GLOBAL ANALYTICAL SOLUTIONS

GERSTEL

AppNote 2/2003

Wine Discrimination using a Mass Spectral Based Chemical Sensor

Vanessa R. Kinton, Edward A. Pfannkoch
Gerstel, Inc., Caton Research Center, 1510 Caton Center Drive,
Suite H, Baltimore, MD 21227, USA

M. Abdul Mabud, Sumer M. Dugar
Alcohol & Tobacco Tax and Trade Bureau (TTB), 6000 Ammendale
Road, Ammendale, MD 20705-1250, USA

Arnd C. Heiden, Carlos Gil
Gerstel GmbH & Co. KG, Eberhard-Gerstel-Platz 1,
D-45473 Mülheim an der Ruhr, Germany

KEYWORDS

Chemometrics, wine, ChemSensor, electronic nose, mass spectrometer (MS), fingerprint mass spectra.

ABSTRACT

Verification of authenticity is a crucial aspect of food quality control, and also important to regulatory organizations. In this study, two wines of known pure varietal along with some commercial wines were examined using a mass spectrometry based chemical sensor. The fast analysis times obtained using this instrument makes this technology ideal for detection of adulteration.

Multivariate statistics were used to create models that discriminate between wine varieties. Exploratory analysis such as principal component analysis (PCA) and hierarchical cluster analysis (HCA) indicated the viability of the data set for classification models. Soft-independent-modeling-

of-class-analogy (SIMCA) and K Nearest Neighbors (KNN) were used to create two classification models.

Both SIMCA and KNN provided a quick identification of unknown samples. Overall, the fast identification of wine varieties demonstrates the usefulness of the MS chemical sensor in detecting samples with close chemical composition.

INTRODUCTION

The usefulness of a mass spectral based chemical sensor has already been proven in several food applications [1]. The benefits of fast and reliable answers that can be obtained with this type of chemical sensor are ideal for applications that require fast sample throughput. By eliminating the chromatographic separation and directly coupling a headspace sampling instrument to a mass spectrometer, runs on the order of 1-2 minutes can be achieved. The separation then becomes a multivariate analysis in which the variables are the sum of abundances for each of the ions selected in the scan range. The scan range can be selected by the user and it usually includes over 100 fragments. In order to easily compare different fingerprints a model with fewer dimensions, less than 100, is needed.

Principal component analysis is a multivariate technique that reduces the dimensionality of the data sets by building a new set of coordinates, principal components or PCs. These PCs are linear combinations of the original variables and they are orthogonal to each other and therefore uncorrelated [2]. They are also built in such a way that each one successively accounts for the maximum variability of the data set. The total number of PCs obtained cannot exceed the number of samples (n) or the number of variables (p) whichever is smaller. Not all these PCs explain systematic variance of the data set; some are simply explaining noise. The effectiveness of a good PCA model depends on keeping only PCs that describe systematic variance. Soft-independent-modeling-of-class-analogy (SIMCA) is a supervised technique that uses PCA to model the shape and position of the samples. An acceptance region is then created for each different type of class.

Besides PCA, another useful exploratory multivariate technique is hierarchical cluster analysis (HCA). By calculating the Euclidean distances between samples a measure of similarity is obtained. The method starts by calculating distances of each sample to all other samples and the groups (or clusters) are formed by agglomeration or division. Although other techniques exist to measure differences or similarities we will concentrate on the Euclidean distance in this paper. Just like a PCA scores plot provides a good indication on the feasibility of the data for a SIMCA model, a single link HCA indicates if the data could be used for a K-Nearest Neighbor (KNN) model. KNN is a supervised technique that classifies unknowns based on their proximity to samples already placed in categories.

In this paper mass fingerprints are obtained from sampling the headspace of wine samples using the GERSTEL Headspace ChemSensor (Figure 1). This instrument integrates the advantages of multivariate analysis with well-known technology like quadrupole mass spectrometry. The GERSTEL Headspace ChemSensor is equipped with a headspace unit coupled directly to an Agilent 5973 mass selective detector (MSD) and Pirouette multivariate software. In this case the variables are the abundances of each m/z fragment obtained from sampling the entire headspace of wine samples without prior chromatographic separation.

Figure 1. Gerstel Headspace ChemSensor.

