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Qualitative Analysis of a Finished Personal Care Product using the GERSTEL MultiPurpose Sampler MPS configured with Multiple Sample Introduction Techniques

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KEYWORDS

ABSTRACT

This study shows the analysis of a commercially available personal care product using the GERSTEL MultiPurpose Sampler (MPS) configured with Thermal Desorption Unit (TDU), Cooled Injection System (CIS) PTV-type inlet, Dynamic Headspace (DHS) and pyrolysis (PYRO) modules in combination with a GC/MS system. Information regarding product composition can be obtained from the chromatographic profiles obtained from one analysis system using a variety of sample introduction techniques.

INTRODUCTION

The GERSTEL MultiPurpose Sampler (MPS) in combination with the GERSTEL Thermal Desorption Unit (TDU) and a programmable temperature vaporizer (PTV) inlet, the GERSTEL CIS 4, provides the user with a multitude of analytical options to utilize for sample analysis. When combining a standard MPS with a CIS 4 inlet, the available techniques include: Liquid and large volume injection (LVI), solid phase micro-extraction (SPME), and static headspace (HS) analysis. When the TDU is added, the list is expanded to

include thermal desorption, thermal extraction, and Stir Bar Sorptive Extraction (SBSE) using the GERSTEL Twister™. Other available options for the MPS include Dynamic Headspace (DHS) and a pyrolysis module, the GERSTEL PYRO. Interchanging the modes of operation of the MPS requires minimal effort, which means that the analyst can take full advantage of the information each technique has to offer when analyzing a particular sample. In addition, the quick change between analysis techniques makes it easier to adapt to changing requirements in the laboratory.

This study describes the use of the GERSTEL MPS with CIS, TDU, DHS, and PYRO for the analysis of a finished personal care product. The product used for this study was a hair heat defense mist.

EXPERIMENTAL

Instrumentation. Analyses were performed on a 7890 equipped with a 5975C Inert XL MSD with triple axis detector (Agilent Technologies), PTV inlet (CIS 4, GERSTEL), Thermal desorber (TDU, GERSTEL), Automated Pyrolyzer (TDU Pyro, GERSTEL) and MPS robotic sampler with 10 uL ATEX syringe (GERSTEL). The equipment is shown in the figure below.

Figure 1. GC/MS system used for automation of all sample introduction techniques.

Analysis conditions pyrolysis.

Time:	Lead: 0.1 min
	Follow up: 0.5 min
	Initial: 0.15 min
Init. Temp.:	350°C;
Rate:	350, 500, or 650°C/s;
Final Temp.:	350, 500, or 650°C
TDU:	splitless
	40°C (0 min); 720°C/min;
	250°C (0.75 min)

Analysis conditions thermal extraction.

TDU:	splitless
	40°C (5 min)

Analysis conditions dynamic headspace DHS.

Trap:	Tenax TA
DHS:	25°C trap temperature
	110°C incubation temperature (2 min)
	300 mL purge volume
	50 mL/min purge flow
	10 mL dry volume
	5 mL/min dry flow
TDU:	solvent venting
	50°C (3 min); 720°C/min;
	280°C (3 min)

Analysis conditions Twister.

TDU:	splitless
	40°C (0 min); 720°C/min;
	280°C (3 min)

Analysis conditions.

CIS:	solvent vent (50 mL/min)
	split 30:1 (pyrolysis 100:1)
	-120°C; 12°C/s; 280°C (3 min)
Column:	30 m Rxi-5Sil (Restek)
	d_i = 0.25 mm d_f = 0.25 μm
Pneumatics:	He, constant flow = 1.0 mL/min
Oven:	40°C (1 min); 10°C/min;
	300°C (3 min)
MSD:	Scan, 50 - 500 amu

Analysis conditions thermal extraction.

TDU:	splitless
	40°C (5 min)

Sample Preparation

Pyrolysis. One to three milligrams of sample were weighed into a short, quartz test–tube-shaped pyrolysis vessel. The quartz tubes used were connected to TDU pyrolysis transport adapters and placed into a 98 position pyrolysis tray.

Direct Thermal Extraction. A 17 mg sample was weighed into a TDU micro-vial. The micro-vial was placed in an empty TDU tube, which was capped with a transport adapter and placed into a 98 position VT-98t tray.

