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Use of a Mass Spectral Based Chemical Sensor to Discriminate Food and Beverage Samples: Olive Oils and Wine as Examples

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ABSTRACT

An accurate but time consuming technique commonly used to analyze samples for quality control applications is Gas Chromatography / Mass Spectrometry (GC/MS). Although GC/MS is a well-known technique, analysis times are usually long and its output (a total ion chromatogram) can be hard to interpret. It is therefore of high interest to provide a faster screening technique that does not compromise the accuracy of results usually obtained with GC/MS. Chemical sensors are ideal for these types of applications because they provide fast chemical analysis with minimal sample preparation. In this study, a ChemSensor that incorporates well-known mass spectrometry technology with multivariate data analysis was used for two different applications.

The first application consists of the analysis of 13 different olive oils. The goal of this application was to classify unknown olive oils as degassed or pure. In order to validate the fast results obtained with the Headspace ChemSensor, traditional headspace GC/MS analyses were also performed. The second application illustrates the use of the ChemSensor to detect a compound not present in the standard samples. In this case, 2,4,6 trichloroanisole, responsible for the corky off-flavor of wine, was spiked into white wine and detected using HeadSpace (HS), Solid Phase Micro-Extraction (SPME) and Stir Bar Sorptive Extraction (SBSE) using the GERSTEL Twister.

For the olive oil application two multivariate models (KNN and SIMCA) were created and all unknown samples were correctly classified. Detection of trichloroanisole was possible at low ppm levels using HS; ppb levels using SPME and ppt levels using Twister sampling. Advantages of using the ChemSensor over traditional GC/MS analysis were faster analysis times and the option of creating customized reports that classified samples as acceptable or rejected.

INTRODUCTION

Detection and assurance of sample integrity is an everyday task performed by companies that provide food products. For example, differences in the origin of raw materials can reflect in perceived differences of the final product by the consumers. Analytical methods are commonly used to analyze food products and certify their quality. A widely used technique involves GC/MS. Although GC/MS has proven to be a reliable analytical technique, its drawbacks include long analysis times and difficult interpretation of results by inexperienced personnel.

In this study, we examine the analysis of two different food products, olive oils and wine samples by a faster technique that also results in easy to interpret results. The use of a ChemSensor retains the benefits of using mass spectrometry but speed the analysis substantially when compared to GC/MS.

The use of a headspace-mass spectrometry ChemSensor for analysis of olive oils has been previously investigated by other studies [1, 2, 3]. These investigations concluded that the mass spectral fingerprints obtained by sampling the static HS of olive oils are characteristic of the oil type and therefore could be used to determine their integrity. For example; Marcos Lorenzo et al. [1] analyzed 61 virgin olive oils of three different cultivars with the ChemSensor and also with a

conventional method in which fatty acids were measured by GC. Their results show that both techniques provided similar results but using the ChemSensor had the advantage of faster analysis times and less sample preparation.

Discrimination between degassed olive oils and pure olive oils is also important because it is used to determine oil quality.

Another food application that has been previously studied by GC/MS is the detection of Trichloroanisole (TCA) in wine samples [4]. Recently a study using HS-mass spectrometry was also published by Marti et al. [5]. In this study, they concluded that using static HS they could detect TCA levels above 100 ng/L using 5 min. runs.

The sensory threshold of TCA is above the detected level by Marti et al. [5]. A more sensitive technique that concentrates TCA prior to introduction to a GC has also been studied. Hayasaka et al. [6] concluded that using SBSE detection of TCA ranges in the part-per-trillion levels.

In this study, we examine two versions of a mass-spectral ChemSensor. For the olive oil application we used an autosampler coupled directly to a mass spectrometer. This version has the flexibility to sample not only static HS but also e.g. SPME. For the wine analysis, we analyzed the samples using the same system used for the olive oils but also a ChemSensor System that couples a thermal desorption system to a GC/MS.

EXPERIMENTAL

A. Olive oils.

Five pure olive oils, three degassed oils and five “unknown” oils were analyzed using the GERSTEL Headspace ChemSensor (Figure 1). 2 g of each oil were weighted into 10 mL vials which were crimped and equilibrated for 20 min. at 80 °C before static HS sampling. Since the ChemSensor does not use a column for a separation, the entire headspace of each sample is introduced into the MSD.



Figure 1. GERSTEL Headspace ChemSensor.

All 13 oils were also analyzed by sampling their static HS using traditional GC/MS.

B. TCA in wine.

2, 4, 6-Trichloroanisole (CAS # 87-40-1) was purchased from Aldrich. A white chardonnay wine box was locally purchased. We decided to use wine available in a box, assuming this has not been in contact with any cork material. We tested our assumption by checking the pure wine for TCA content. Using SBSE, we did not detect any TCA in the pure wine.