EXPERIMENTAL

One Merlot and one Cabernet Sauvignon wine from the same winery were purchased at a local store; these will be referred in this study as M-C (Merlot commercial) and CS-C (Cabernet Sauvignon commercial). Besides the commercially available wines, the Alcohol & Tobacco Tax and Trade Bureau (TTB) provided pure varietal Merlot and Cabernet Sauvignon wines. These wines will be referred as M-PV (Merlot pure-varietal) and CS-PV (Cabernet Sauvignon-pure varietal). Seven replicas of each wine were analyzed using 5 ml aliquots. The aliquots were placed in 10 mL vials which were crimped and equilibrated for 20 minutes at 80 °C before headspace sampling. Since the GERSTEL Headspace ChemSensor does not use a column for chromatographic separation prior to the mass selective detector (MSD), the entire headspace of each sample is introduced into the MSD.

The mass spectrum of each of the four wine samples was acquired in 1.20 minute runs in the scan mode using the GERSTEL Headspace ChemSensor (Figure 1). The carbon dioxide peak (from the air in the sample) and the ethanol peaks were avoided by setting the scan range from 48 m/z to 150 m/z.

All four wine samples were also analyzed using a GC (6890, Agilent Technologies) coupled to a MSD (5973, Agilent Technologies). This instrument was equipped with a Thermal Desorption autosampler (TDS A, Gerstel). The samples were diluted 10-fold in water and extracted for one hour at room temperature using stir bar sorptive extraction (Twister, Gerstel).

RESULTS AND DISCUSSION

The entire headspace volatiles of each of the 4 wines were sampled and a characteristic fingerprint mass spectrum was obtained for each one of them. For example, Figures 2 and 3 represent the TIC and MS obtained for the commercial and pure varietal wines respectively. The major ions are the same for the two commercial wines (M-C and CS-C); visual inspection of these fingerprint mass spectra (Figure 2) reveals very little differences between these two wines.

