.

Trap:	Tenax TA
MPS 2:	25°C trap temperature
	25 or 40°C incubation temperature
	200 or 300 mL purge volume
	20 mL/min purge flow
PTV:	10:1 solvent venting
	-100°C; 12°C/sec, 280°C (8 min)

In SPME mode, the samples are incubated and extracted in the MPS 2 agitator. A 50/30 µm DVB/Car/PDMS SPME fiber was exposed to the headspace of the sample, then desorbed in the Agilent split/splitless injector.

SPME conditions.

Fiber:	DVB/Car/PDMS; 50/30 µm
MPS 2:	30 or 40°C (30 min) incubation
S/SL:	250°C; 10:1 split

In SHS mode, samples are incubated in the MPS 2 agitator. A 1.0 mL aliquot of the headspace was taken using a gas tight syringe. It was injected into the split/splitless inlet.

SHS conditions.

Injection:	1 mL
MPS 2:	30 or 40°C (30 min) incubation
S/SL:	250°C; 10:1 split

In ITEX mode, samples are heated and extracted in the MPS 2 agitator. The ITEX module consists of a special headspace needle, partly filled with Tenax TA. The headspace of the sample is pumped through this adsorbent bed using a heated gas tight syringe that is mounted in the autosampler tower. Following analyte trapping on the bed, the needle is inserted into the split/splitless inlet, the adsorbent bed is heated, and the analytes transferred to the GC column by moving the plunger of the gas tight syringe down.

ITEX conditions.

Trap:	Tenax
MPS 2:	30 or 40°C (5 min) incubation
	80 or 120 x 2500 µL extraction vol.
S/SL:	280°C; 10:1 split

Following extraction in the large sample DHS unit, the Tenax-TA filled TDU tubes (traps) were manually loaded into a VT-98t tray on the MPS 2 autosampler and subsequently thermally desorbed in the TDU.

DHS-Large Sample conditions.

Trap:	Tenax TA
MPS 2:	25°C trap temperature
	25 or 60°C incubation temperature
	750 mL purge volume
	25 mL/min purge flow
PTV:	20:1 solvent venting
	-120°C (0.2 min); 12°C/sec,
	280°C (3 min)
Column:	10 m Rtx-5 (Restek); MACH-format
	d_i = 0.18 mm d_f = 0.40 µm
Pneumatics:	He, constant flow = 2 mL/min
Oven:	40°C (2 min); 15°C/min;
	250°C (2 min)
MSD:	scan mode; 35-350 amu

Results and Discussion

Figure 1 shows a picture of the GERSTEL DHS Module. Figure 2 shows several views of the prototype DHS module for large items.

