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## Analysis of Flavors using a Mass Spectral Based Chemical Sensor

Vanessa R. Kinton

*Gerstel, Inc., 701 Digital Drive, Suite J,  
Linthicum, MD 21090, USA*

Kevin L. Goodner

*USDA, Citrus & Subtropical Products Lab, 600 Ave S,  
NW Winter Haven, FL 3388, USA*

### **KEYWORDS**

Flavors, chemsensor, chemometrics, principal component analysis

### **ABSTRACT**

Development of flavor formulations can be a challenging task. Individual components of different flavor formulations can be varied in composition and quantity depending on the final product desired. For example, if a new formula needs to be developed that matches a certain target a series of trial formulations can be developed and a method that compares samples is needed.

A technique widely used in flavor analysis is gas chromatography coupled with mass spectrometry (GC/MS). The output, a total ion chromatogram (TIC), can be challenging to compare between many samples. This technique can also be time consuming with sample analysis between 30-60 min/sample. In order to simplify the comparison and decrease analysis times, a mass spectrometry based chemical sensor was investigated.

The chemical sensor consists of an x, y, z robot autosampler that is capable of sampling headspace, solid phase

microextraction (SPME) or liquids. The autosampler is directly coupled to a mass spectrometer without a GC which results in MS analysis times of 1-3 min/sample. Multivariate data analysis is then applied to the samples' mass spectral fingerprint and comparison of samples profiles can be easily done with exploratory data analysis.

Different flavor formulations were easily compared against each other by visual inspection of their fingerprint projections into a three-dimensional principal component space. These results were validated by running the same samples with a GC/MS instrument. The GC/MS data was also analyzed in the same manner as the MS-only data and compared. Overall, the fast and easy to interpret output of the chemical sensor was found to be an advantage over the traditional GC/MS analysis.

## INTRODUCTION

Nowadays new flavors appear in a great variety of food products. For example, coffee, teas, yogurts, etc can be purchased in many different flavors. The chemical analysis of these new and exotic flavors can be demanding. A traditional approach widely used in the flavor industry is the use of Gas Chromatography/Mass spectrometry (GC/MS).

Although, GC/MS is a reliable technique, the analysis times can be long (30-60 minutes) and its output (a total ion chromatogram, TIC) can be difficult to compare when many samples are analyzed. In order to simplify the comparison and decrease analysis times, a mass spectrometry based chemical sensor was used in this study. Mass fingerprints were used for comparison instead of the traditional TICs.

The chemical sensor used in the static headspace mode provides high sample throughput. The autosampler is directly coupled to a mass spectrometer without a GC which results in MS analysis times of 1-3 min/sample. Multivariate data analysis is then applied to the samples' mass spectral fingerprints and comparison of samples profiles can be easily done with exploratory data analysis such as principal component analysis (PCA).

The same data analysis that is applied to the ChemSensor data can also be used to examine traditional GC/MS data. This is accomplished by using special macros (ChemSensor macros, Gerstel) that create the samples' fingerprints by adding all the scans present in the TIC. The resulting two-dimensional data set can be analyzed with multivariate software.

## EXPERIMENTAL

Eight different lime and lemon flavor formulations were provided by a customer. Six replicas of each flavor were analyzed using 7.5 uL aliquots. The aliquots were placed in 10 mL vials which were crimped and equilibrated for 15 minutes at 60 °C before static headspace sampling. Since the GERSTEL ChemSensor does not use a column for a 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 eight flavor samples was acquired in 1.20 minute runs in the scan mode using the GERSTEL ChemSensor (Figure 1 GERSTEL ChemSensor, Gerstel). The carbon dioxide peak (from the air in the sample) and the ethanol peaks were avoided by scanning from 48 m/z to 160 m/z range.