Dynamic Headspace Analysis. A 17 mg sample was weighed into a 20 mL screw cap vial, which was then capped and placed into a VT-32-20 tray.

Twister. A 60 mg sample was weighed into a 10 mL screw cap vial. The sample was diluted with 10 mL of bottled water. A Twister™ stir bar was placed in the vial, which was then capped. The sample was extracted for 1 hour at a speed of 1200 rpm. After extraction, the Twister was removed from the sample, rinsed with water, dried, and placed in an empty TDU tube. The TDU tube was capped with a transport adapter and placed into a 98 position VT-98t tray.

Headspace Sorptive Extraction (HSSE). A 60 mg sample was weighed into a 20 mL crimp cap vial. An HSSE insert with a Twister was placed in the vial and the vial was capped. The sample was extracted for 1 hour at 40°C at an agitator speed of 500 rpm in the MPS agitator. After extraction, the vial was de-capped, and the Twister was removed from the sample and placed in an empty TDU tube. The tube was capped with a transport adapter and placed into a 98 position VT-98t tray.

RESULTS AND DISCUSSION

Pyrolysis. The new PYRO pyrolysis module for the TDU is an option that enables automated pyrolysis in combination with the GERSTEL MPS . Samples can be heated to user-selectable temperatures up to 1000°C. Pyrolysis GC/MS can provide information regarding polymers, additives, and other compounds contained in the sample.

In figure 2, three pyrograms obtained after pyrolysis at 350, 600, and 750°C respectively of the hair mist sample are shown. The pyrogram obtained at the lowest temperature shows siloxanes and other compounds, most likely associated with the fragrance used in the product. At 750°C, secondary pyrolysis products, such as benzene, toluene, styrene, indene, and naphthalene are formed, indicating that the pyrolysis temperature is too high. The best pyrolysis temperature, of the three utilized for this sample, is 600°C.