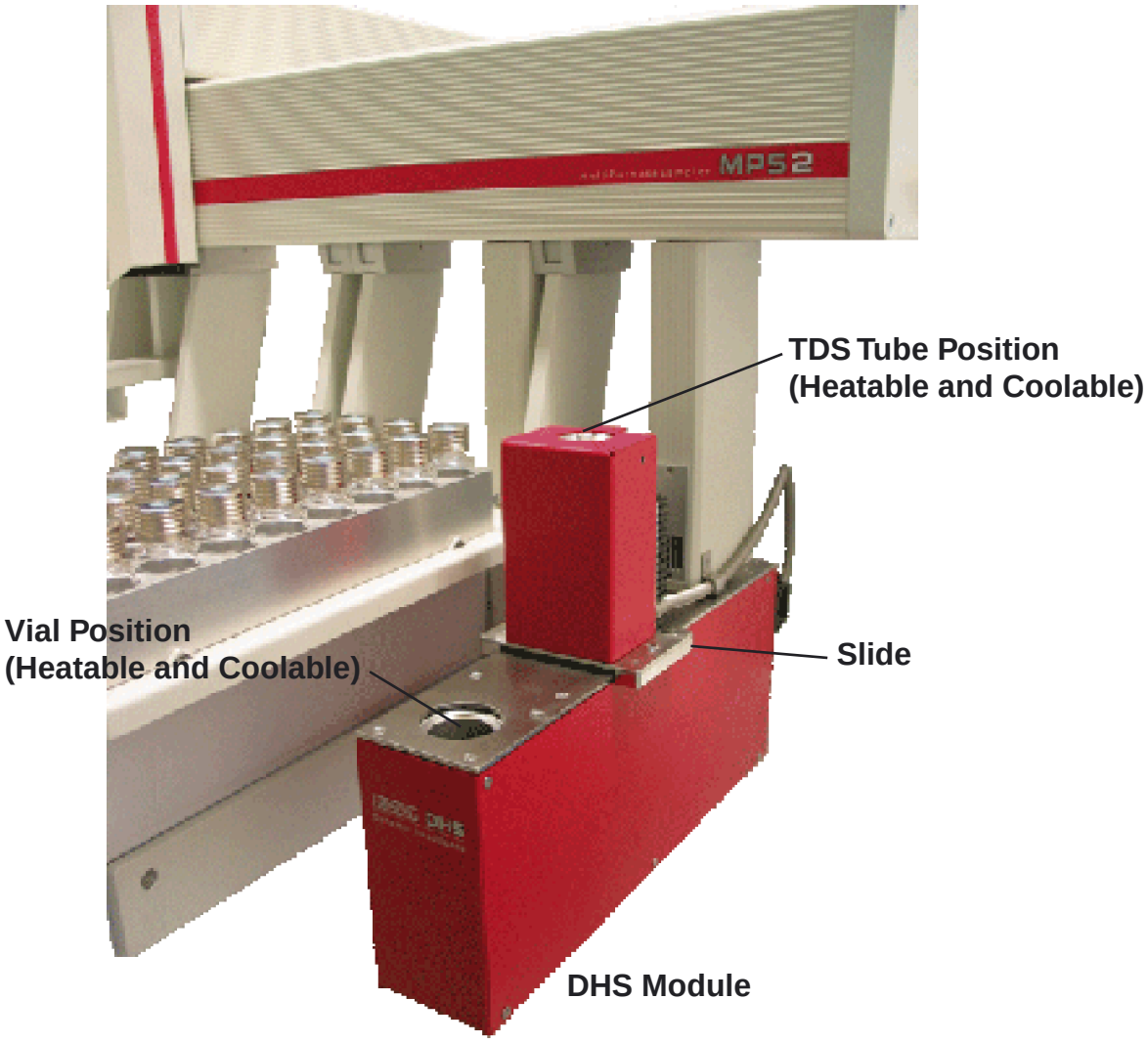

Figure 1. Photo of automated DHS module.

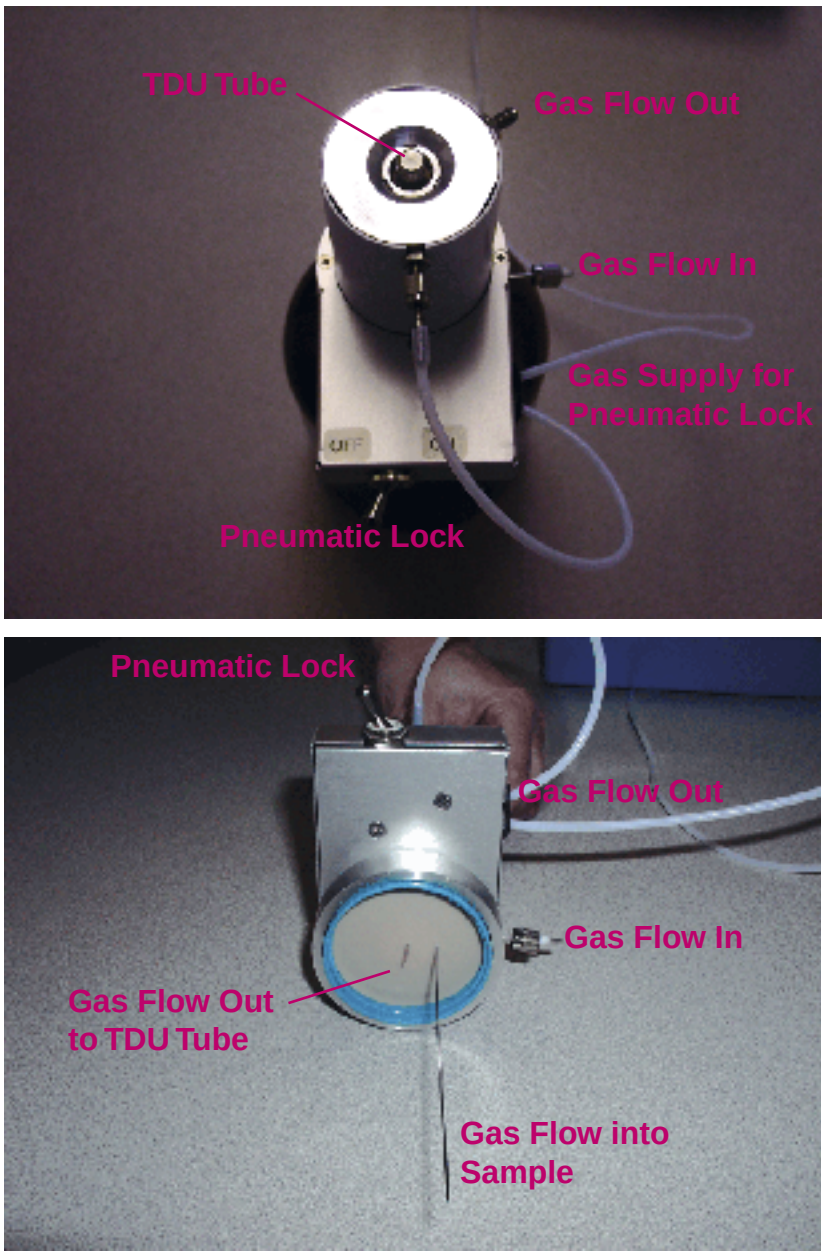

Figure 2. Photos of prototype Large Sample DHS unit.

For the cheese, coffee powder, and shower gel, six replicates were analyzed by each extraction technique. Figure 3 shows representative total ion chromatograms (TICs) for each extraction technique for the coffee powder.

