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Fast Analysis of Beverages using a Mass Spectral Based Chemical Sensor

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ABSTRACT

Detection of adulteration, contamination or inconsistencies in food and flavor samples should be accurate and fast. Chemical sensors are ideal for these types of applications because they provide fast measurements. While analysis times are crucial, accuracy and precision of the analysis should never be compromised. It is therefore desirable to use a reliable and stable technology that is robust to environmental changes such as humidity or temperature. Quadrupole mass spectrometry is a robust technique that has been widely used in food and flavor applications.

In this study, mass spectral fingerprints of orange juice and wine samples were obtained by direct transfer of their headspace into a mass spectrometer without chromatographic separation. For the beer samples a GERSTEL ChemSensor System that includes a GC was used. Stan-

dard samples were used to train the chemical sensor with acceptable mass spectral profiles. Adulteration of wine samples was modeled with two different types of wines; contamination was detected by spiking orange juice with diacetyl and inconsistencies in products was modeled by analyzing beer samples freshly opened and aged 3 and 6 days.

Detection of contamination, adulteration and product inconsistencies was easily determined using chemometric models. In particular, principal component analysis (PCA) easily detected anomalies by projection of the mass spectral fingerprints into the space of the first three or two principal components. Adulteration of the wine standards was detected in the percentage range while diacetyl concentrations in orange juice were detected at the low ppm range. Slight differences between beer samples freshly opened and aged 3 and 6 days were also detected and identified.

INTRODUCTION

Identification of product adulteration, contamination or inconsistency in food samples greatly benefits when the total analysis times are short. This includes sample preparation and instrument time. Chemical sensors are ideal for these types of applications because they provide fast results with minimal sample preparation. For example, a robust chemical sensor is obtained when well-known mass spectrometry technology is coupled with multivariate data analysis.

Mass spectrometry is a robust technology that is unaffected by moisture in the sample, ambient humidity, or ambient temperature fluctuations. It is also immune to sensor poisoning. Ions associated with dominant sample components, such as ethanol in wine, can be ignored and ions that model only the critical factors that differentiate samples are used. Also, ions present in an unusual sample that are not part of a standard sample can be detected.

The use and popularity of multivariate analysis has increased due to the availability of fast computers with virtually unlimited memory coupled with instruments such as a mass spectrometer that generate megabytes of data quickly. The advances in computer and instrumental technology result in complex data sets where useful information needs to be extracted. For example, a normal mass spectrum could consist of over 250 m/z fragments. These m/z ions carry information that could be used as a fingerprint for a certain compound. In order to easily compare different fingerprints a model with fewer dimensions, less than 250, is needed.

In this study, headspace (HS) volatiles from wine and orange juice are introduced without chromatographic separation to a quadrupole mass selective detector (MSD) using a GERSTEL Headspace ChemSensor (Figure 1A). Also, volatiles from beer samples concentrated in a SPME fiber are introduced to a GERSTEL ChemSensor System (Figure 1B). The resulting composite mass spectrum of each sample is used to train the chemical sensor using multivariate pattern recognition techniques. Unknown samples are easily compared to standards using integrated multivariate analysis software that can be easily customized to reflect pass or fail decisions.



Figure 1a. Gerstel ChemSensor.



Figure 1b. Gerstel ChemSensor System.

EXPERIMENTAL

A: Wine. Merlot and Cabernet Sauvignon wine samples from the same winery were purchased at a local store. Pure samples along with three different blends were prepared according to Table 1. The goal of this experiment was to create models that could predict if an unknown was a pure wine (either merlot or cabernet) or a blend.

Table 1. Levels used for wine mixtures.

| Level | % Merlot | % Cabernet |
|-------|----------|------------|
| 1 | 0 | 100 |
| 2 | 30 | 70 |
| 3 | 50 | 50 |
| 4 | 70 | 30 |
| 5 | 100 | 0 |

B: Orange juice. Orange juice samples were purchased at a local store. Diacetyl standard was obtained from Sigma-Aldrich (Allentown, PA). Solutions of diacetyl in water at 10,000 and 2,000 ppm were used to spike

orange juice at 10, 50, 100, 500 and 2000 ppm levels. The goal of this experiment was to detect diacetyl in an orange juice matrix.

C: Beer. Five different German Pilsner beer samples were purchased in Mülheim an der Ruhr, Germany. All samples were purchased in glass bottles, the Koenig beer was also purchased in the can form. SPME extractions were carried out using a 75 μm Carboxen/PDMS fiber (CAR/PDMS). Headspace SPME extractions were carried out for 15 min at 45 $^{\circ}\text{C}$ and the fiber was desorbed for 3 min at 220 $^{\circ}\text{C}$. The objective of these experiments was to discriminate between the different beer samples and to detect differences in chemical composition in beers aged 3 and 6 days.