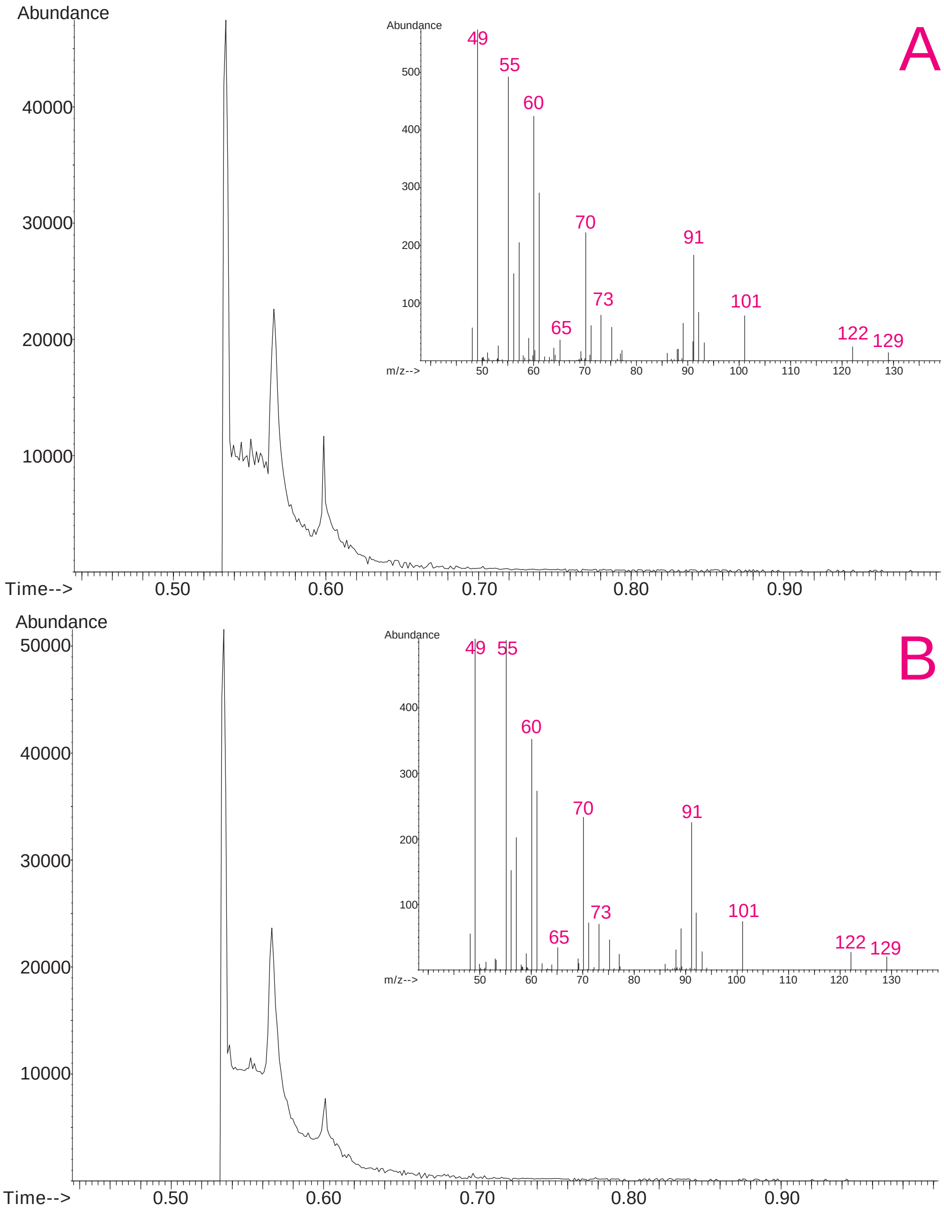

Figure 2. TIC and MS of commercially available wines. (A) Merlot and (B) Cabernet Sauvignon obtained with the GERSTEL Headspace ChemSensor.

Visual inspection of the pure-varietal wines mass spectra (Figure 3) indicates differences in abundance for some ions. For example, ions 88, 91, 101 and 129 appear to have different abundance in the Merlot (M-PV) than in the Cabernet Sauvignon (CS-PV).

Comparison of the mass spectra of commercial Merlot (M-C; Figure 2A) and pure-varietal Merlot (M-PV; Figure 3A) indicates higher abundance of ions 88 and 101 in the pure-varietal wine. Visual inspection of the fingerprint mass spectra of the Cabernet Sauvignon commercial (CS-C; Figure 2B) and the Cabernet Sauvignon pure varietal (CS-PV; Figure 3B) indicates little differences between the fragmentation patterns between these two wines. The relative abundance of all the ions appears to be higher in the pure-varietal Cabernet Sauvignon wine.