**Figure 1.** GERSTEL HeadSpace ChemSensor.

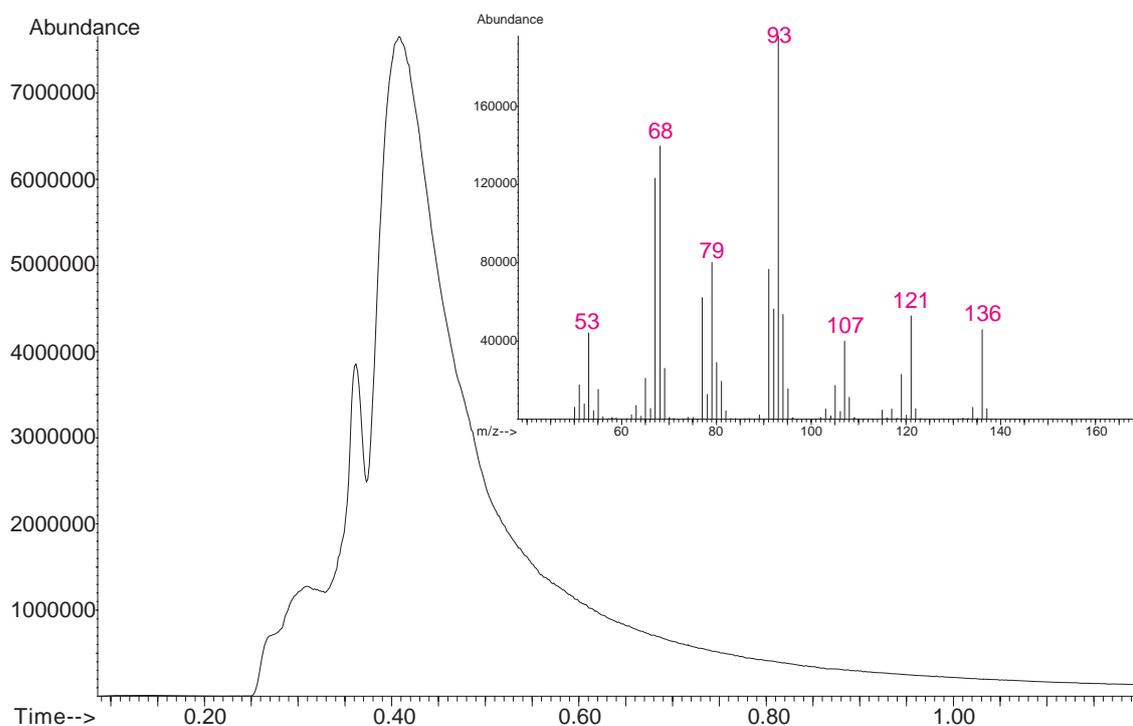
All the eight flavor samples were also analyzed using a GC (6890, Agilent Technologies) coupled to a MSD (5973, Agilent Technologies). This instrument was equipped with a Thermal Desorption autosampler (TDS A, Gerstel). The samples were diluted 10,000 fold and extracted for one hour with stir bar sorptive extraction; SBSE (Twister, Gerstel).

The two data matrices, one for the static HS and another one for SBSE, were created using ChemStation DA with Gerstel macros. For multivariate data analysis Pirouette 3.11 and InStep 2.11 were used. Both data