In the resulting pyrogram, 1-vinyl-2-pyrrolidinone and 2-pyrrolidinone are seen from the VA/VP copolymer listed as one of the ingredients in this product. Siloxanes which dominate the pyrogram are produced from several of the listed ingredients including Dimethiconol, Dimethiconol/Silsequioxone copolymer, and PEG/PPG-20/15 Dimethicone. Extracted Ion Chromatograms at m/z = 45 amu show a series of ethoxyethanol peaks, which indicate the presence of polyethylene glycol in the formulation. The peak shape for these compounds could be enhanced by performing derivatization pyrolysis GC/MS. A series of C6-C10 alkane/alkene pairs were also observed in this study.
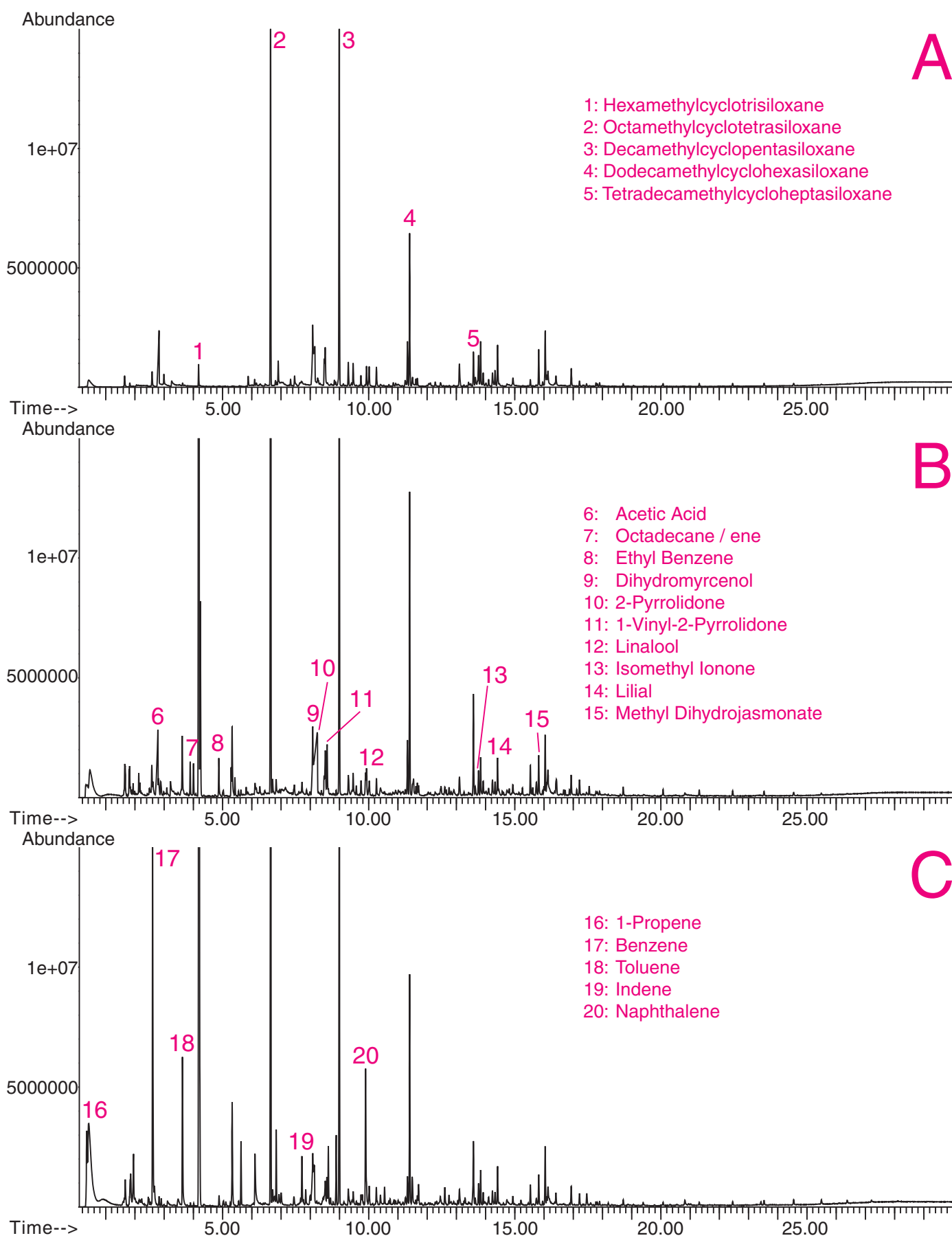
Figure 2. Stacked View of Pyrograms resulting from pyrolysis at 350 (A), 600 (B), and 750°C (C).

Direct Thermal Extraction. Direct thermal extraction of solid or liquid samples can easily be accomplished with the TDU. Sample sizes typically range from 10-50 mg. Liquid or solid samples can be loaded into TDU μ-vials, which are typically used as disposable sample containers. The μ-vials have a volume of 250 μL. Solid samples can also be placed in fritted TDU tubes, enabling the analysis of larger sample amounts. Samples can be heated up to 350°C in the TDU.