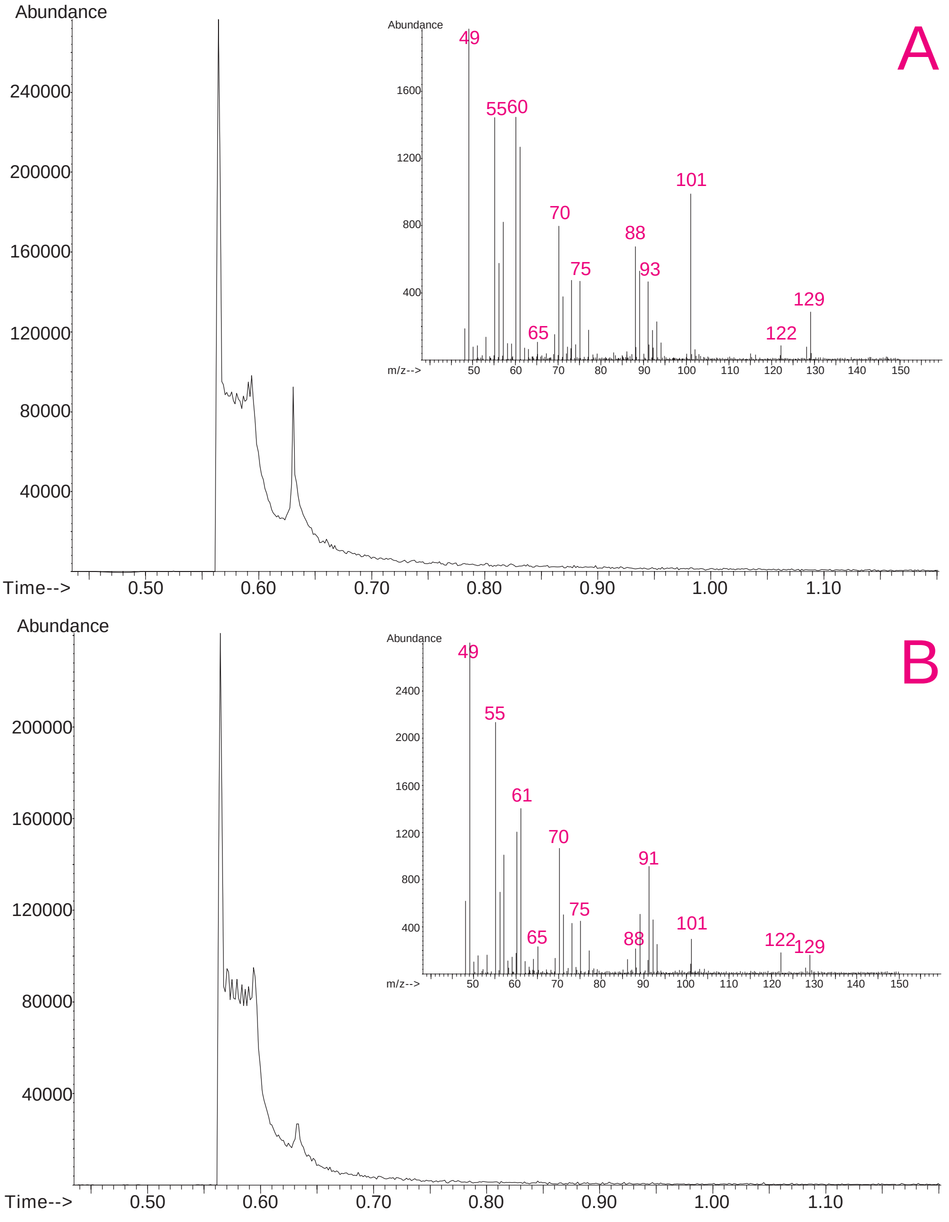

Figure 3. TIC and MS of pure varietal wines. (A) Merlot and (B) Cabernet Sauvignon obtained with the GERSTEL Headspace ChemSensor.

The mass spectrum obtained for each of the wines was converted by the ChemSensor software into a composite mass fingerprint (ASCII file) which can be easily imported into a chemometrics modeling software such as Pirouette. Figure 4 shows an overlay of these composite mass spectra for the four wine samples. Note that each band of samples is actually 7 to 8 replicas for each wine indicating excellent sample repeatability. It is also evident that the pure-varietal Merlot has higher abundance for ions 88, 101 and 129 as previously observed. This figure also indicates that the overall intensity for the majority of ions is much higher in the pure varietal wines.