RESULTS AND DISCUSSION

A: Wine. The mass spectral fingerprint of the two different wines was obtained and it is shown in Figure 2. It can be seen that the profiles are pretty similar but there are some subtle differences in some ion ratios (e.g. 61, 92).

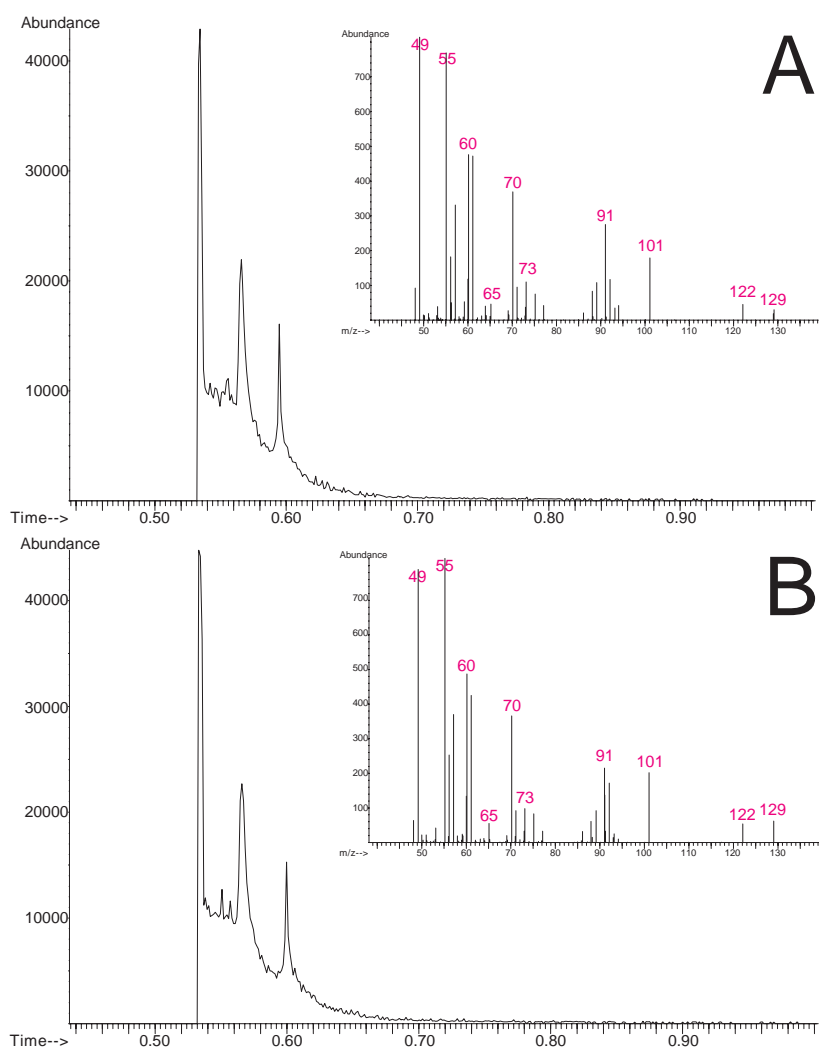


Figure 2. TIC and MS for A) merlot and B) cabernet wine obtained using the Gerstel Headspace ChemSensor.

Exploratory analysis was carried out using principal component analysis (PCA) and hierarchical cluster analysis. These analyses indicate the feasibility of the data for possible classification or regression analysis. The projection of the samples into the space of the first three principal components is shown in Figure

3. A cascading model was created for these types of samples in which the first model (KNN) classified the samples as either pure or as a blend, if the samples were classified as a blend then a PLS model was used to predict the percentage of blending.