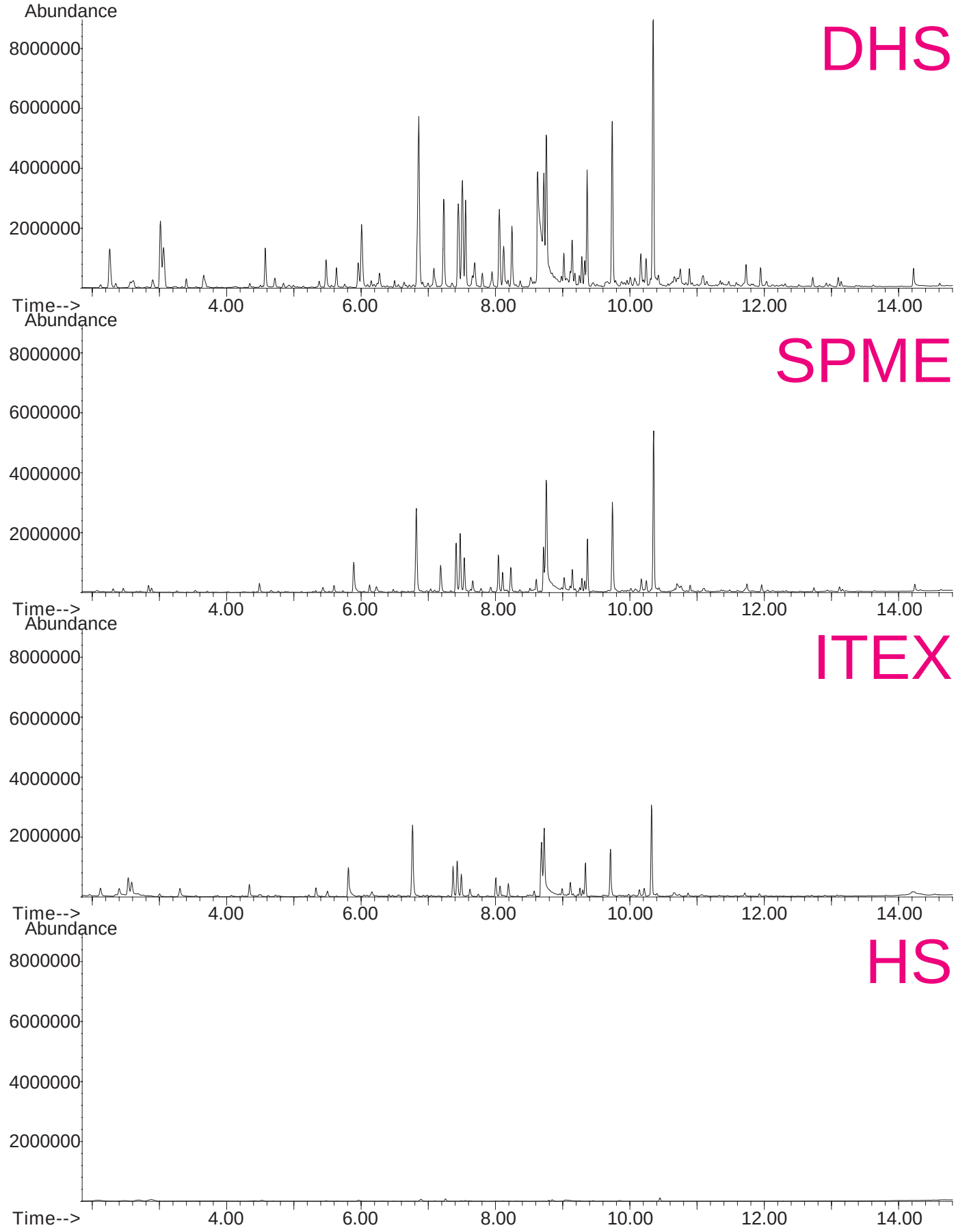

Figure 3. Total ion chromatograms for each extraction technique of the coffee powder.

Figures 4 and 5, show TICs for each extraction technique for the shower gel and cheese samples, respectively. For each sample type, the DHS extraction shows the highest sensitivity.