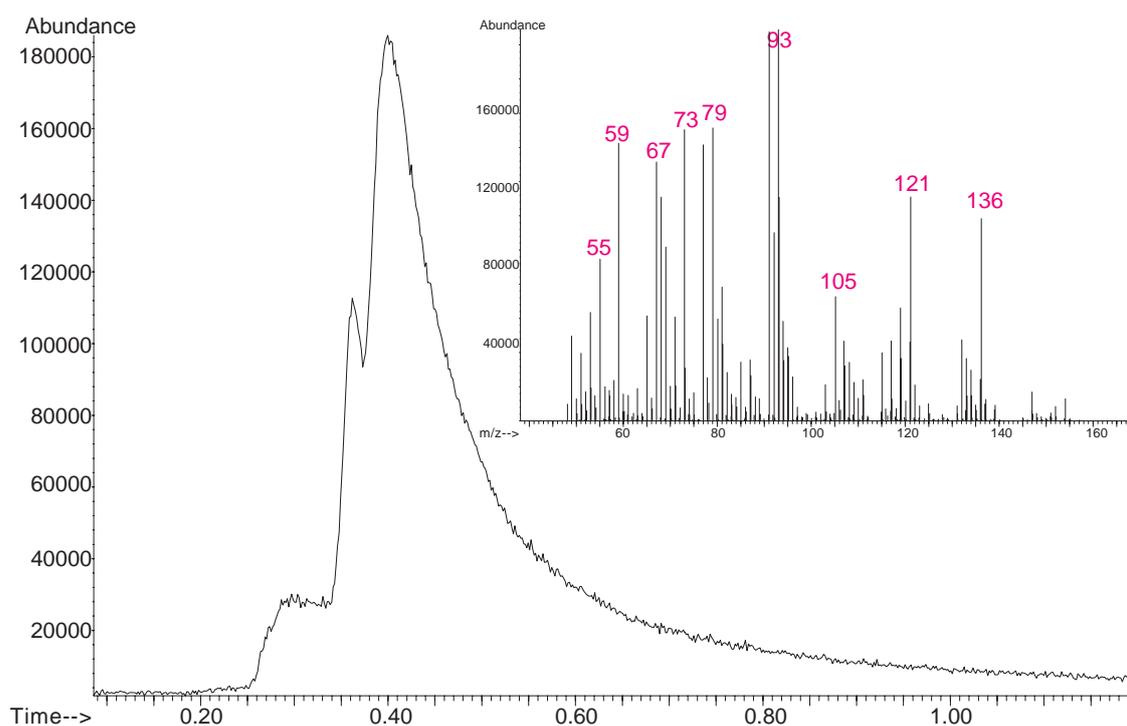
sets were mean-centered and normalized before creating the PCA and SIMCA models

## RESULTS AND DISCUSSION

*Static Headspace analysis.* The entire headspace volatiles of each of the 8 flavor samples were sampled and a characteristic fingerprint mass spectrum was obtained. For example, Figures 2 and 3 represent the TIC and MS obtained for formulations #1 and #8 respectively. From these two figures it can be seen that each flavor sample has a characteristic mass spectrum. Similar results were observed with the mass spectrum from the rest of the flavors formulations.