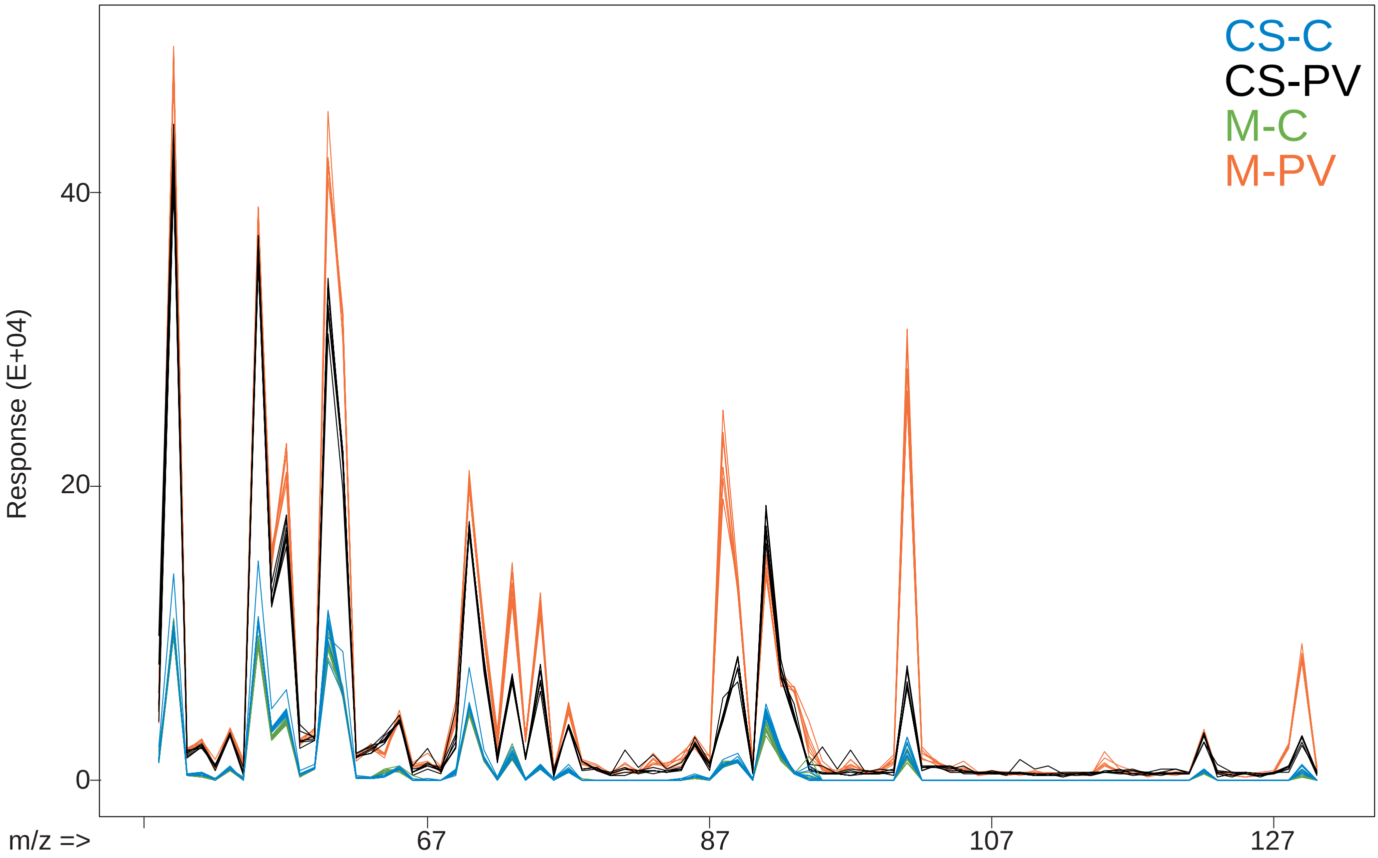

Figure 4. MS fingerprint data for the four different wines.

Principal component analysis was performed using the mean-centered data set. Since 99.69% of the total variance was captured within the first three principal components we can be confident that differences in the samples mass spectral projections (Figure 5) reflect differences present in the headspace composition of the four wine samples. Figure 2 indicated very small differences in the fingerprint mass spectra between the two commercially purchased wines; this is corroborated in the PCA scores plot that shows M-C and CS-C clustering together. The first PC (horizontal axis in Figure 5B) explains the difference between pure varietal wines and commercially purchased wines. The second PC (vertical axis of Figure 4B) indicates differences between the pure varietal Cabernet (negative scores) and the other three wines (positive scores).