The pure wine was spiked with TCA at different levels depending on the sampling technique. A stock solution of TCA of 1000 ppm in Methanol was prepared and aliquots were taken to obtain the different concentrations.

TCA in wine - Static Headspace. For static HS, we spiked the pure wine with TCA at 40 and 10 ppm. 1.5 g of sodium chloride was added to all solutions, including the blank ones.

Static headspace conditions.

Incubation 80°C (20 min)
Injection 2 mL, split 10:1, at 180°C
MSD scan mode, 50-250 amu, 1.0 min runs

TCA in wine-Headspace Solid Phase MicroExtraction.

For headspace SPME, we spiked the pure wine with TCA at 40, 75 and 100 ppb. 1.5 g of sodium chloride was added to all the solutions, including the blanks.

Headspace SPME conditions.

Fiber 100µm PDMS
Equilibration 60°C (15 min)
Extraction 60°C (15 min)
Injection 0.8 min splitless, at 250°C
MSD scan mode, 50-250 amu, 1.5 min runs

TCA in wine-Stir Bar Sorptive Extraction. For SBSE, we spiked the pure wine with TCA at 40 ppb and 40 ppt.

A Twister was added to the samples and the vial was crimp capped. The sample was stirred for 90 min. at room temperature. The Twister was removed, rinsed with water, dried and placed directly in a conditioned thermal desorption tube for analysis.

Twister desorption (SBSE).

TDS 2 splitless,
20°C, 60°C/min, 250°C (5 min)
PTV 0.2 min solvent vent (50 mL/min),
split ratio 30:1 (ppb-level)
splitless (ppt-level)
-120°C, 12°C/s, 280°C (3 min)
Column: 30m HP-5 (Agilent),
 $d_i = 0.25\text{mm}$, $d_f = 0.25\mu\text{m}$
Pneumatics: He, constant flow = 1.2 mL/min
Oven: 40°C, (2 min), 10°C/min,
280°C (5 min)
MSD scan mode, 35-350 amu

RESULTS AND DISCUSSION

A. Olive oils.

Traditional total ion chromatograms (TIC) obtained by sampling the static HS of the olive oils are shown in Figure 2. Visual inspection of this figure indicates some similarities between the TICs of the degassed and pure oils. This comparison becomes more complicated when we try to analyze replicas between samples.