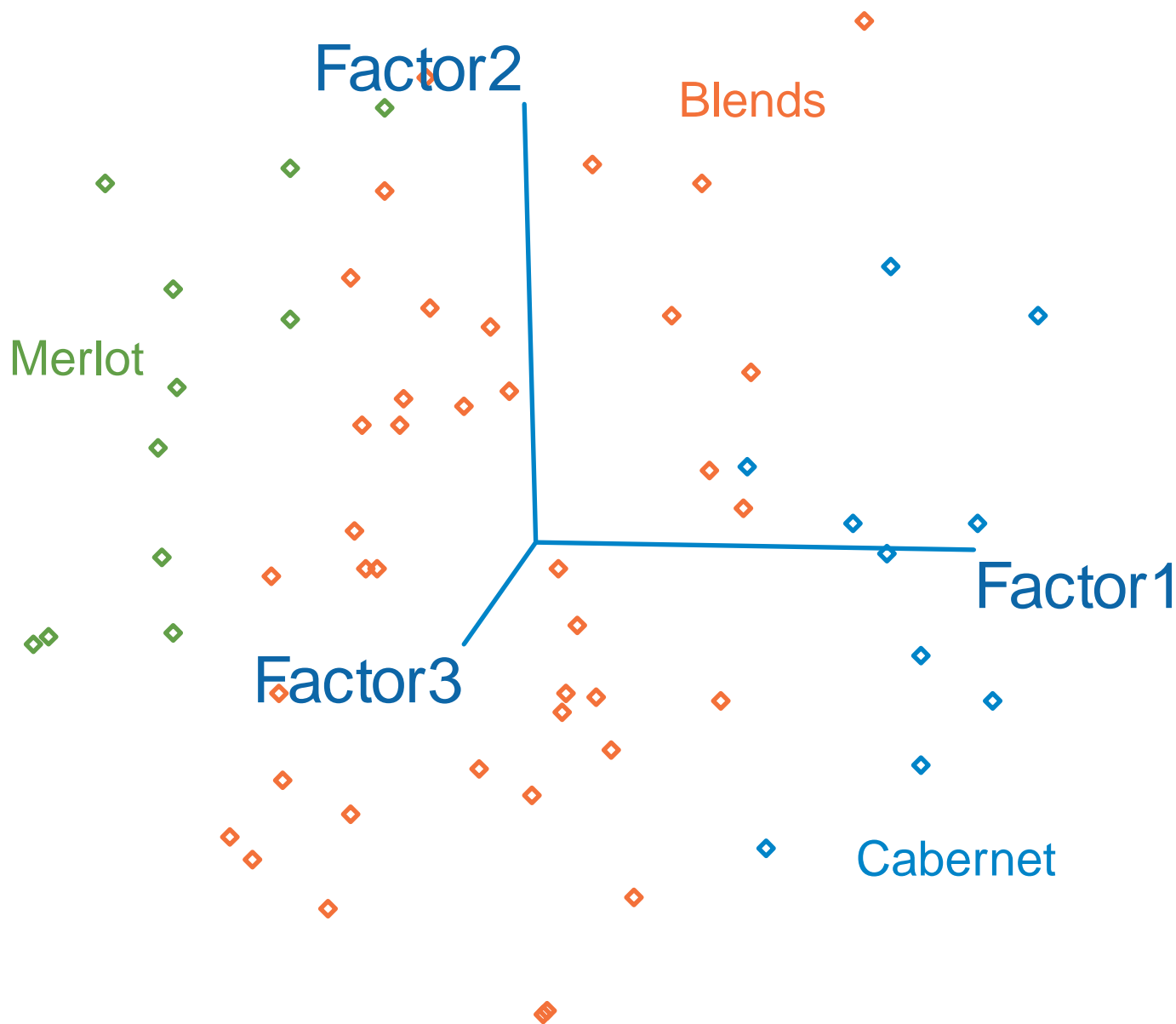


Figure 3. Projection of the wine solutions into the space of the first three principal components.

The output for a testing data set (not used in model creation) using the cascading models is shown in Table 2. It can be seen that the predictions are 100% accurate when the model predicts as Cabernet or Merlot. For the blended samples we decided to examine the stan-

dard error of calibration (SEC, 4.01) obtained with an 3-factor PLS model and the r_{cal} (0.996). Both diagnostic values indicate that the PLS model (Figure 4) could be used in the prediction of blending.

Table 2. Predictions for a wine testing data set using a cascading model.

| % Merlot | Class | Predicted | Known [% Merlot] |
|----------|-------|---------------|------------------|
| 37.28 | | Blend | 30 |
| | 3 | 100% Merlot | 100 |
| | 3 | 100% Merlot | 100 |
| 69.12 | | Blend | 70 |
| 27.92 | | Blend | 30 |
| | 3 | 100% Merlot | 100 |
| | 1 | 100% Cabernet | 0 |
| | 3 | 100% Merlot | 100 |
| 39.58 | | Blend | 50 |
| | 3 | 100% Merlot | 100 |
| | 1 | 100% Cabernet | 0 |
| | 3 | 100% Merlot | 100 |
| 41.77 | | Blend | 50 |
| 53.77 | | Blend | 50 |
| | 3 | 100% Merlot | 100 |
| | 3 | 100% Merlot | 100 |
| | 1 | 100% Cabernet | 0 |
| | 1 | 100% Cabernet | 0 |
| | 3 | 100% Merlot | 100 |
| 63.94 | | Blend | 70 |
| 64.89 | | Blend | 70 |
| | 1 | 100% Cabernet | 0 |