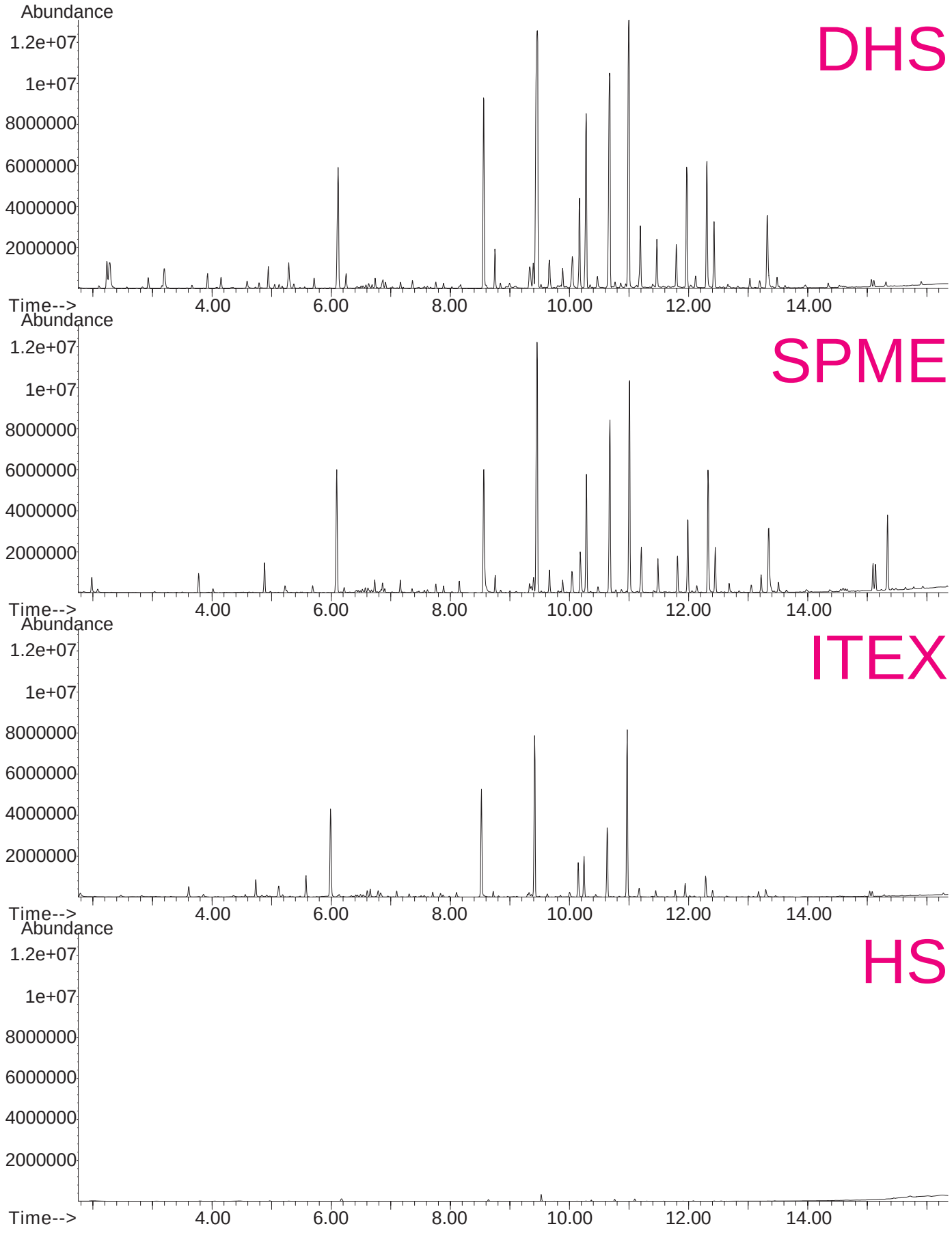

Figure 4. Total ion chromatograms for each extraction technique of the shower gel.