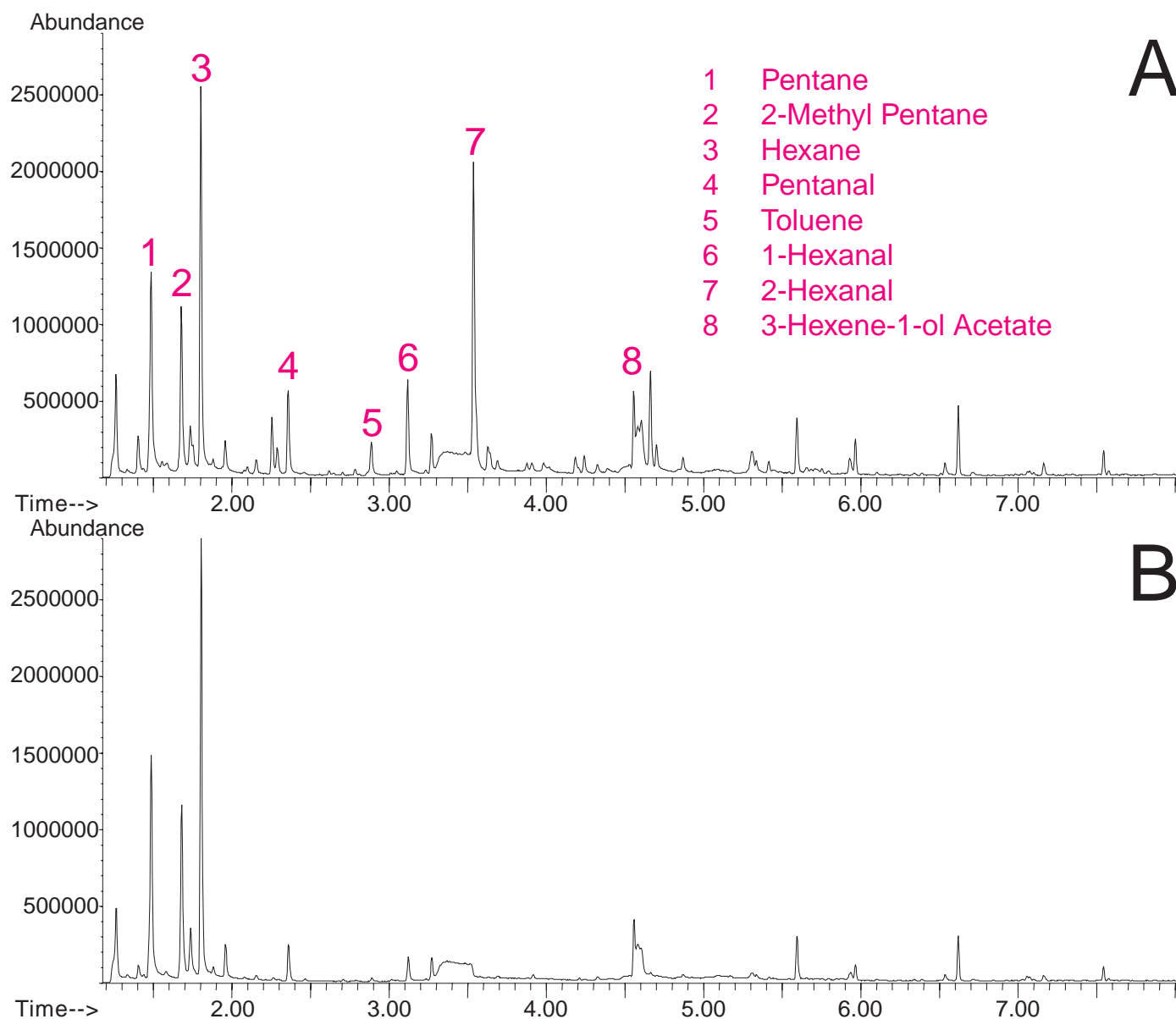


Figure 2. TIC of pure (A) and degassed (B) olive oils using traditional HS-GC/MS analysis.

After optimizing the equilibration temperature of the oils with the Headspace ChemSensor, a clear increase in sensitivity was seen when the samples were equilibrated at higher temperatures. Figure 3 shows the mass fingerprints of all 13 olive oils obtained after static HS sampling at 80 °C. A visible difference between the degassed and pure olive oils is seen at m/z 48 and 51.

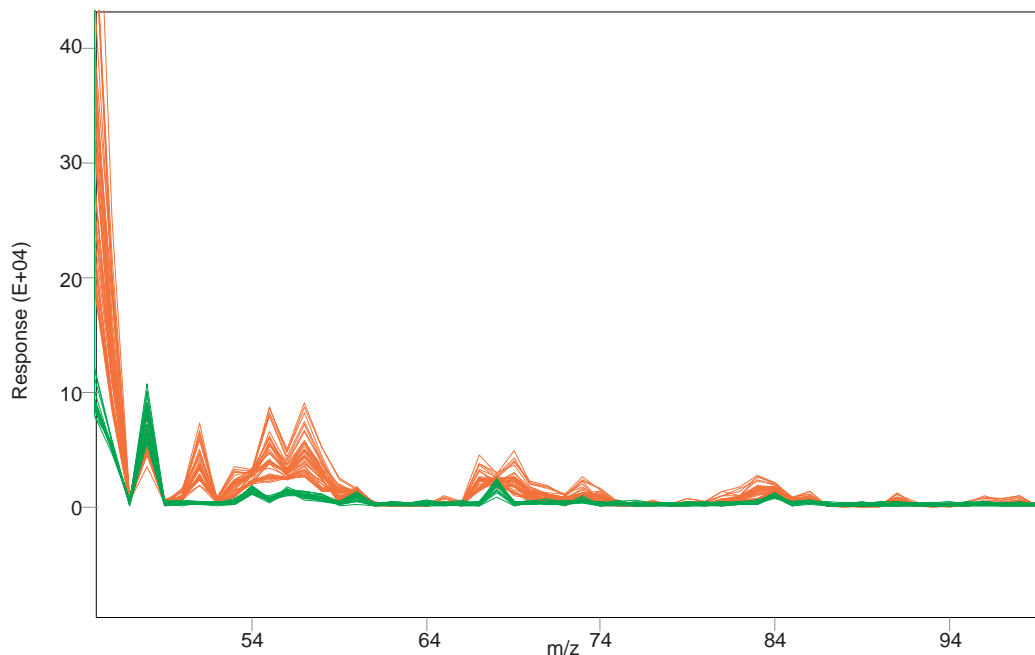


Figure 3. Lineplots of pure (orange traces) and degassed (green traces) olive oils using traditional HS-MS ChemSensor.

