GERSTEL Application Note No. **202**, *2019*

Analysis of Food Samples using Thin Film Solid Phase Microextraction (TF-SPME) and Thermal Desorption GC/MS

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Keywords

Thin Film Solid Phase Micro-Extraction (TF-SPME), Gas Chromatography, Mass Spectrometry, Flavor Compounds

Abstract

Food products are routinely monitored for quality, authenticity, and safety. Analysis of food products may also be necessary due to off flavor or odor complaints. The aroma and flavor profiles of each product are unique and made up from a variety of semi-volatile and volatile compounds including aldehydes, ketones, acids, alcohols, terpenes, esters and other trace level components. The wide range of concentrations, polarities, and functional groups used in the composition of a flavor/aroma profile can make the analysis of the sample difficult. Techniques which are simple, use little or no solvent and encompass a wide range of analytes are desirable.

TF-SPME is an extension of regular SPME. It is more sensitive than regular SPME due to the increased surface area and phase volume, both of which lead to improved analyte recovery. The TF-SPME device is a 20 mm x 4.8 mm carbon mesh sheet impregnated with a sorptive phase. The TF-SPME devices can be used in headspace or immersive mode.

In headspace mode, the TF-SPME device is suspended above a solid or liquid sample inside a sealed sample vial. In immersive mode, it is placed directly in a liquid sample. In both cases, the sample is agitated by stirring. After extraction, the devices are blotted dry and placed in an empty thermal desorption tube. They are then analyzed by thermal desorption GC/MS, a technique that is easy to automate, simple to use and requires no solvent.

The work presented here demonstrates the application of Thin Film Solid Phase Microextraction (TF-SPME) to the determination of aroma and flavor components in a variety of high fat food products.

Introduction

The GERSTEL Multipurpose Sampler (MPS) in combination with the GERSTEL Thermal Desorption Unit (TDU 2) and programmable temperature vaporizer (PTV) inlet (CIS 4) provides the user with a multitude of analytical options to utilize for chemical analysis. This study describes the use of the GERSTEL MPS in combination with a CIS 4 inlet and TDU for automated thermal desorption of TF-SPME devices with a divinylbenzene/polydimethylsiloxane coating (DVB/PDMS) that have been used to extract flavor components from a variety of food samples. Among these are: blue cheese, dark chocolate, Caesar dressing, and strawberry cream cheese. Monitoring of key flavor components is important for quality control and product development of foods. Identification of off-aromas can help pinpoint and find a remedy for product defects.

Experimental

Instrumentation

Agilent 7890A GC / 5977B MSD
GERSTEL MPS, TDU 2 & CIS 4

Analysis conditions

TDU:	splitless
	40°C (0.5 min); 720°C/min;
	280°C (3 min)
PTV:	solvent vent (50 mL/min), split 5:1
	-150°C; 12°C/sec; 280°C (3 min)

Dark chocolate:

Pneumatics:	He, constant flow, 1 mL/min
Column:	30 m Rxi-5Sil MS (Restek)
	d_i = 0.25 mm d_f = 0.25 µm
Oven:	40°C (3 min); 7°C/min; 280°C (3 min)

Other samples:

Pneumatics:	He, constant pressure, 336 kPa
Column:	30 m DB-Wax (Agilent)
	d_i = 0.25 mm d_f = 0.25 µm
Oven:	40°C (1 min); 10°C/min; 230°C (5 min)

Sample Preparation. All analyzed food products were purchased at a local store. A 2.0 g aliquot of each sample was weighed and placed in an empty 20 mL screw cap vial. A TF-SPME device was suspended in the headspace of the vial. The vial was placed into the GERSTEL agitator/stirrer and extracted at 40°C for 3 hours at 250-500 rpm agitation speed. The strawberry cream cheese sample was also extracted at room temperature (25°C) for 15 hours.

Results and Discussion

All food samples, apart from dark chocolate, were separated using a DB WAX column. The dark chocolate food sample was separated used a Rxi-5Sil MS column.