For this study, approximately 17 mg of sample was weighed into a micro-vial. The sample was extracted at 40°C for 5 minutes with a flow of 50 mL/min across the tube. Analytes were trapped in the CIS 4 inlet at -120°C in a liner packed with quartz wool. A low extraction temperature was used to avoid driving too much water into the inlet since this could cause freezing. In figure 3, the resulting chromatogram is shown. This approach yields a fairly clean chromatographic profile of the volatiles given off from the sample without too much interference. Octamethylcyclotetrasiloxane is the largest peak. Given the low temperature used for the extraction, it is reasonable to assume that this compound is present in the formulation and is not just a product of pyrolysis, as indicated above.
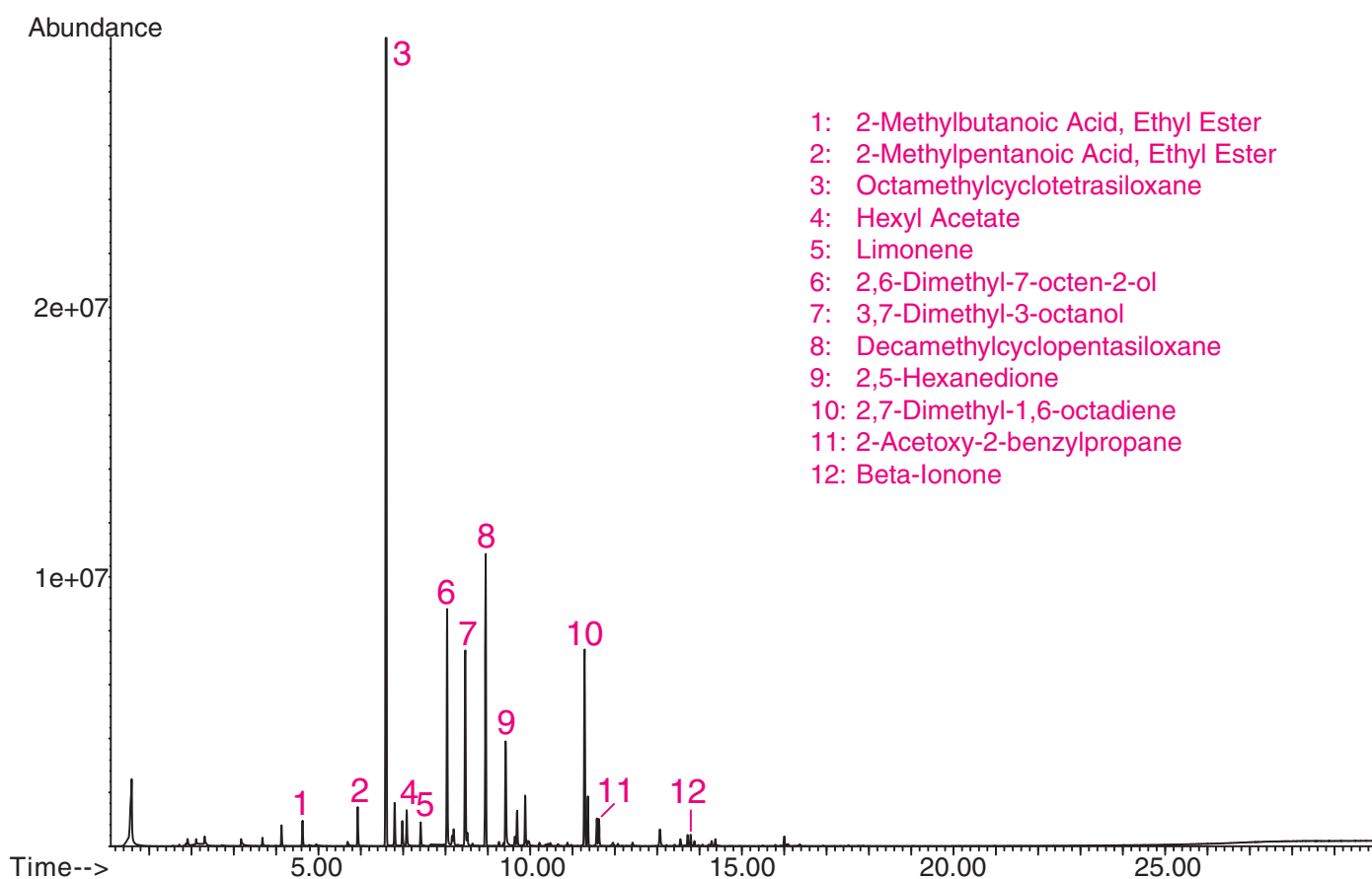

1: 2-Methylbutanoic Acid, Ethyl Ester
2: 2-Methylpentanoic Acid, Ethyl Ester
3: Octamethylcyclotetrasiloxane
4: Hexyl Acetate
5: Limonene
6: 2,6-Dimethyl-7-octen-2-ol
7: 3,7-Dimethyl-3-octanol
8: Decamethylcyclopentasiloxane
9: 2,5-Hexanedione
10: 2,7-Dimethyl-1,6-octadiene
11: 2-Acetoxy-2-benzylpropane
12: Beta-Ionone

Figure 3. Total Ion Chromatogram resulting from Direct Thermal Extraction.

Twister HSSE. Headspace sorptive extraction (HSSE) is a technique used for the analysis of volatiles above a solid or liquid sample in a closed container. A Twister is suspended above the sample. The temperature, time and agitator speed used for the extraction can be varied. One advantage of this technique over headspace SPME is the higher capacity of the Twister stir bar, which typically results in increased sensitivity.