Figure 4 shows the projections in the space of the first three principal components. Speculation of identity of the unknown oils from inspection of Figure 4 indicates that unknowns N and E could be degassed oils and unknowns B, G and U could be pure olive oils.

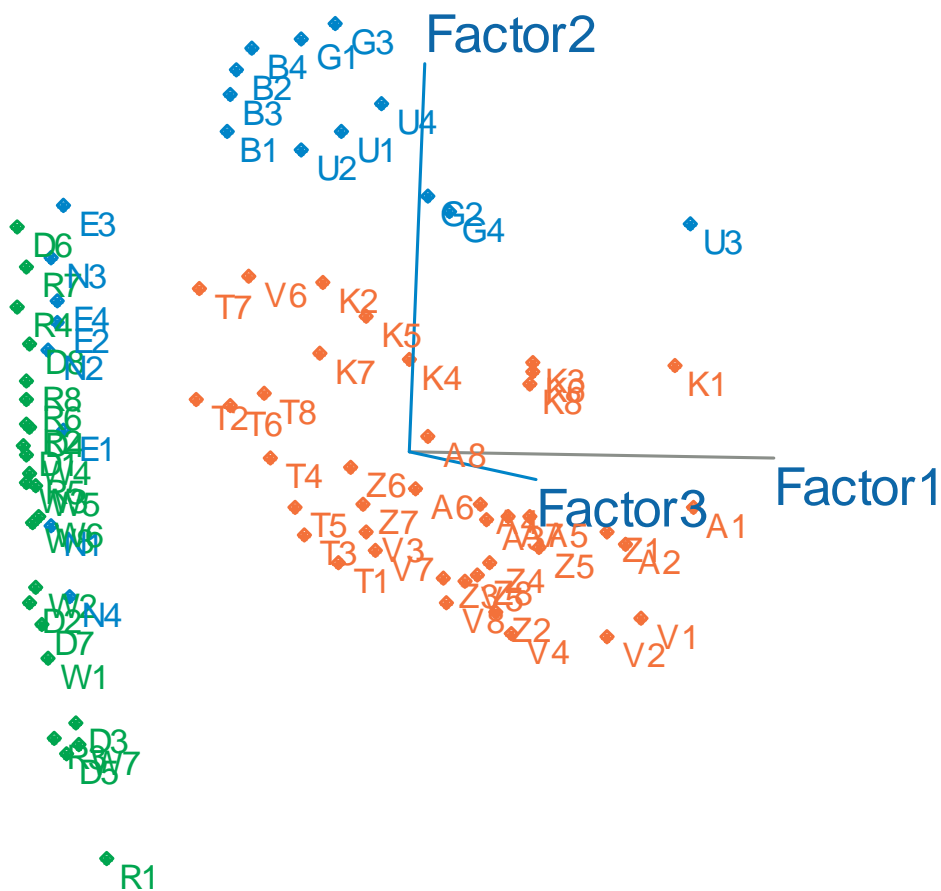


Figure 4. Projection of the mass spectral fingerprints of pure (orange), degassed (green) and unknown (blue) olive oils into the space of the first three principal components (data collected using HS-MS ChemSensor).

In order to classify the unknown oils into defined categories we used a KNN model. KNN is a model that classifies unknown samples based on their proximity to samples already placed in categories. Table 1 lists the classification of the unknown samples (four replicas each) as either degassed or pure. After this study was finished, the customer who provided the samples confirmed samples B, G, and U as olive oils and samples E and N as degassed ones. Correct classifications for all the 5 unknowns using KNN models can be obtained at 45 °C as well (data not shown).

Table 1. Classification of unknown samples.

		KNN Predicted Class	
		Olive Oils	Degassed
Sample	B	4 x	
	G	4 x	
	U	4 x	
	E		4 x
	N		4 x

B. TCA in wine.

TCA in wine - Static Headspace. Using the Gerstel ChemSensor in the HS mode, we detected TCA at the low ppm levels. Figure 5 shows the detection of TCA using the Data Analysis program of ChemStation Software (Agilent Technologies). The presence and identification of TCA was corroborated by subtracting the mass spectrum of the spiked sample (Figure 5-A) minus the spectrum of the blank wine (Figure 5-B). The resulting spectrum (Figure 5-C) was compared to the mass spectral profile of TCA (Figure 5-D) and a tentative match was obtained using the Wiley 138 mass spectral library (Match Quality = 95 %).