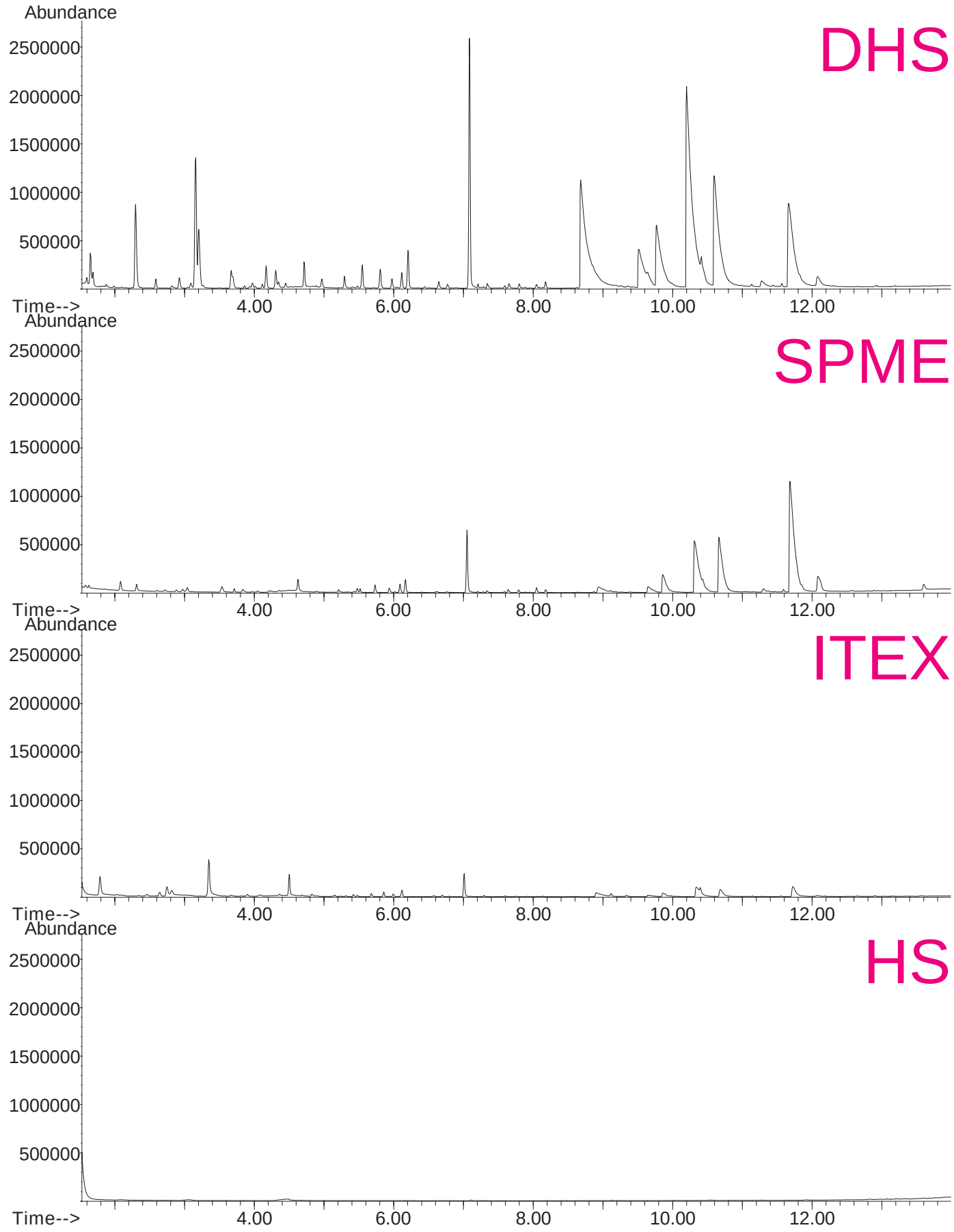

Figure 5. Total ion chromatograms for each extraction technique of the cheese.

Figure 6 shows the relative abundance for the 4 extraction techniques for select analytes in the coffee sample. The area responses are normalized to the DHS response.

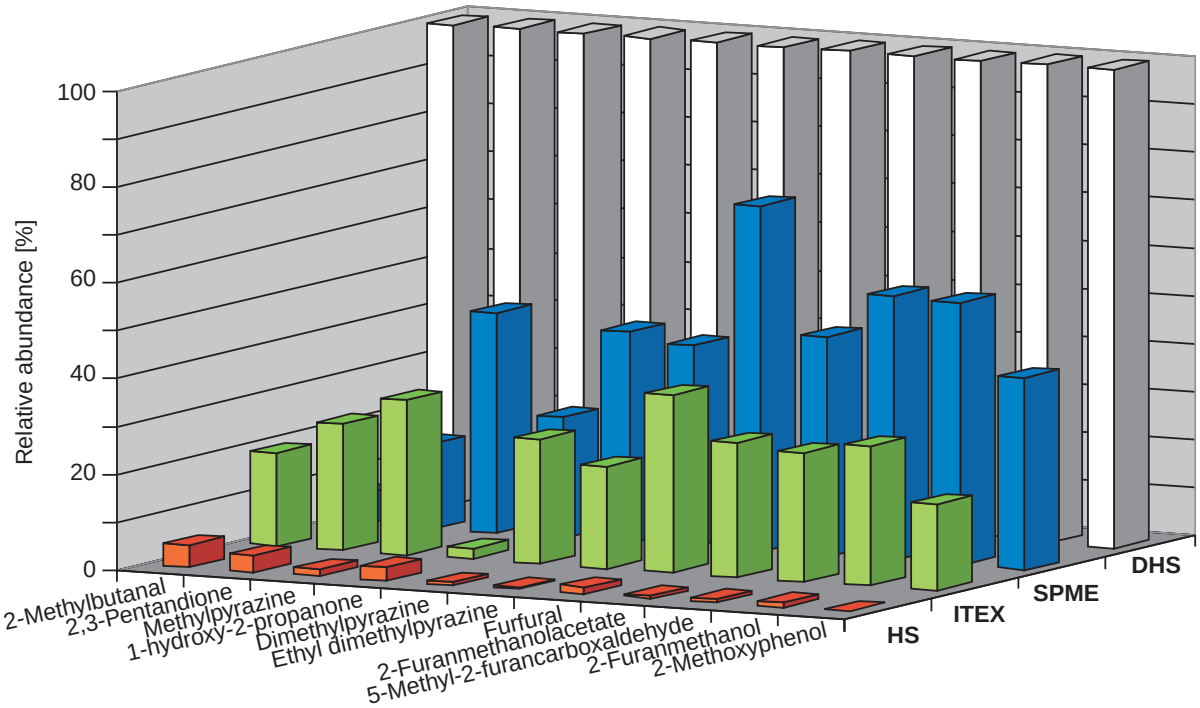

Figure 6. Relative Response for Select Compounds in Coffee Powder.