Dark Chocolate. TF-SPME was applied to the headspace of the dark chocolate sample. Figure 1 shows the resulting total ion chromatogram with identified peaks labeled. A wide variety of volatile and semi volatile flavor compounds were observed including pyrazines, esters, alcohols, acids, aldehydes, ketones, furans, etc. Several pyrazine compounds, which impart important cocoa/nutty flavors to the chocolate, were observed: 2,5-dimethyl-2-(3-methylbutyl)-pyrazine, 3-ethyl-2,5-dimethyl-pyrazine, tetramethyl pyrazine (roasty note) and 2,3,5-trimethyl-6-ethylpyrazine. Other key aroma compounds present in large quantities include acetic acid, isovaleraldehyde, 2-methylbutyraldehyde, 2,3-butandiol, tetrahydrofurfuryl alcohol and alpha-pinene.

The results show that TF-SPME is a highly useful technique for assessing off-aromas or quality defects in dark chocolate with very little sample preparation.

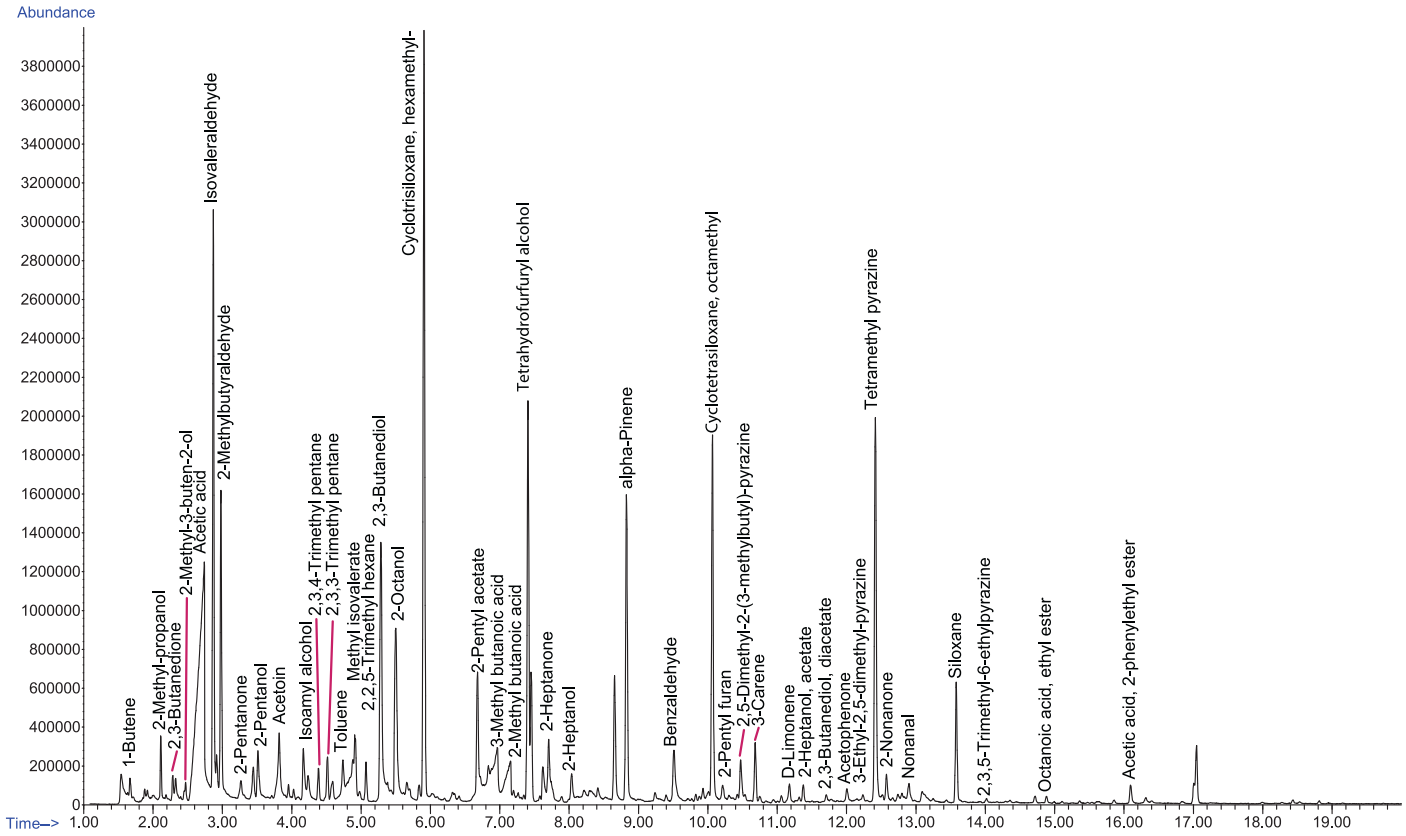

Figure 1. Total Ion Chromatogram resulting from Thin Film Solid Phase Microextraction of Dark Chocolate.

Blue Cheese. TF-SPME was applied to the headspace of a blue cheese sample. Figure 2 shows the resulting total ion chromatogram with identified peaks labeled. A wide variety of compound types were observed including aldehydes, alcohols, esters, acids and phenols. The predominant compounds are 2-pentanone, 2-heptanone and 2-nonanone, which are metabolites formed by Penicillium mold. These methyl ketones are responsible for the characteristic flavor of mold-ripened cheese. Other flavor compounds that were observed in the chromatogram include the secondary alcohols 2-pentanol, 2-heptanol, 2-nonanol, as well as the fatty acids butanoic acid, hexanoic acid, octanoic acid, nonanoic acid and n-decanoic acid. These results show that TF-SPME is a highly useful technique for assessing aroma compounds in blue cheese.