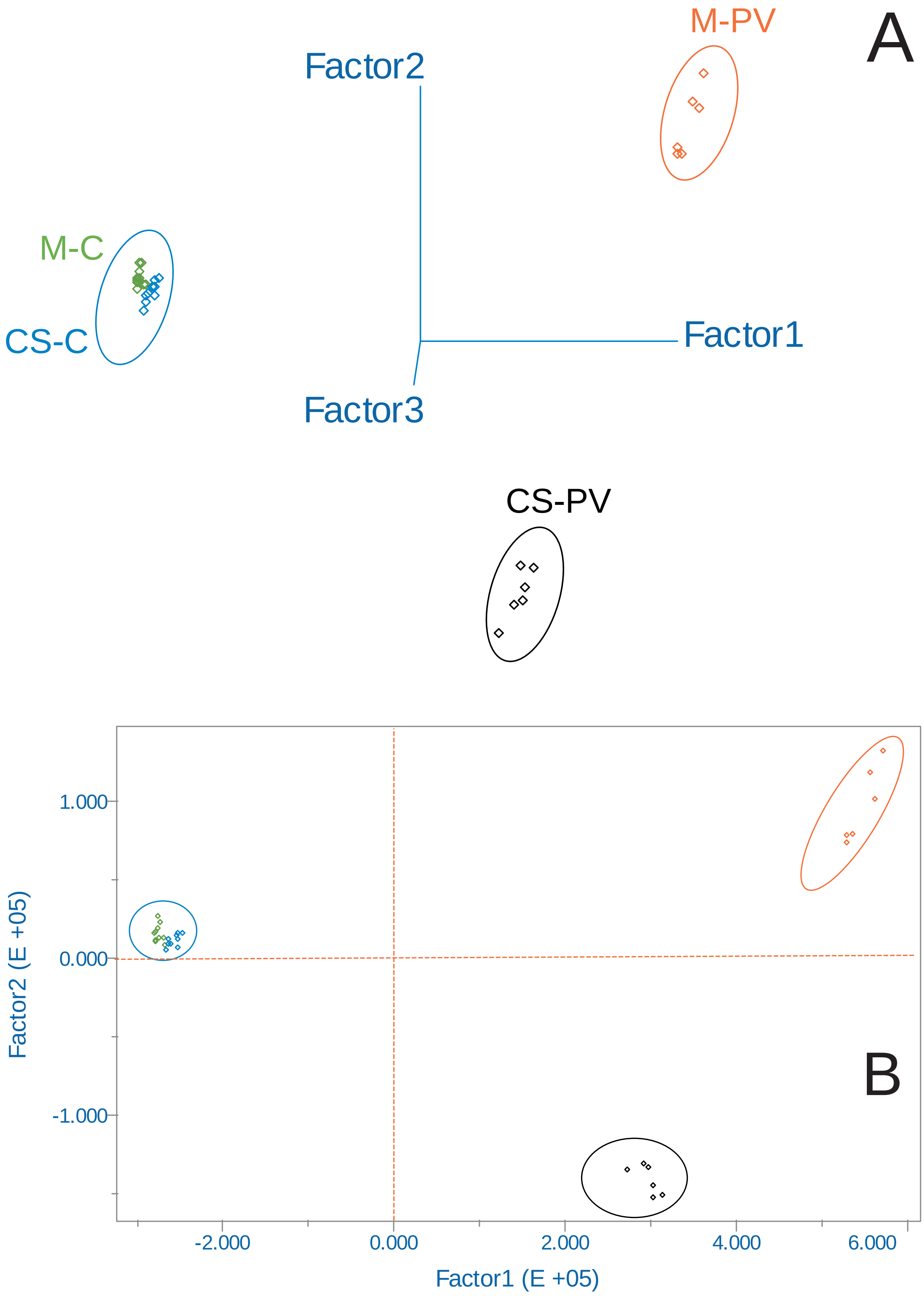

Figure 5. Projection of the wines mass spectra into the space of the first three (A) and two (B) principal components.

By inspecting the associated loadings plot to its score plot, one can find the ions that were important in constructing the principal component. For example, inspection of Figure 6 indicates that ions 49, 55, 60 and 70 were important in constructing the first PC while ions 49, 55, 88, 91, 101, and 129 were important for building the second principal component.

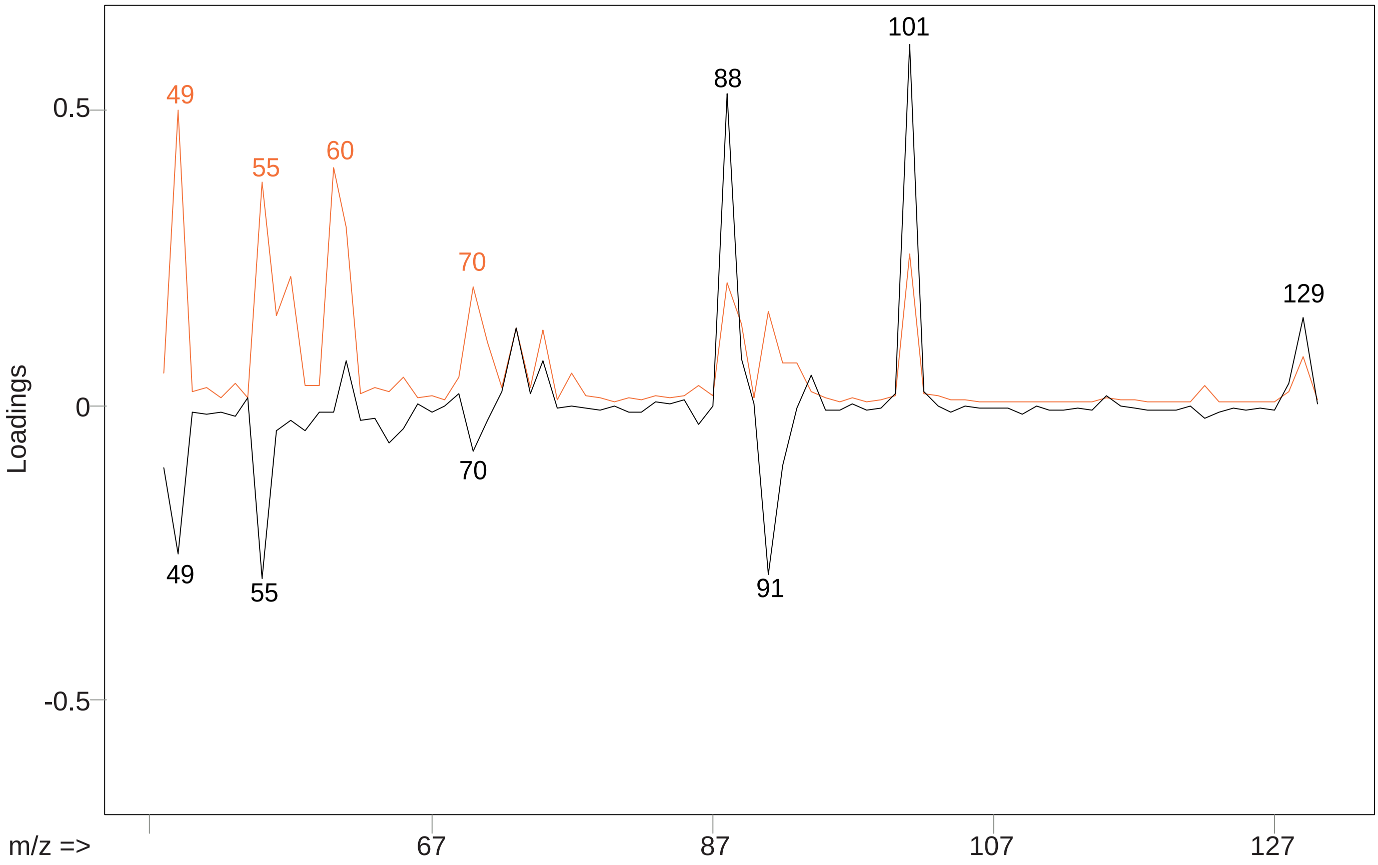

Figure 6. Loadings plot of the first principal component (red trace) and second principal component (black trace).