Table 1 lists the %RSD for select analytes in the three sample types for the four extraction techniques. For the coffee sample, 50 analytes were identified and for the shower gel sample more than 30 analytes. The %RSDs for the DHS extracts were mostly below 5%, which was comparable to the SPME, HS, and ITEX results. More than 20 analytes were identified in the cheese sample with %RSDs below 10%. This was better than the results obtained with the other 3 extraction techniques.

Table 1. %RSD for selected analytes comparing four different extraction techniques.

Analyte	DHS [% RSD]	SPME [% RSD]	ITEX [% RSD]	HS [% RSD]
Coffee Powder				
Methyl Acetate	11	10	8	ND
2,3-Pentandione	5	9	5	21
4-Methylthiazole	3	4	7	10
Furfural	2	2	2	7
Pyrrole	2	3	5	6
Pyrazinamide	4	2	2	6
2-Methoxyphenol	5	2	2	11
Shower Gel				
2-Methyl-2-propanol	7	6	8	9
α-Pinene	6	3	3	3
Eucalyptol	3	4	2	6
Linalool	2	1	1	1
Caryophyllene	5	6	3	6
Lillial	3	9	3	ND
Piperonal	2	4	2	4

Analyte	DHS [% RSD]	SPME [% RSD]	ITEX [% RSD]	HS [% RSD]
Cheese				
Ethanol	7	9	12	8
2-Butanol	6	18	16	ND
Dimethyldisulfide	17	14	14	14
Acetoin	7	14	17	15
2-Butoxyethanol	6	11	10	ND
2-Methyl propanoic acid	6	11	5	ND
Phenol	3	6	4	25

Figure 7 shows the results for a 50 mL sample in 500 mL jar of herbal liqueur analyzed by DHS and a 2 mL sample in 10 mL vial analyzed by HS. The DHS shows a significantly higher signal level.

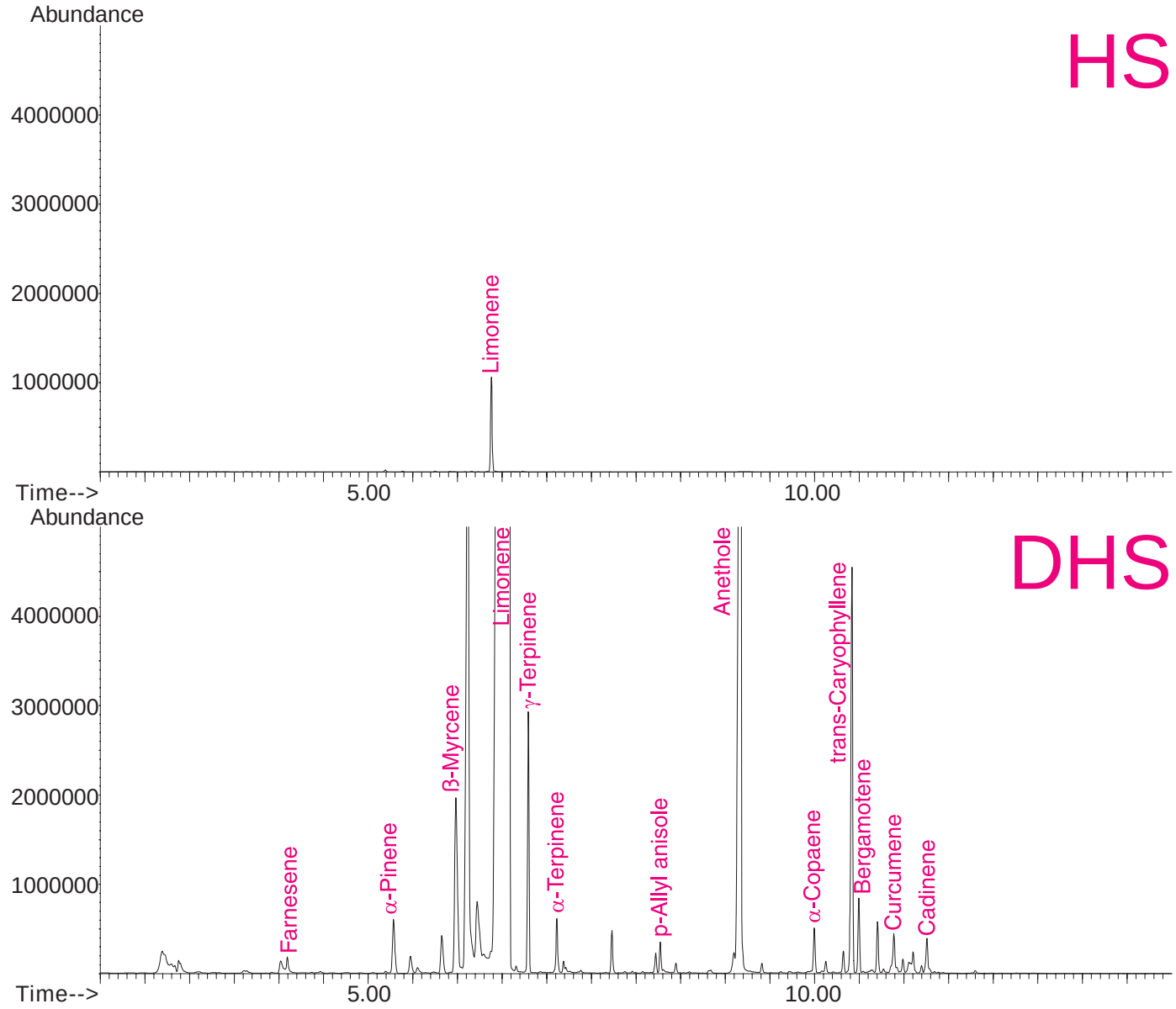

Figure 7. Total Ion Chromatograms of HS (Top) and DHS (Bottom) of Herbal Liqueur.