For this study, approximately 60 mg of sample was placed in a 20 mL vial. A Twister was suspended in the headspace above the sample for 60 minutes at 40°C in the MPS agitator with the agitator speed set to 500 rpm. The resulting chromatogram is shown in Figure 4 (Top), the peaks are identified in Table 1. HSSE results in a much more complex chromatogram than direct thermal extraction. Many of the compounds identified in the HSSE chromatogram are associated with the fragrance used in this product.
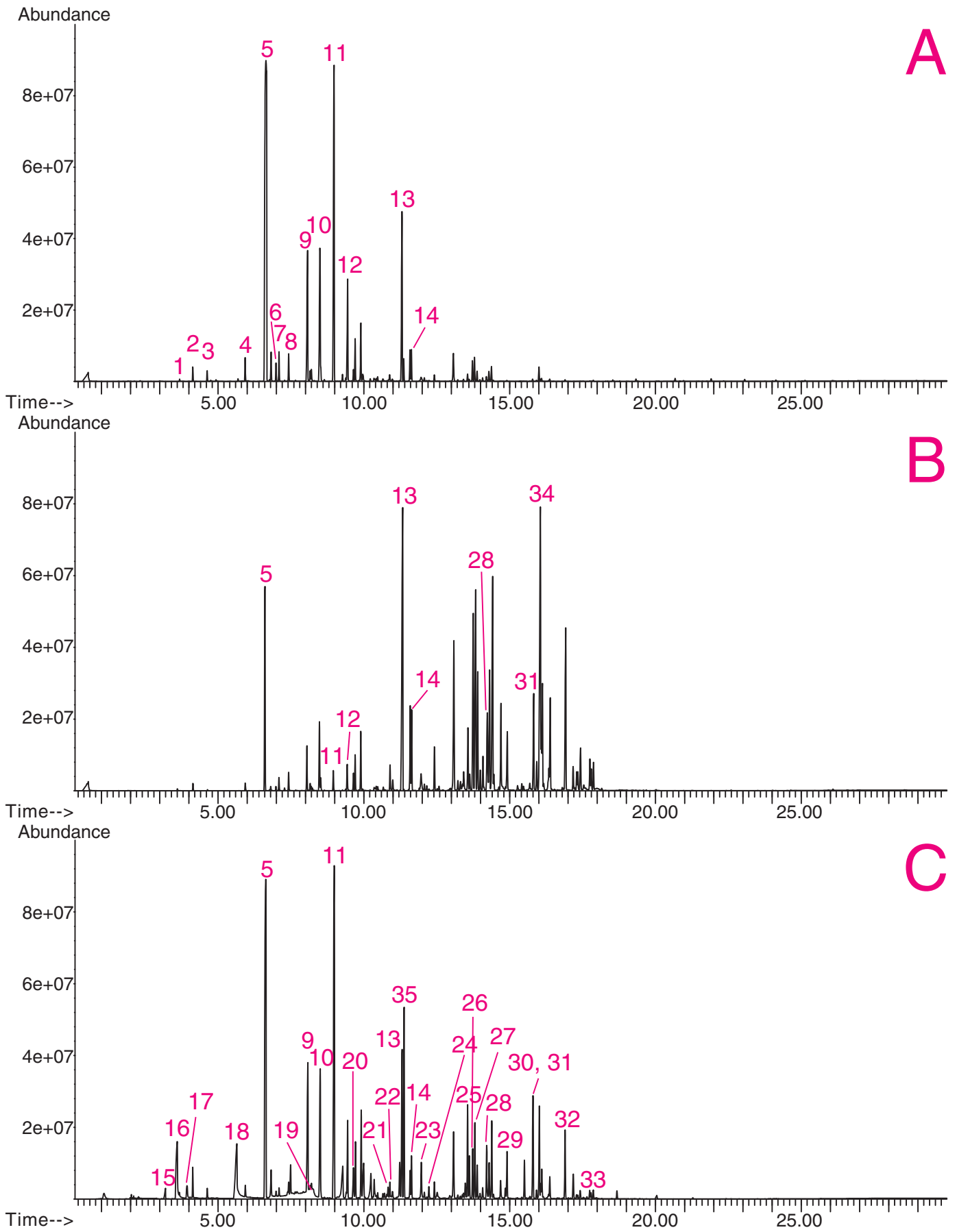
Figure 4. Stacked View of Total Ion Chromatograms obtained from HSSE- (A), SBSE- (B) and DHS- (C) analysis of the sample.