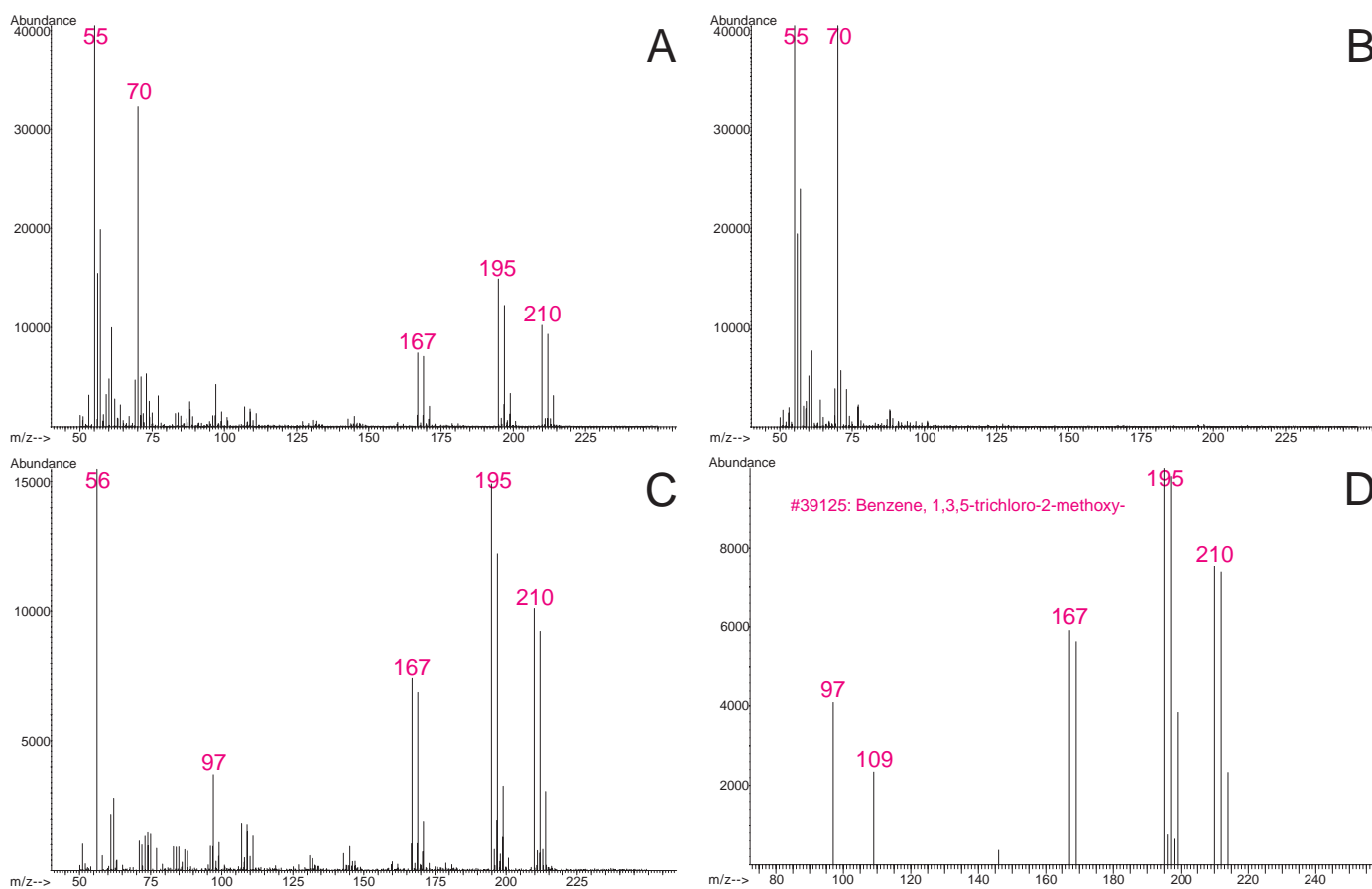


Figure 5. Detection of TCA in the 10 ppm level using the data analysis program of the ChemStation software (Agilent Technologies). A: Spiked wine; B: Blank wine; C: Spectrum obtained by subtraction of A minus B; D: TCA spectrum.

In order to estimate the level of TCA in the wine, a Partial Least Square (PLS) model was created. Figure 6 shows that with a 5 factor PLS model, good linearity is observed. Using a testing set (data not used for model construction) we obtained accurate predictions.