A total ion chromatogram overlay (TIC, Figure 7) obtained using a GC/MS instrument with Twister extraction indicates that the pure-varietal Merlot has a higher abundance for peaks at retention times of 10.096, 13.042 and 15.473 minutes. The tentative identity of these peaks was found using the Wiley138 MS library as Butanedioic acid diethyl ester (main fragments 101, 129), Decanoic acid ethyl ester (main fragments 88,101), and Dodecanoic acid ethyl ester (main fragments 88,101), respectively.

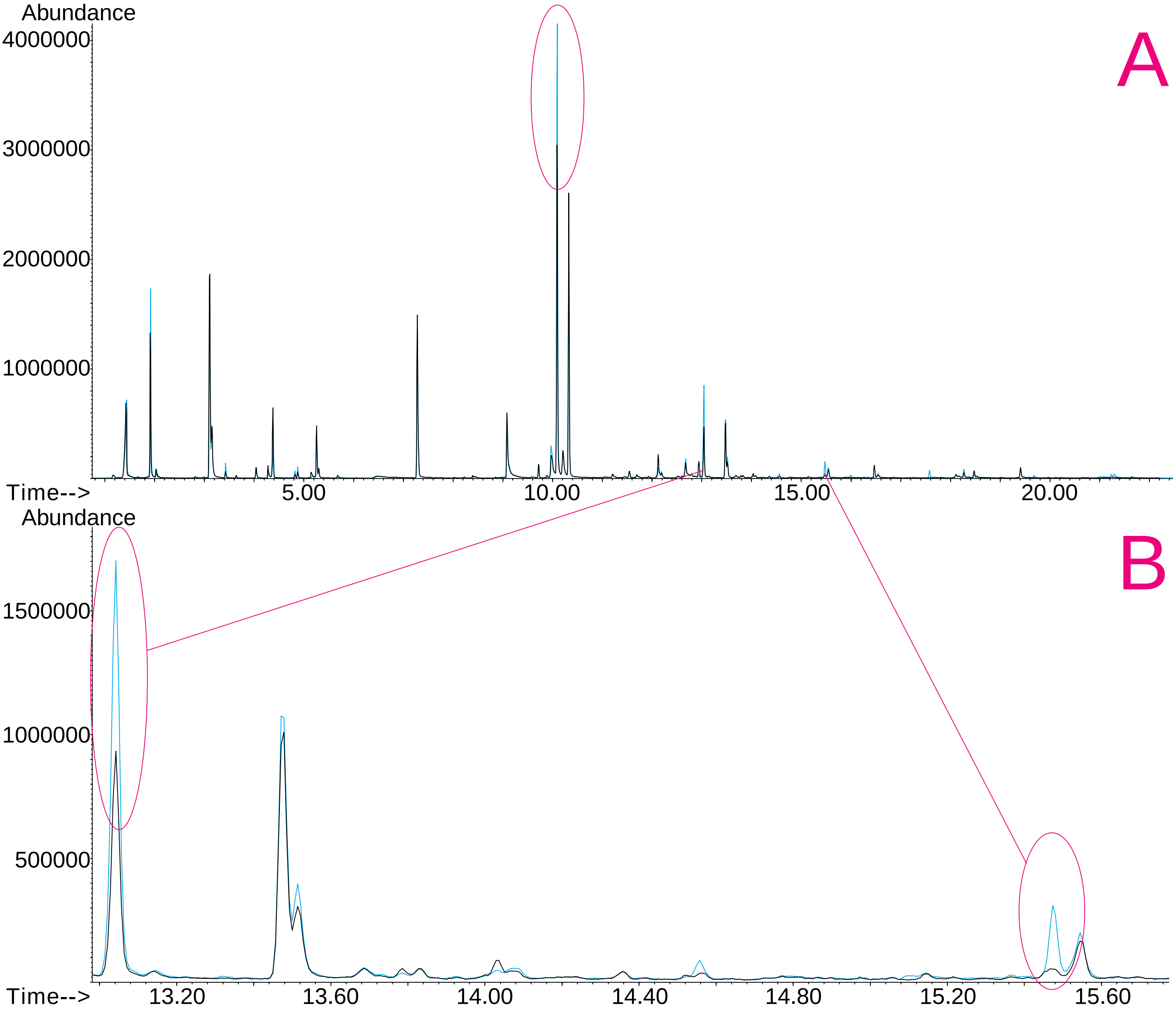

Figure 7. TIC for the pure-varietal wine samples obtained using Twister extraction, GC/MS.