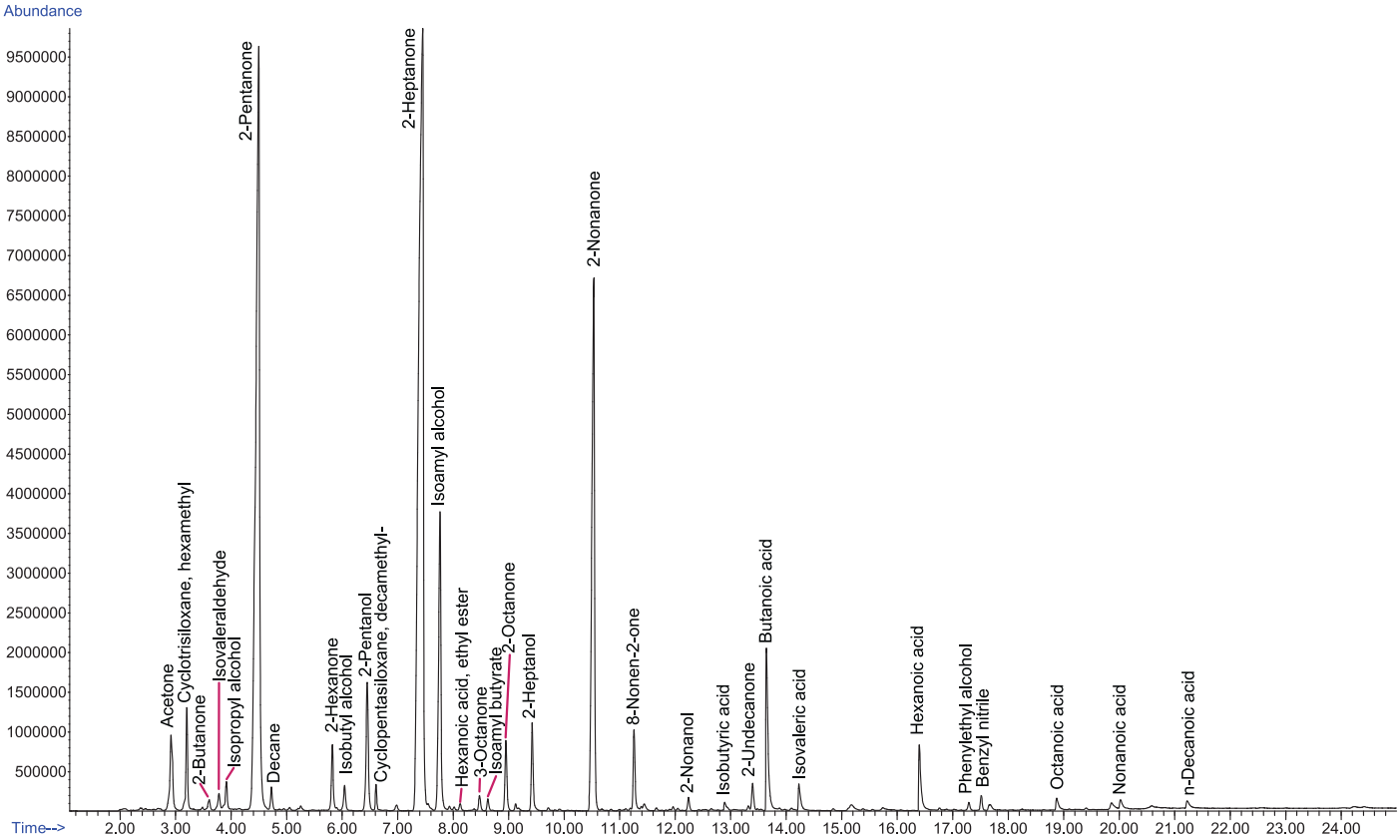

Figure 2. Total Ion Chromatogram resulting from Thin Film Solid Phase Microextraction of Blue Cheese.

Caesar Dressing. TF-SPME was applied to the headspace of a Caesar dressing sample. Figure 3 shows the resulting total ion chromatogram with identified peaks labeled. A wide variety of compounds were observed including terpenes/terpenoids, alcohols, acids and aldehydes. The predominant compounds are sorbic acid, which is a food preservative and ethyl acetate, a solvent used for flavors. A wide variety of terpenes and terpenoids are also found in the chromatogram, due to the presence of black pepper in the dressing. These include pinene, limonene, phellandrene, and caryophyllene, key aroma compounds found in the outer fruit layer of black pepper. Fatty acids such as butanoic acid, hexanoic acid, heptanoic acid, octanoic acid and n-decanoic acid are also present, likely due to the presence of parmesan and Romano cheese listed as ingredients in the dressing. These results show that TF-SPME is a highly useful technique for assessing off-aroma and quality defects in dressing samples.