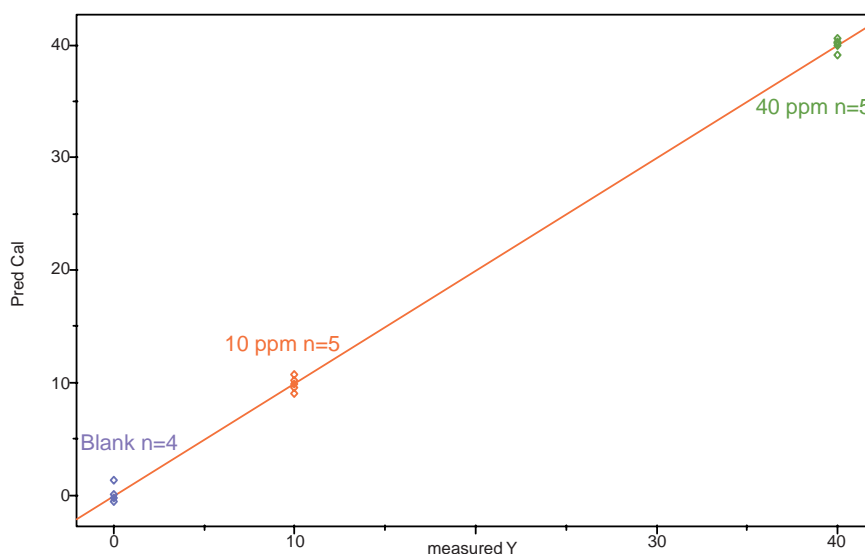


Figure 6. PLS model for HS-MS ChemSensor. Y fit obtained using 5 factors.

TCA in wine- Headspace SPME. The results obtained with static HS were encouraging at the low ppm level. We decided to explore the ChemSensor capability and examine a concentrating technique that could allow detection at the ppb level.

Previous studies using SPME to detect TCA in the ppb levels have been published. These studies used traditional GC/MS detection and therefore are time consuming; furthermore detection of TCA will still require close inspection of the data by an experienced operator. By using direct SPME coupled to an MSD, the time limitation lies in the incubation and extraction time of the samples. Detection of TCA is displayed in the computer screen as soon as samples are processed by the sensor therefore alleviating the data analysis process. Figure 7 shows the displayed report after running unknown samples in the ChemSensor prediction mode.

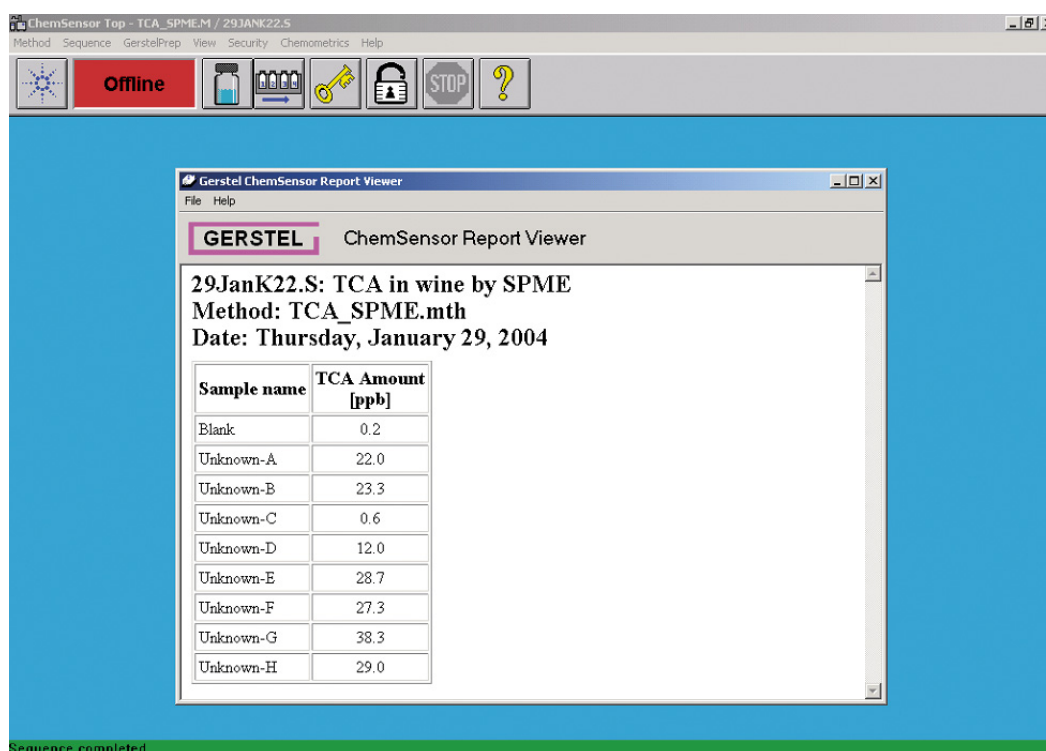


Figure 7. Customized report obtained after analysis of SPME-MS ChemSensor samples.

TCA in wine- Stir Bar Sorptive Extraction. SBSE is an enrichment technique that has also been applied to the detection of TCA in wine. We decided to use a ChemSensor System to speed the analysis and automate the data analysis report of unknown samples.