Table 1. Peak identities for figure 4.

Peak #	Identification	Peak #	Identification
1	2-Methylbutanoic acid, methyl ester	19	1,2,3-Propanetriol
2	Hexamethylcyclotrisiloxane	20	2-Methyl-3(2H)-isothiazolone
3	2-Methylbutanoic acid, ethyl ester	21	Gamma-Octalactone
4	2-Methylpentanoic acid, methyl ester	22	4-Methoxybenzaldehyde
5	Octamethylcyclotetrasiloxane	23	Piperonal
6	3-Hexen-1-ol, acetate	24	Gamma-Nonalactone
7	Hexyl acetate	25	Tetradecamethylcycloheptasiloxane
8	Limonene	26	Gamma-Decalactone
9	2,6-Dimethyl-7-octen-2-ol	27	Beta-Ionone
10	3,6-Dimethyl-3-octanol	28	Phenoxyethyl isobutyrate
11	Decamethylcyclopentasiloxane	29	Gamma-Undecalactone
12	Benzyl acetate	30	Ethyl citrate
13	4-t-Butylcyclohexyl acetate	31	Dihydromethyljasmonate
14	2-Acetoxy-2-benzylpropane	32	2-(Phenylmethylene)-octanol
15	Acetic Acid	33	Hexadecadienal isomers
16	Trimethylfluorosilane	34	2,4-di-t-Amylphenol
17	1,2-Propanediol	35	Dodecamethylcyclohexasiloxane
18	Methoxyphenyl oxime		

Twister SBSE. Stir bar sorptive extraction (SBSE) relies on the GERSTEL Twister, a PDMS coated magnetic stir bar that is used to extract analytes from a liquid sample into the PDMS phase while stirring the sample. Following the extraction step, the Twister is removed, rinsed with water, dried, and the analytes are transferred to the GC/MS system using thermal desorption. The recovery of analytes from aqueous solutions can be predicted based on their octanol/water partition coefficients.

For this study, approximately 60 mg of sample was diluted with 10 mL water. A Twister stir bar was added and the sample extracted at room temperature for 1 hour at 1200 rpm. The stir bar was thermally desorbed in the TDU and the analytes transferred to the GC/MS. The resulting chromatogram is shown in figure 4 (B). Compared with HSSE, the SBSE technique results in much better recovery of semi-volatile organic compounds (SVOCs), as one would expect. Among the SVOCs seen in the SBSE chromatogram are long chain alcohols and substituted phenols. In figure 5, an overlay of 2 replicates is shown, illustrating the excellent precision, which can be achieved using the SBSE technique.
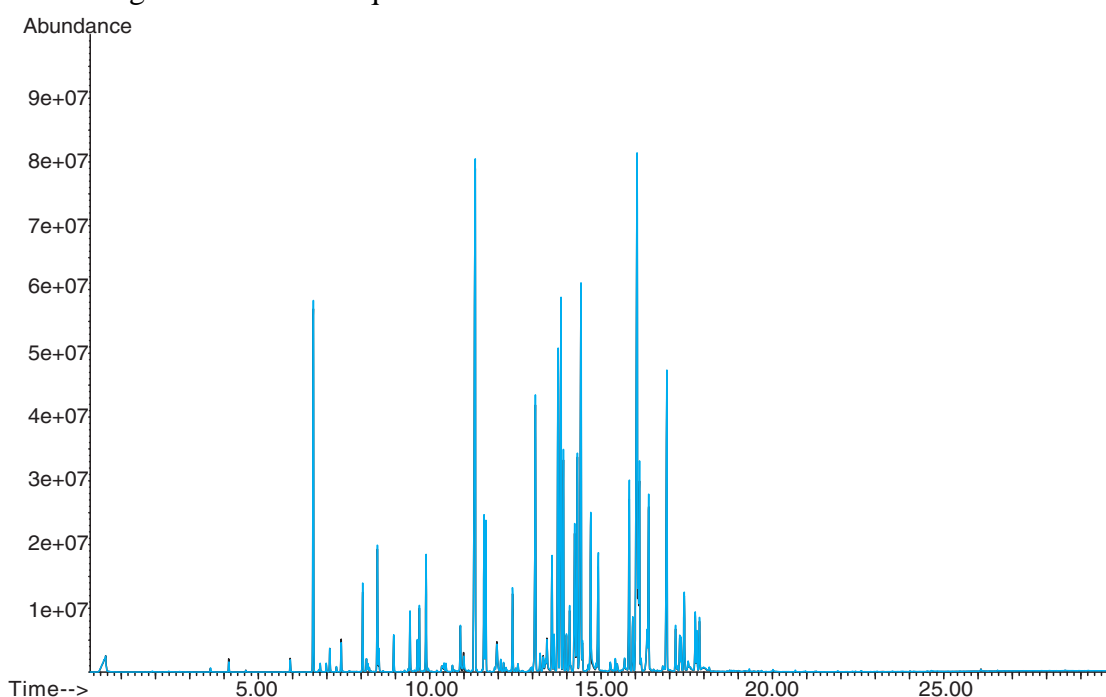
Figure 5. Overlay chromatograms from two individual SBSE extractions.