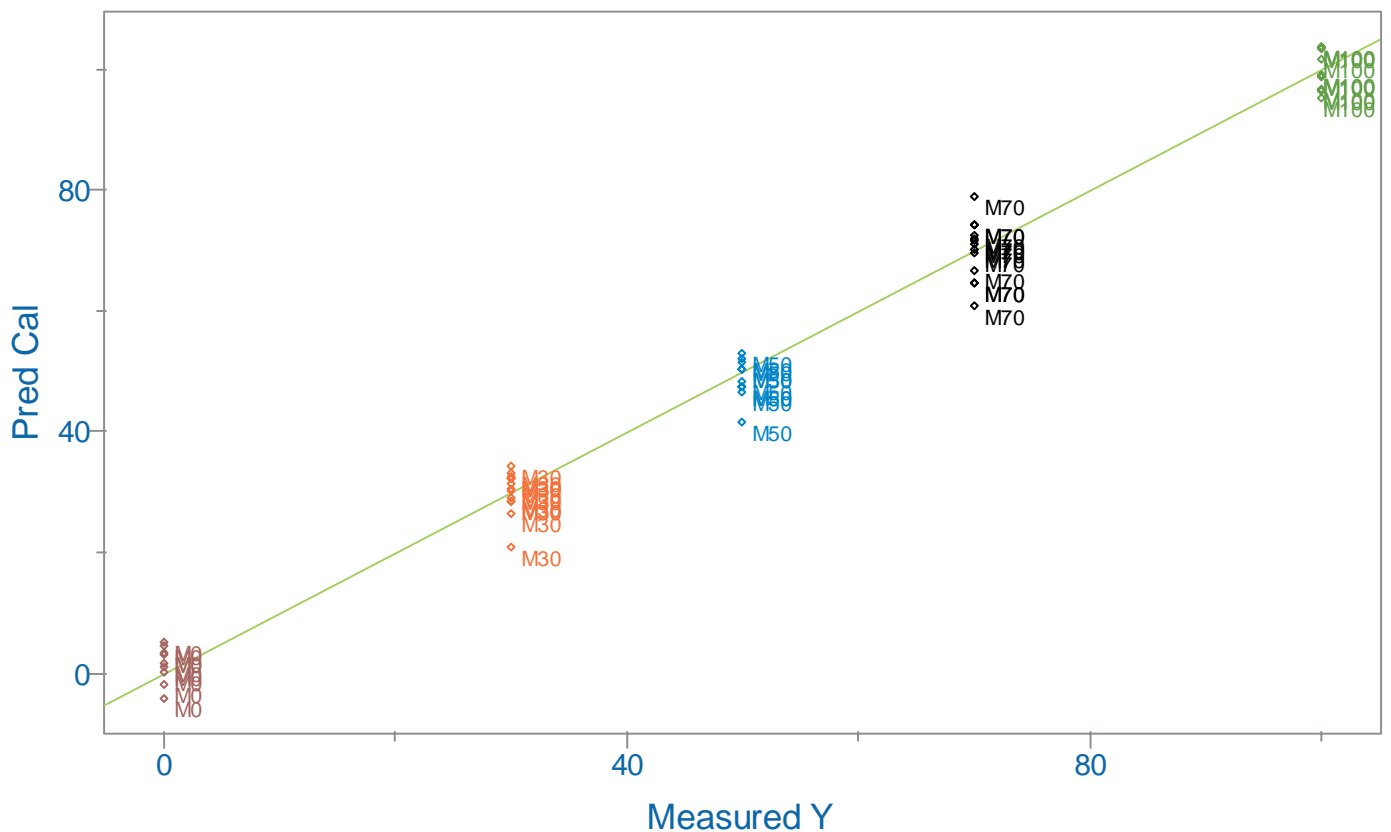


Figure 4. Y-Fit for a PLS 3 factor regression model for the wine mixtures.

B: Orange juice. The mass spectra of each of the orange juice samples were examined using the Data Analysis program of ChemStation software (Agilent Technologies). The presence and identification of diacetyl at the 100 ppm concentration was corroborated

by subtracting the mass spectrum of a spiked sample minus the spectrum of the non-spiked sample. Figure 5 shows how it is possible to detect with ChemStation Data Analysis software the presence of diacetyl.