Using the ChemSensor System in the traditional GC/MS mode we were able to detect TCA at ppb and ppt levels. Figure 8 shows a TIC in which TCA elutes at 12.94 minutes. Using the GC/MS in the ChemSensor mode, the mass spectral fingerprints are also obtained.

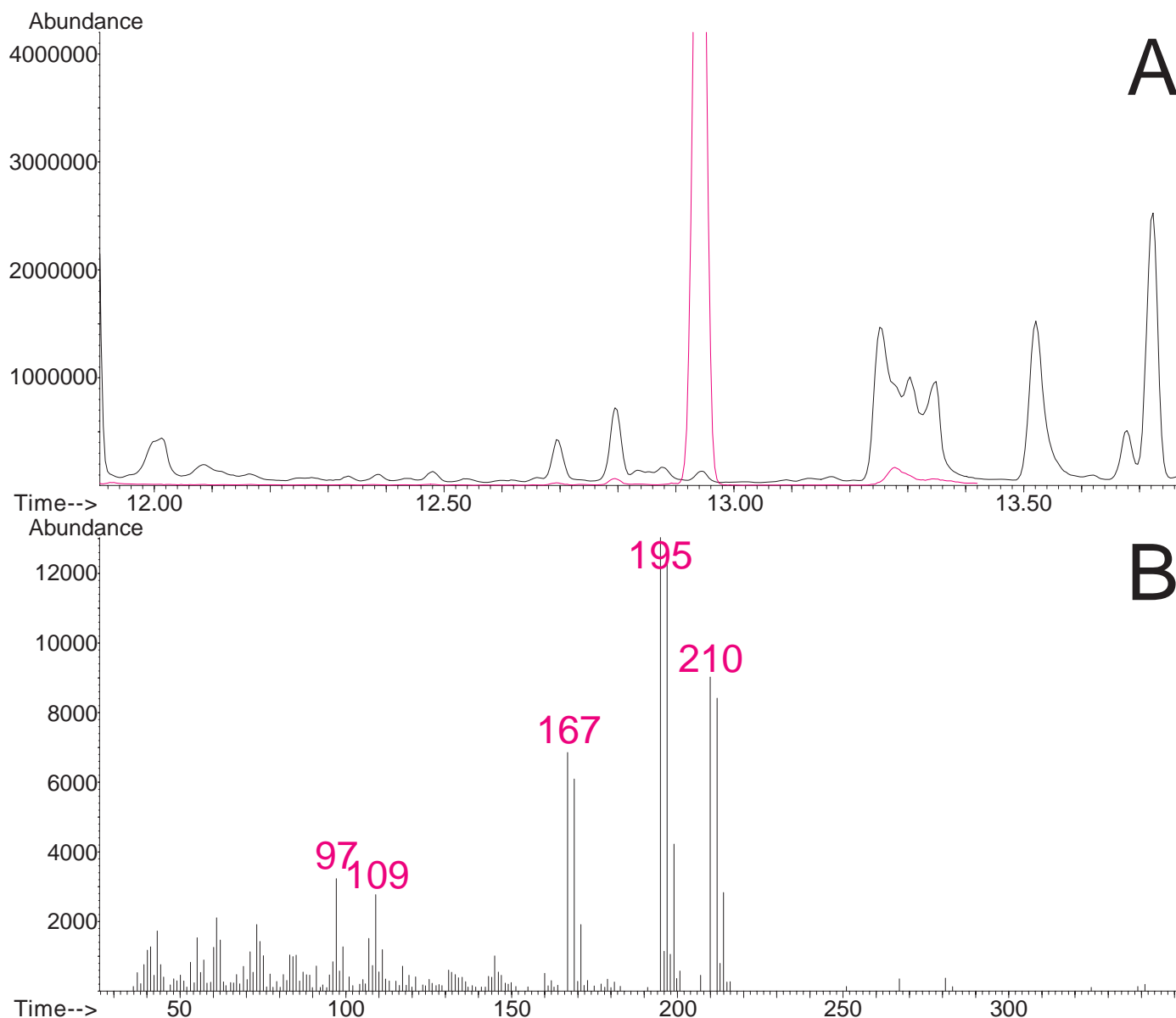


Figure 8. A: TIC of spiked wine solutions obtained after sampling with SBSE using the MSD in the scan mode. The red trace is the TCA spiked at 40 ppb (split 30:1) and the black trace at 40 ppt (splitless). B: Mass spectrum of TCA obtained at 40 ppt.

Figure 9 shows the projections of the samples' fingerprints into the space of the first three principal components. It can be seen that the samples cluster according to the level of TCA and there is enough separation to create a multivariate model.