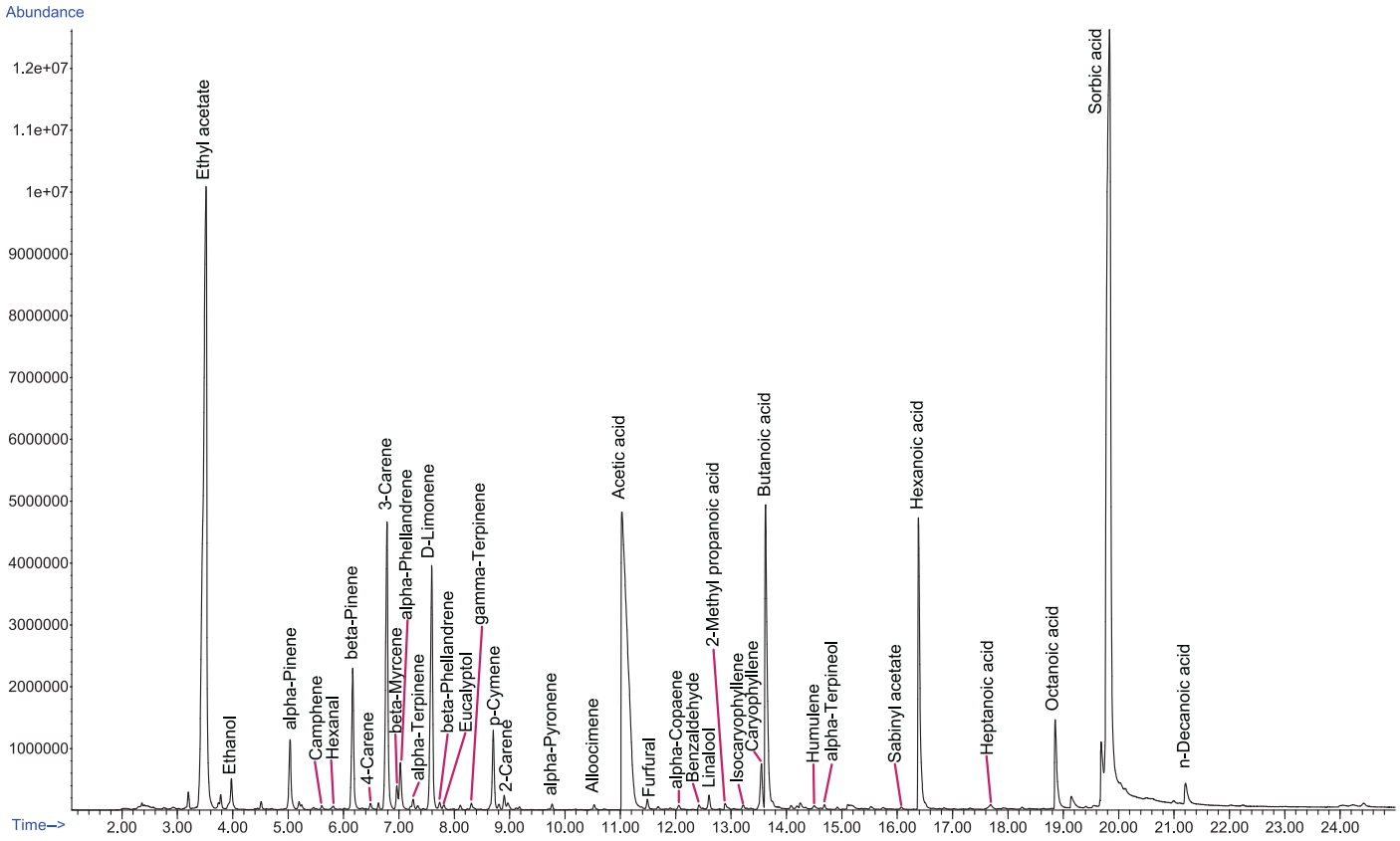

Figure 3. Total Ion Chromatogram resulting from Thin Film Solid Phase Microextraction of Blue Cheese.

Strawberry Cream Cheese. TF-SPME was applied to the headspace of a strawberry flavored cream cheese sample. Figure 4 shows a chromatogram resulting from an extraction at 25°C that lasted 16 hours. A wide variety of compounds were observed including alcohols, esters, aldehydes, acids, furans, and lactones. The largest peaks in the chromatogram were identified as ethyl acetate, a flavor solvent; ethyl butyrate, a commonly used artificial flavoring for fruit-flavored foods; ethyl 2-methyl butyrate, a fruity flavoring agent; and acetoin, a food flavoring agent with a pleasant, buttery aroma.