The heated zone of the TDU is large enough to accommodate 2 Twisters in each TDU liner. This means that Twisters from HSSE and SBSE of the same sample can be combined in a single GC/MS run to give a more complete picture of the composition of the sample across the volatility range from VOC to SVOC. In the GERSTEL MAESTRO software, multi-desorption mode can be selected and multiple tubes desorbed for a single GC/MS run, resulting in enhanced sensitivity. The same or two different sets of desorption conditions can be used.

Dynamic Headspace Analysis. Dynamic Headspace (DHS) is a technique used to extract and concentrate VOCs from liquid or solid samples placed in standard headspace vials. The headspace above the sample is purged and analytes are concentrated on a replaceable, user selectable adsorbent-filled trap. Analytes are subsequently introduced into the GC/MS system by thermal desorption of the trap in a GERSTEL TDU.

Tenax-TA® was the adsorbent material chosen for this study. Carboxen® and Carbotrap® filled tubes are also available. The Full Evaporation Technique (FET[1,2]) combined with DHS was used for the analysis: A small amount of liquid sample is placed in a sealed headspace vial. The vial is then heated above the boiling point of the solvent, which is fully evaporated. This means that volatile compounds are quantitatively transferred to the vapor phase independent of their solubility in the liquid phase since there is no liquid phase left. The headspace of the vial is then purged with inert gas and analytes are swept onto an adsorbent trap. Non-volatile residue is left at the bottom of the vial and discarded with the used vial when the extraction has been completed.

In figure 4 (C) a chromatogram resulting from a FET-DHS extraction of the sample is shown. Compared with HSSE and SBSE, DHS results in better sensitivity for volatile compounds, especially for highly water soluble VOCs. As an example, the methoxyphenyloxime peak at retention time 3.6 minutes is clearly larger in the FET-DHS chromatogram. The SVOC peaks, however, are not as large as those seen in the SBSE chromatogram, but late eluters, such as the hexadecadienal isomers at retention time 17.5-18.0 minutes, are clearly identified. Another peak of interest in the FET–DHS-GC/MS chromatogram at retention time 9.6 minutes is methylisothiazolinone. This compound is listed in the ingredients for the product and is typically added as a biocide. The octanol/water partition coefficient for this compound is -0.83, which means it is highly soluble in water. It is therefore no surprise that the compound is not found in the SBSE and HSSE chromatograms.

CONCLUSIONS

The GERSTEL MPS/TDU/CIS-GC/MS combination provides a versatile platform for sample analysis. Several techniques can be applied quickly to the analysis of a sample in order to provide the necessary data for R&D, quality control, troubleshooting, or competitive analysis. The addition of a DHS or PYRO module can provide additional, complimentary data. With the appropriate use of standards, any of the above techniques can be used for quantitative analysis.

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