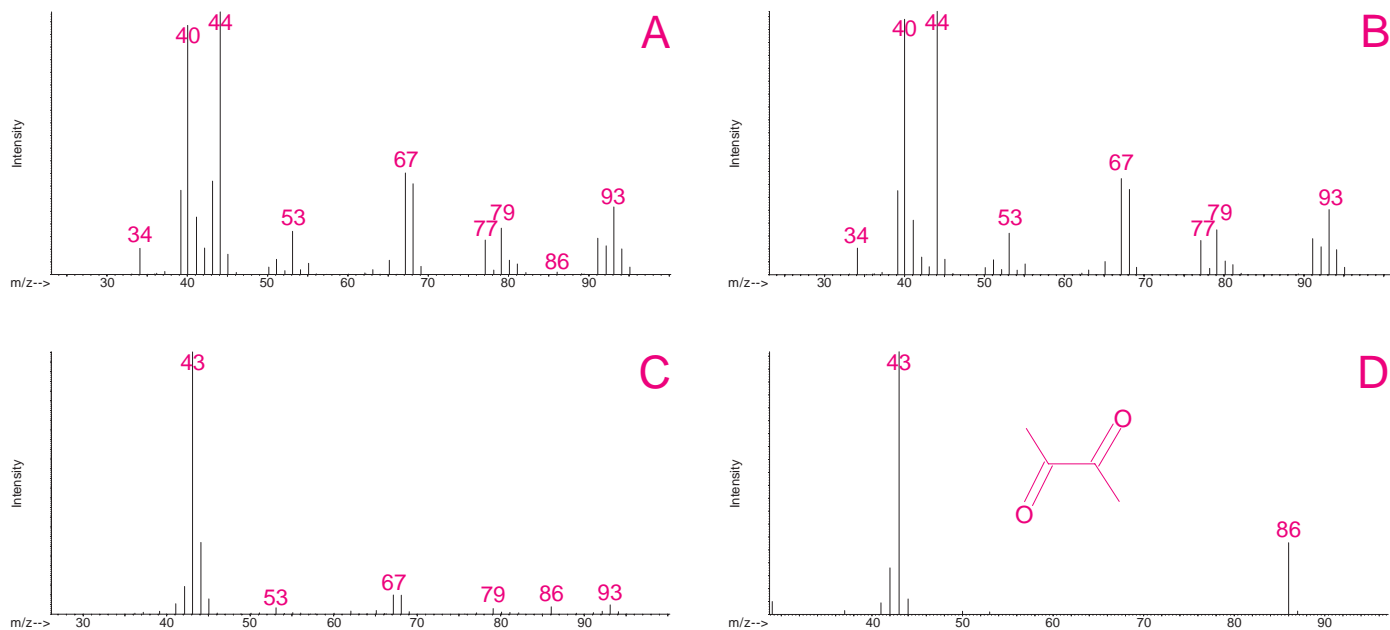


Figure 5. Mass spectra of orange juice. A) OJ with 100ppm diacetyl; B) pure OJ; C) subtraction of pure OJ from OJ with diacetyl; D) diacetyl standard.

A PCA model was created to determine if the presence of diacetyl was possible. As seen in Figure 6, PCA scores for the orange juice samples indicate that the first

PC (horizontal axis in Figure 6) describes the difference between samples containing marker (positive scores on the first PC) and no marker (negative scores).

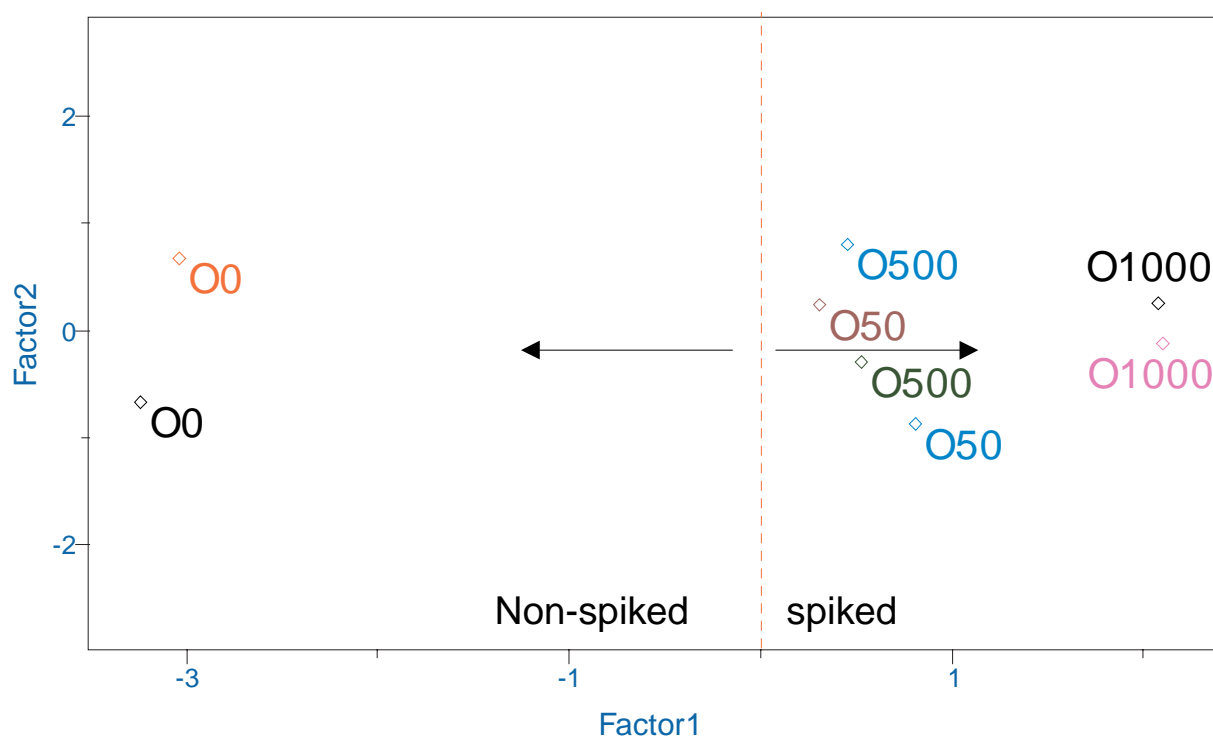


Figure 6. Projections of the orange juice mass spectra into the space of the first two principal components.