Table 2 lists the %RSD for n=3 for 4 compounds identified in the herbal liqueur extract.

Table 2. %RSD for four compounds identified in herbal liqueur extract.

	ß-Myrcene	γ-Terpinene	Anethole	trans-Caryophyllene
Average Area	40228996	32292965	215179377	62424594
% RSD	4.3	6.2	4.6	6.5

Figure 8 compares the results for a dryer sheet analyzed by HS (Top) and DHS (Middle). There is no signal obtained using HS, whereas the DHS extraction results in a large number of peaks in the TIC. The last Chromatogram (Bottom) of Figure 8, shows a DHS analysis of a fabric sheet after use. The technique is sensitive enough to see many of the same peaks, even after the fabric sheet has been through the dryer.

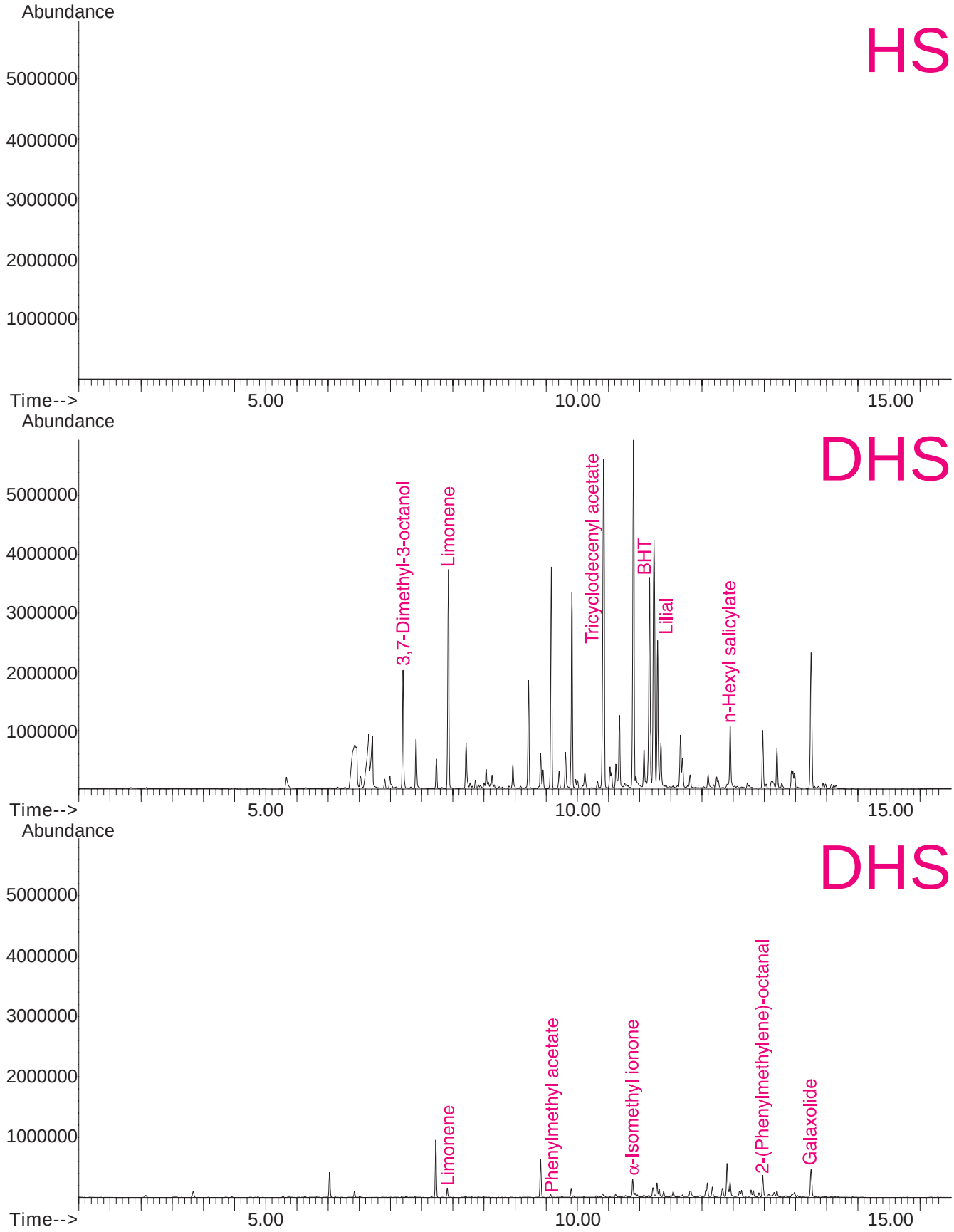

Figure 8. Total ion chromatograms of HS (top) and DHS (middle) of new and DHS (bottom) of used dryer sheet.