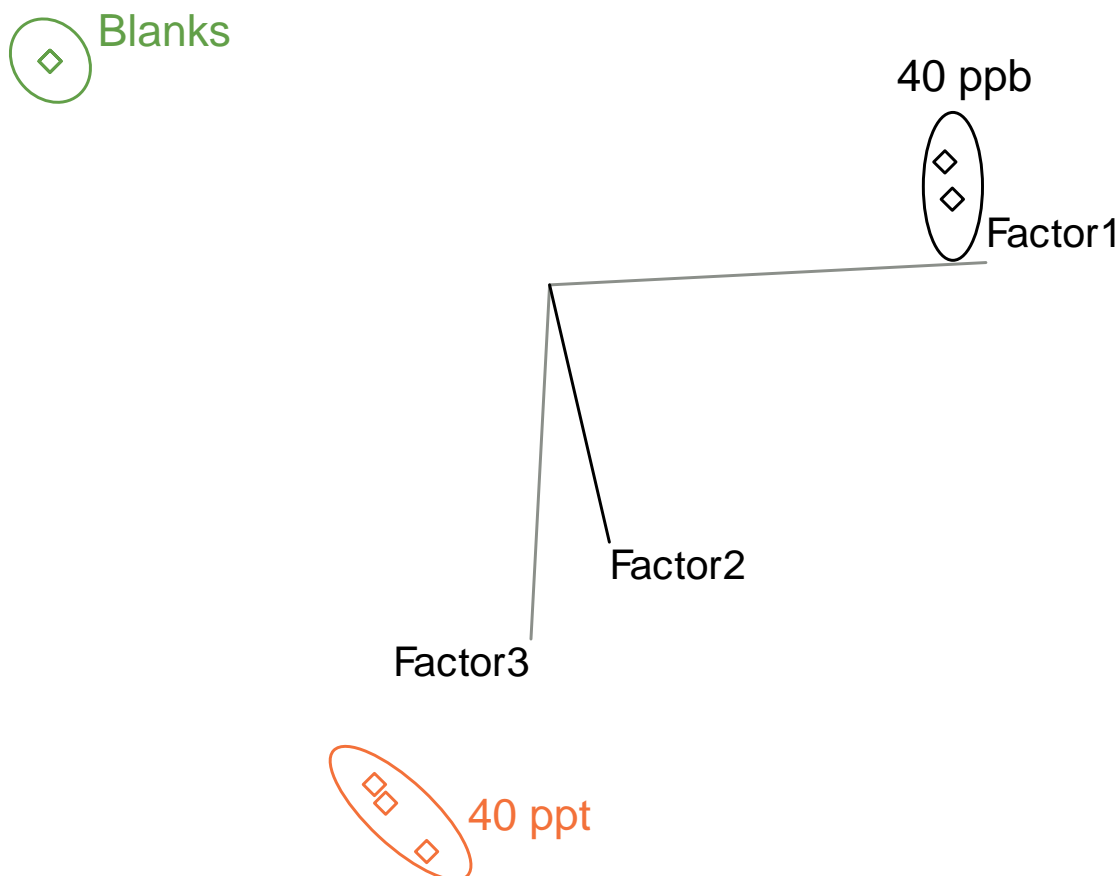


Figure 9. Projection of the mass spectral fingerprints of the wine samples into the space of the first three principal components (data collected using Twister-Thermal Desorption-GC/MS).

We decided to desorb the Twister without chromatographic separation by using a fast GC oven ramp. The mass spectral fingerprints obtained were similar to the mass spectral fingerprints obtained with chromatographic separation. Using this fast GC method we were able to detect TCA levels in the ppb level but the signal-to-noise ratio was not adequate to detect TCA in the ppt levels.

CONCLUSIONS

Differences between pure and degassed olive oils were detected using a mass spectral based chemical sensor with static HS introduction. Results were validated using traditional GC/MS. Advantages of using the ChemSensor include fast sample throughput and easy to interpret results. For this particular application, unknown oils were correctly classified as either pure or degassed. This result was also confirmed by the supplier.

Detection of TCA in white wine was possible at the low ppm level using the ChemSensor in the HS mode, in the ppb level using the ChemSensor in the SPME mode. Parts-per-Trillion levels of TCA were possible

using SBSE sampling and analysis with a ChemSensor System that includes a Thermal Desorption System coupled to a GC/MS. Easy to interpret reports as samples are analyzed is a benefit of this technique over the traditional GC/MS data analysis. Detection of TCA at lower levels than the ones we observed in this study could have been improved by using the MS in the SIM mode.

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