C: Beer. The beer samples were analyzed using a GERSTEL ChemSensor System. This configuration allows switching between rapid screening and comprehensive GC/MS analysis depending if a short transfer

line or a capillary column is on-line. Figure 7 shows six TICs obtained using this configuration in the SPME mode. Visual inspection of these five TICs reveals few differences between these six types of beers.

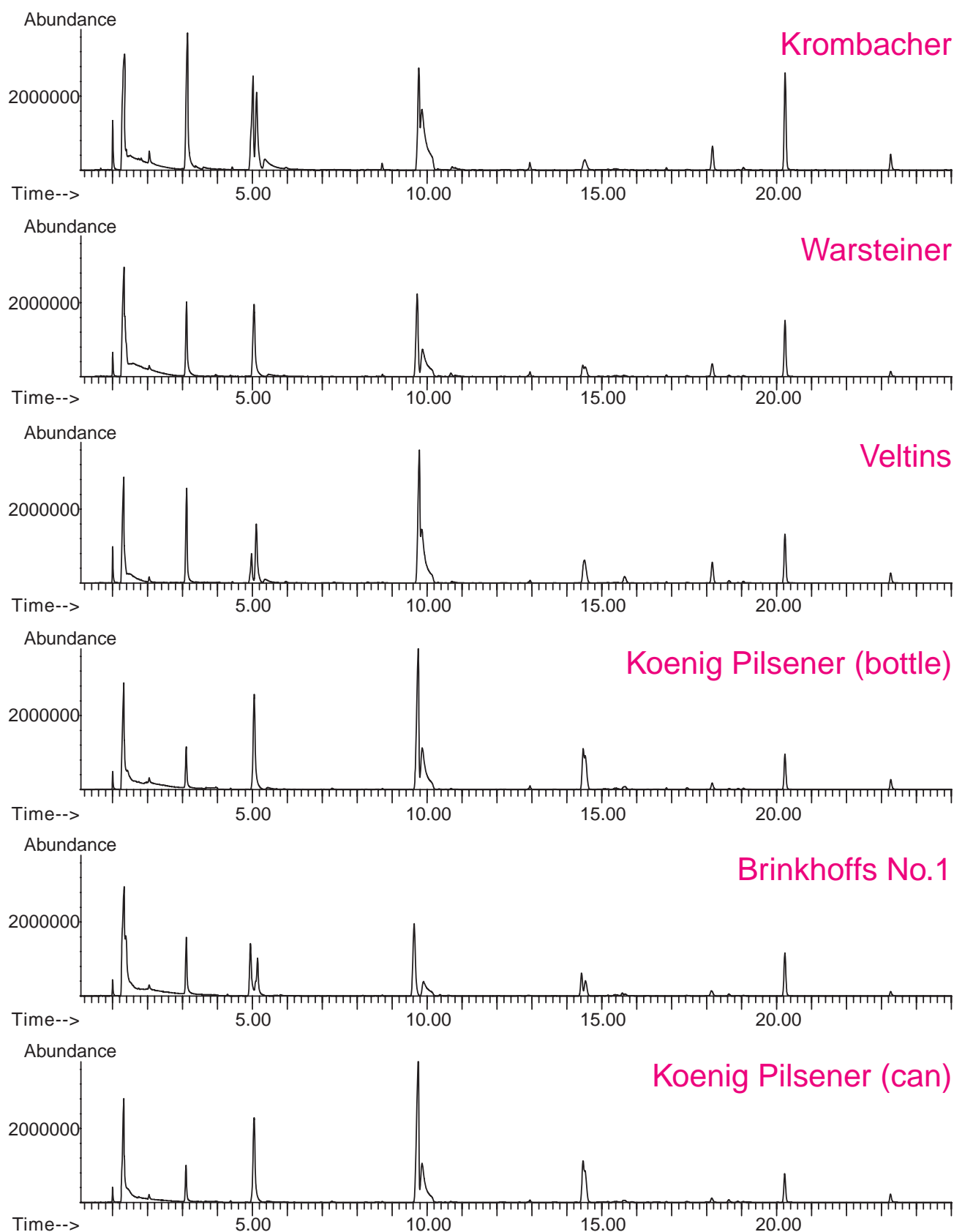


Figure 7. GC-MS total ion chromatograms of the different beer types.