Ions with high loadings in the first principal component appear to discriminate between pure varietal and commercial wines. For example, ion 49 was found present in the commercial wines at RT=1.90 min but was missing in the pure varietal wines, the peak was unidentified using the Wiley 138 MS library. The specific compounds responsible for ions 55, 60 and 70 were not possible to identify since these were present in several compounds. Ion 91 appears to be present only in M-PV at RT=22.85 min and its tentative identification appears to be an ester (CAS #85-68-7) These findings are also in agreement with the ones obtained using the chemical sensor.

Two classification models were created using the pure varietal wines: SIMCA and KNN. A series of “unknown samples” were created to test the prediction ability of these models. Using pure varietal “unknowns” the models successfully identified them according to the grape type. Using the commercial wines as unknowns neither model was able to classify the wines as Merlot or Cabernet Sauvignon. This is not a surprise, since previous figures (Figures 4 and 5) indicated minor differences between these samples. A KNN model created using the four wines successfully identified all the unknowns correctly.

CONCLUSIONS

The fast classification of wine samples using an instrument that integrates multivariate statistics with mass spectrometry technology is now possible. It has been shown how the results obtained with the Gerstel ChemSensor also relate to the results obtained with Twister extraction.

Our results indicate that the two commercially purchased wines, labeled as M-C and CS-C did not have major differences in their headspace composition. Pure varietal wines contained the same type of components but the Merlot (M-PV) appears to have higher content for some of the ester compounds. Overall the fragmentation pattern of the pure varietal wines appears to have much higher raw ion abundance than the commercial types.

The reason why the two commercially purchased wines (M-C and CS-C) appear to have relatively the same headspace composition was not investigated at the time of this writing. Our goal was to assess the feasibility of using a mass spectral based chemical sensor in wine discrimination. It is possible that the compounds responsible for differentiating the commercial wines are present at very low concentrations not detected with headspace sampling.

REFERENCES

[1] GERSTEL, application notes, http://www.gerstelus.com/apntes.html (accessed February2003).

[2] K. Beebe, R. Pell and M.B. Seasholtz, Chemometrics: a practical guide, John Wiley & Sons (1998).

GERSTEL
AppNote

GERSTEL GmbH & Co. KG
Eberhard-Gerstel-Platz 1
45473 Mülheim an der Ruhr
Germany
☎ +49 (0) 208 - 7 65 03-0
📠 +49 (0) 208 - 7 65 03 33
@ gerstel@gerstel.com
🌐 www.gerstel.com

GERSTEL Worldwide

GERSTEL, Inc.
701 Digital Drive, Suite J
Linthicum, MD 21090
USA
☎ +1 (410) 247 5885
📠 +1 (410) 247 5887
@ sales@gerstelus.com
🌐 www.gerstelus.com

GERSTEL AG
Wassergrabe 27
CH-6210 Sursee
Switzerland
☎ +41 (41) 9 21 97 23
📠 +41 (41) 9 21 97 25
@ swiss@ch.gerstel.com
🌐 www.gerstel.ch

GERSTEL K.K.
1-3-1 Nakane, Meguro-ku
Tokyo 152-0031
SMBC Toritsudai Ekimae Bldg 4F
Japan
☎ +81 3 5731 5321
📠 +81 3 5731 5322
@ info@gerstel.co.jp
🌐 www.gerstel.co.jp

GERSTEL LLP
10 Science Park Road
#02-18 The Alpha
Singapore 117684
☎ +65 6779 0933
📠 +65 6779 0938
@ SEA@gerstel.com
🌐 www.gerstel.com

GERSTEL (Shanghai) Co. Ltd
Room 206, 2F, Bldg.56
No.1000, Jinhai Road,
Pudong District
Shanghai 201206
☎ +86 21 50 93 30 57
@ china@gerstel.com
🌐 www.gerstel.cn

GERSTEL Brasil
Av. Pascoal da Rocha Falcão, 367
04785-000 São Paulo - SP Brasil
☎ +55 (11)5665-8931
📠 +55 (11)5666-9084
@ gerstel-brasil@gerstel.com
🌐 www.gerstel.com.br

ISO 9001
ISO 9001:2015
CERTIFICATE NO. 0086 D

ECOPROFIT®
Awarded for the
active pursuit of
environmental sustainability