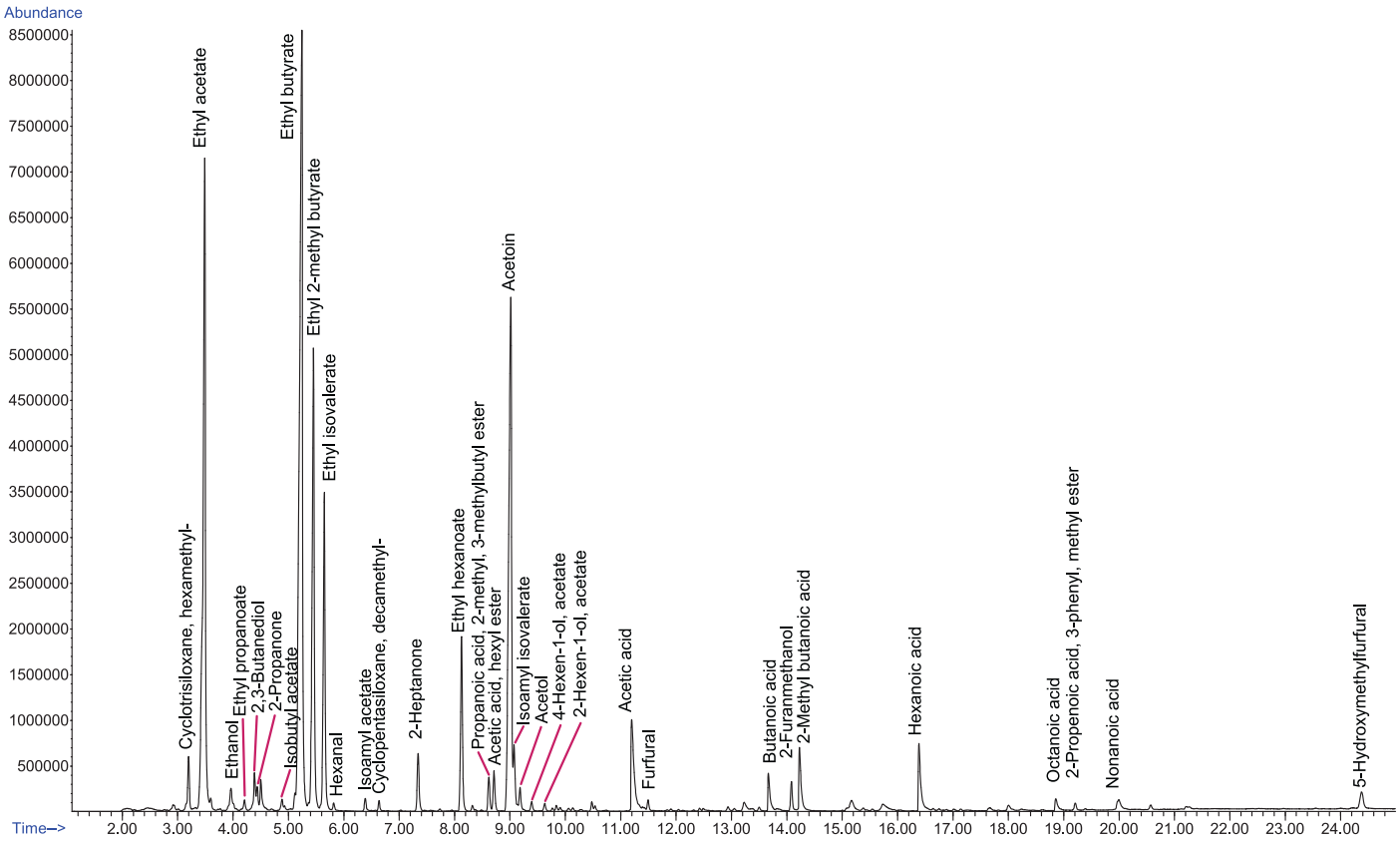

Figure 4. Total Ion Chromatogram resulting from Thin Film Solid Phase Microextraction of Strawberry Flavored Cream Cheese, extraction at 25°C for 15 hours.

Figure 5 shows the resulting chromatogram following extraction at 40°C for 3 hours. This chromatogram showed an increase in peak areas corresponding to Maillard reaction products: furfural, 2-furanmethanol, maltol, 3,5-dihydroxy-6-methyl-2,3-dihydro-4H-pyran-4-one and 5-hydroxymethylfurfural. This indicates that TF-SPME is well suited for monitoring undesirable Maillard reaction products that may occur due to food processing or heating of food products, such as strawberry cream cheese.

The results show that TF-SPME is well suited for quantification as well as assessment of quality defects that may arise due to food processing or packaging, while requiring very little sample preparation.