Since visual separation of the samples using TIC is difficult, the mass spectral fingerprint was used to develop chemometric models. Figure 8 shows the projection of the mass fingerprints into the space of the first three principal components. The total variance captured within the first three principal components was over 98%, this implies that differences in the

samples projections are due to differences in the chemical composition obtained with SPME sampling. Five different clusters are evident in the scores plot (Figure 8), beer sampled from the can and bottle appears to cluster together. A separate model was created for this type of beer (inset of Figure 8) in which separation was obtained using 3 PCs.

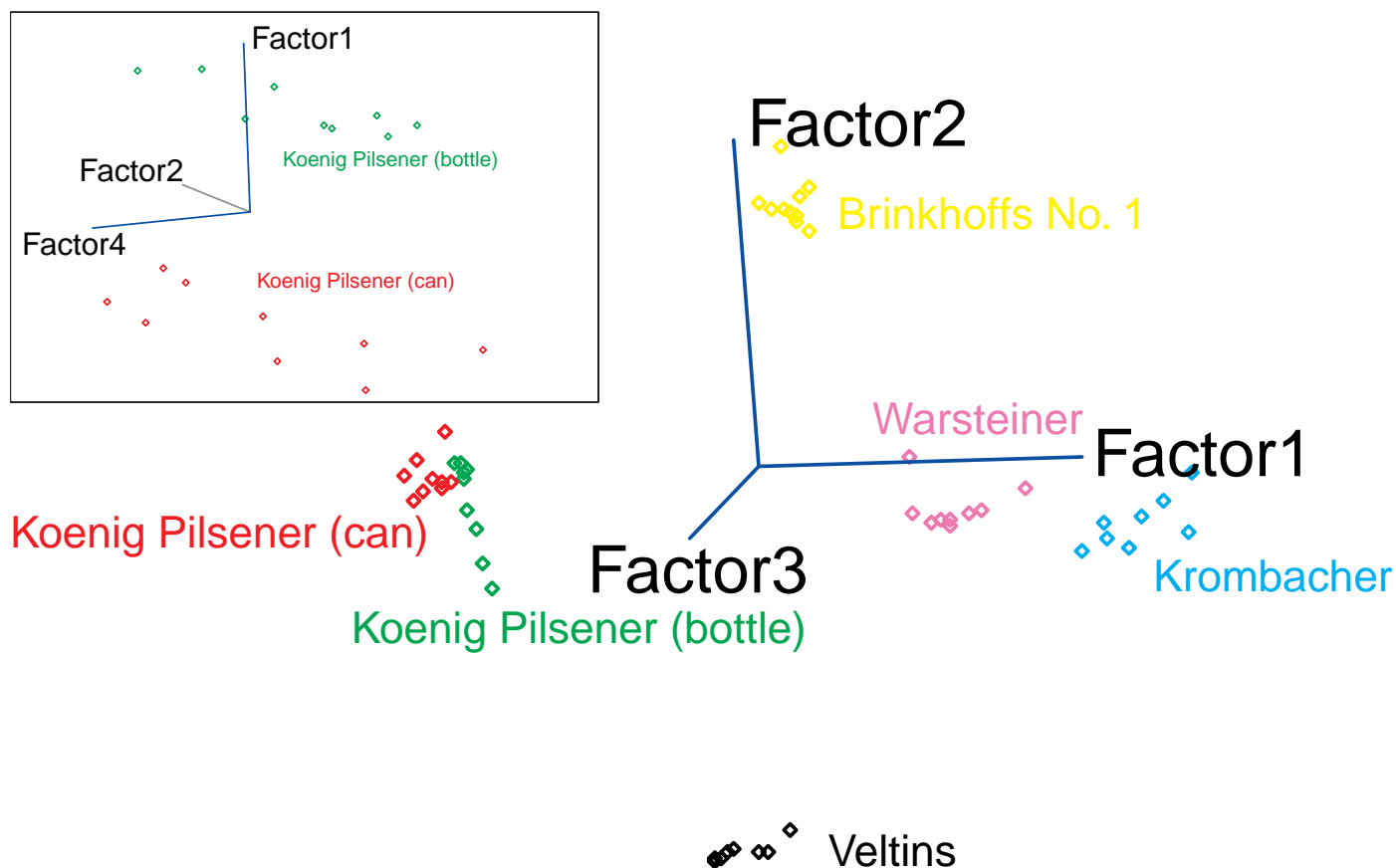


Figure 8. PCA scores plot (4 factors) of the 6 beers fingerprint mass spectra.

Change in composition as the beer aged was easily detected using the GERSTEL ChemSensor system. Figure 9 shows the projection of the fresh and aged Warsteiner beer into the space of the first two principal components. Examination of the corresponding

loadings for these PCs reveals key ions responsible for the different projections. Using these ions as a guide, extracted ion chromatograms were inspected using ChemStation Data Analysis software.