Figure 9, shows the TIC for a carnation heated to 60°C, and extracted for 30 minutes at a flow rate of 25 mL/min.

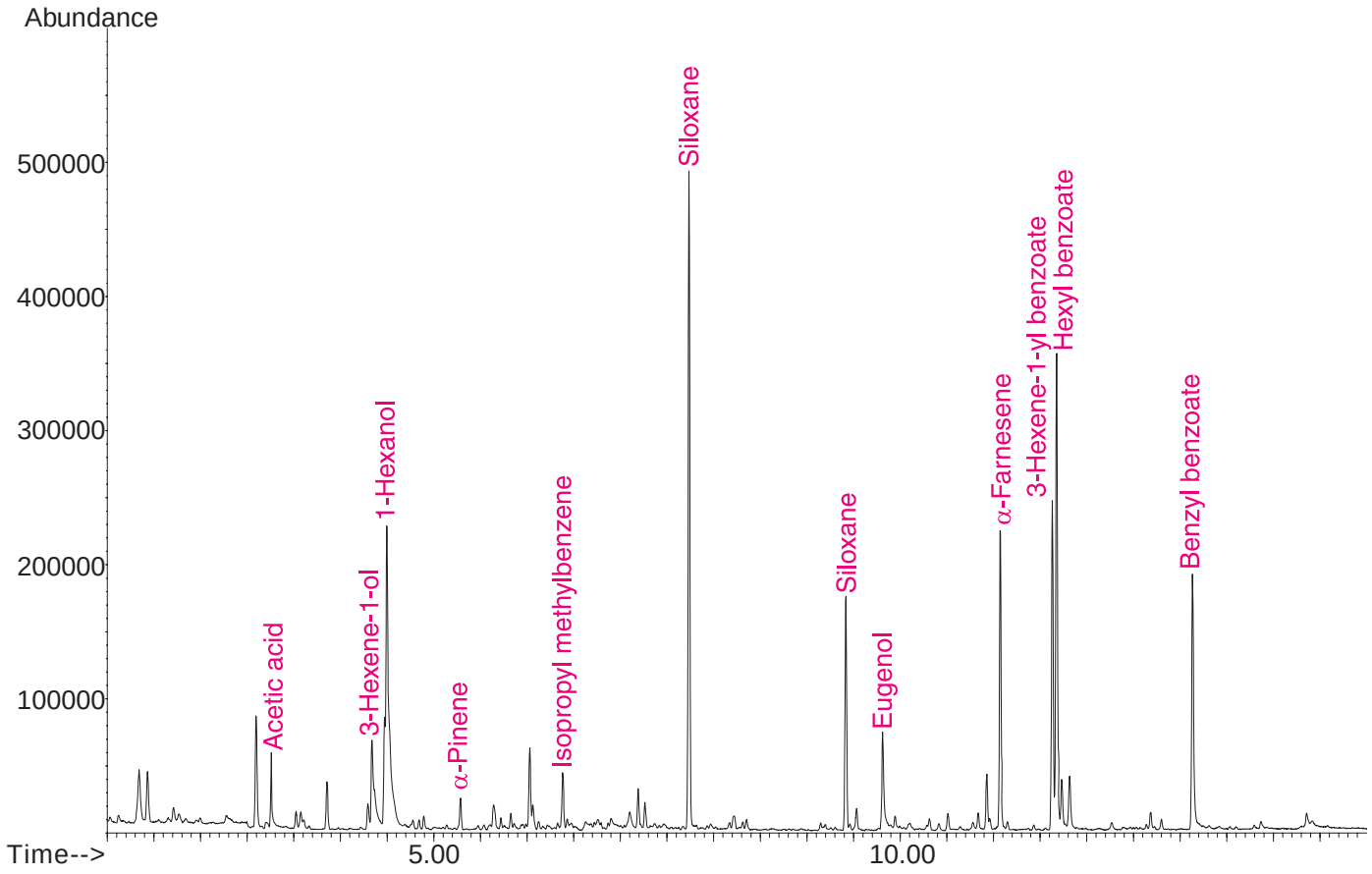

Figure 9. Total ion chromatograms of DHS extract of carnation.

Conclusions

The new GERSTEL Dynamic Headspace Module provides a simple and reliable tool for analysts to concentrate low levels of analytes from solid or liquid matrices. It is fully automated for standard 10 and 20 mL vials. Carry-over is minimized or eliminated by the ability to change traps for each sample. A wide variety of trapping materials are available including carbon based adsorbents, Tenax TA, and PDMS foam. The DHS module can provide higher sensitivity relative to other extraction techniques with equivalent precision. A prototype DHS module for extraction of large samples further expands the range of this technique.

References

[1] B.Kolb and L.S.Ettre, Static Headspace Gas Chromatography, Wiley-VCH, Inc., New York, 1997.

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