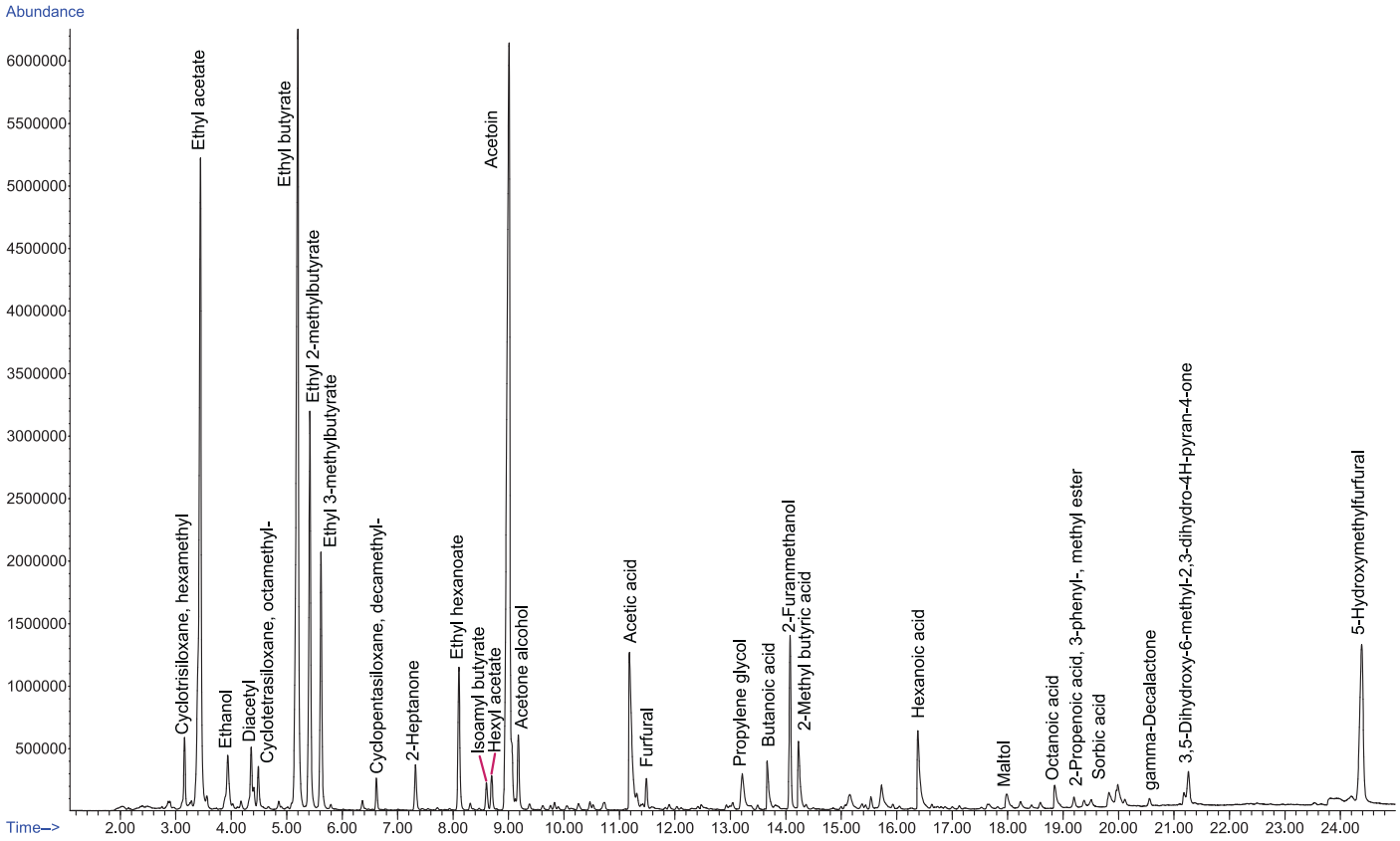

Figure 5. Total Ion Chromatogram resulting from Thin Film Solid Phase Microextraction of Strawberry Flavored Cream Cheese, extraction at 40°C for 3 hours.

Conclusions

The GERSTEL MPS/TDU/CIS provides a versatile platform for qualitative analysis of a wide variety of food products. Thin Film Solid Phase Microextraction (TF-SPME) is a robust technique that allows the user to quickly identify and quantify a wide variety of compound types in food samples. In addition to TF-SPME, the versatile GERSTEL MPS/TDU/CIS system allows several techniques to be applied quickly to the same samples, rapidly providing the necessary data for quality control, product development, troubleshooting, or competitive analysis. With the appropriate use of standards, any of the techniques can be used for quantitative analysis.

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