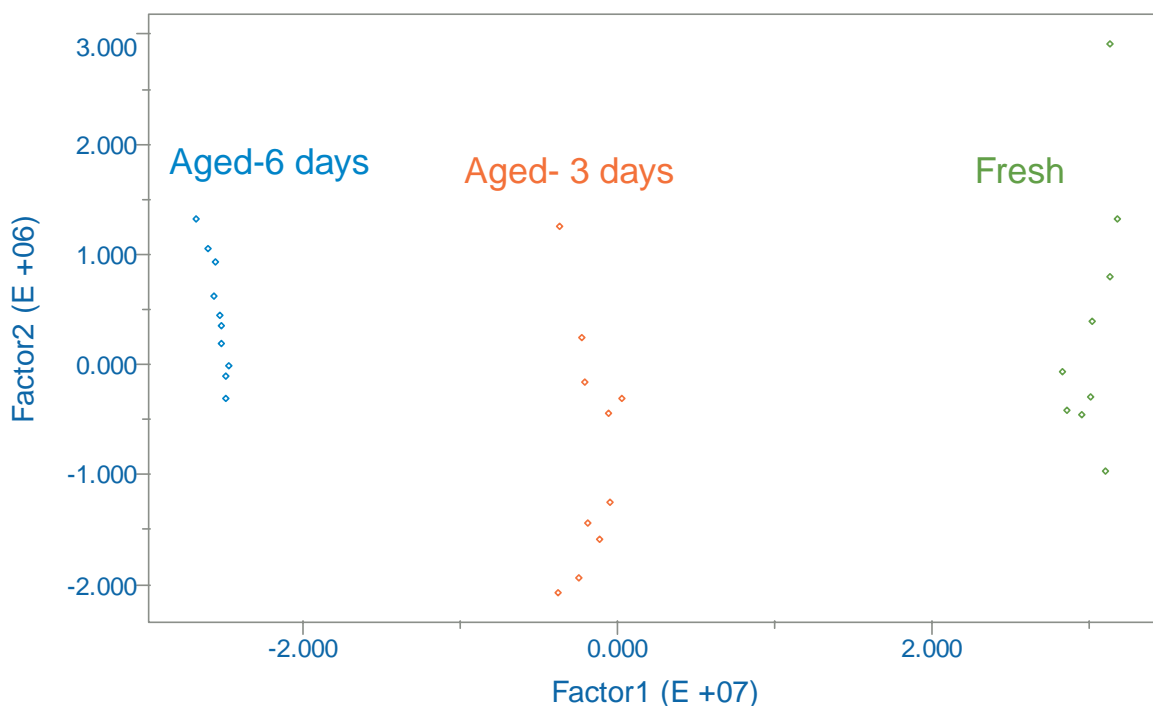


Figure 9. Projections of the mass spectral fingerprints of Warsteiner aged beers into the space of the first two principal components.

Table 3 shows the compounds that decrease over time as the Warsteiner beer was aged. Ions with high loadings for the first PCs are highlighted. It appears that the first principal component in this case is explaining the difference between the content of the compounds

from Table 3 in the different aged samples. Since the GERSTEL ChemSensor System includes a GC, detection of the specific compound is easily done when a capillary column with slow temperature ramp is used.

Table 3. Compounds that decrease overtime as the Warsteiner beer was aged. Ions highlighted have high loadings in the first principal component.

| RT [min] | Compound | CAS # | Ions |
|----------|----------------------------|----------|------------------|
| 1.00 | Ethyl acetate | 141-79-6 | 43, 61, 70, 88 |
| 3.11 | 1-Butanol-3-methyl acetate | 123-92-2 | 43, 55, 70, 61 |
| 5.05 | Ethyl caproate | 123-66-0 | 60, 71, 88, 99 |
| 9.71 | Octanoic acid ethyl ester | 106-32-1 | 88, 101, 127, 57 |

CONCLUSIONS

The fast and accurate classification of samples using an instrument that integrates multivariate statistics with mass spectrometry technology is now possible. The GERSTEL Headspace ChemSensor and GERSTEL ChemSensor System have both been proven to be capable of detecting differences in the composition of three beverages: wine, orange juice and beer.

For the wine samples, it has been shown that it is possible to develop cascading models that can predict wine samples as pure or blends using the GERSTEL Headspace ChemSensor. The blending percentage was also possible to predict with a PLS model.

For the orange juice study, these preliminary re-

sults indicate the possibility of using a mass spectral based chemical sensor to predict the level of diacetyl. More research with more markers and more levels is necessary. Also, the possibility of using the Chemical sensor in the single ion-monitoring mode (SIM) could improve the sensitivity below 10 ppm.

Finally, it has been shown that visual comparison of total ion chromatograms of beer samples was cumbersome. Comparison of chemical composition is more objective and faster using a GERSTEL ChemSensor System with multivariate analysis.



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