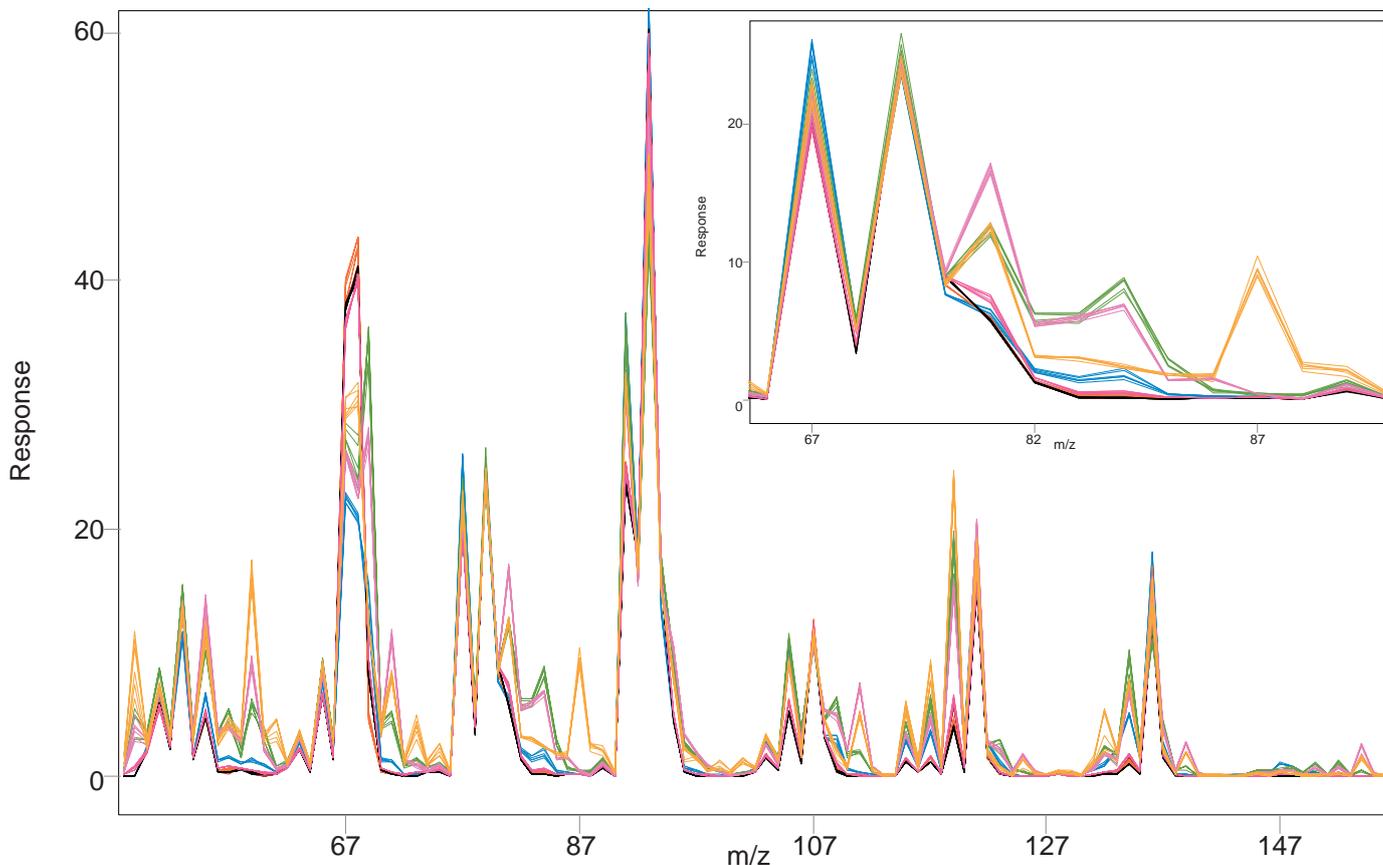


**Figure 2.** TIC and MS of flavor formula #1 obtained with GERSTEL Headspace ChemSensor.



**Figure 3.** TIC and MS of flavor formula #8 obtained with GERSTEL Headspace ChemSensor.

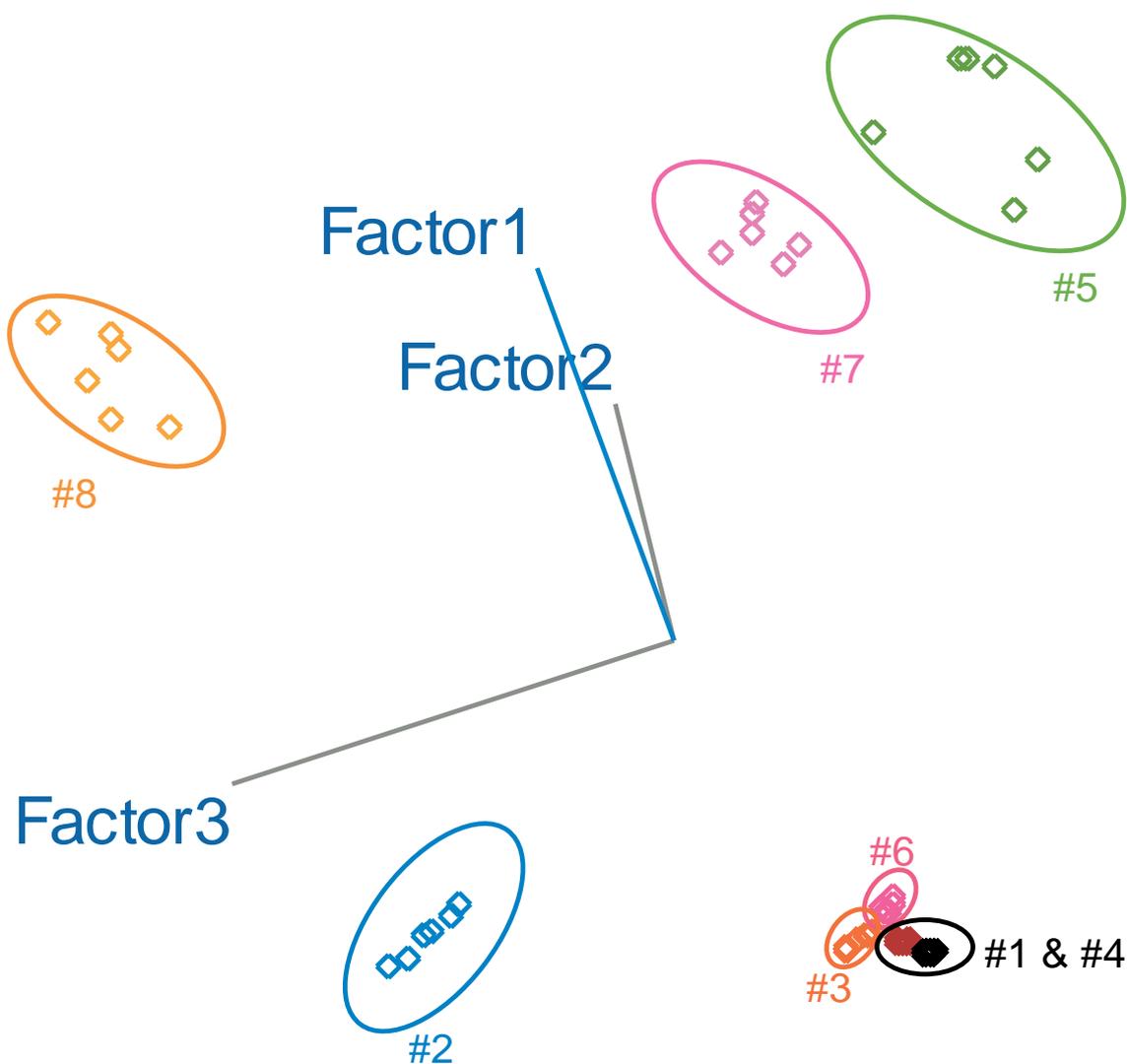
Figure 4 contains the mass spectra line plot of all 8 formulations used for developing the chemometric models. A closer look of the profile is seen in the inset that shows how the different flavor samples have different ion abundance and therefore different mass spectral fingerprints. These results also indicate excellent sample reproducibility since each band represents 6 replicas for each sample.



**Figure 4.** Normalized MS data for the eight different flavor samples.

Exploratory data analysis was carried out with principal component analysis (PCA). Exploratory analysis indicates if the data is appropriate for building a classification model. PCA searches for correlations among all m/z abundances simultaneously and extracts linear combinations of highly correlated m/z abundances (principal components, or PCs) that describe the greatest amount of sample variability. In this particular data set, 95 % of the variance was captured within the first three PCs.

A PCA scores plot is shown in Figure 5, in this plot close distance between points indicates close similarities in the samples mass spectra. For example, formulas #1, #4, #3 and #6 cluster close together which suggests similar chemical composition. On the other hand, samples far away from others such as formula #2 indicate very unique composition. A close examination of the mass spectrum of this sample (light green trace, Figure 4) indicates differences in ion abundances compared to the other samples. Inspection of Figure 5 also indicates very little differences between formulas #1 and #4.



**Figure 5.** Projection of flavor samples into the space of the first three principal components with data acquired using the GERSTEL Headspace ChemSensor.

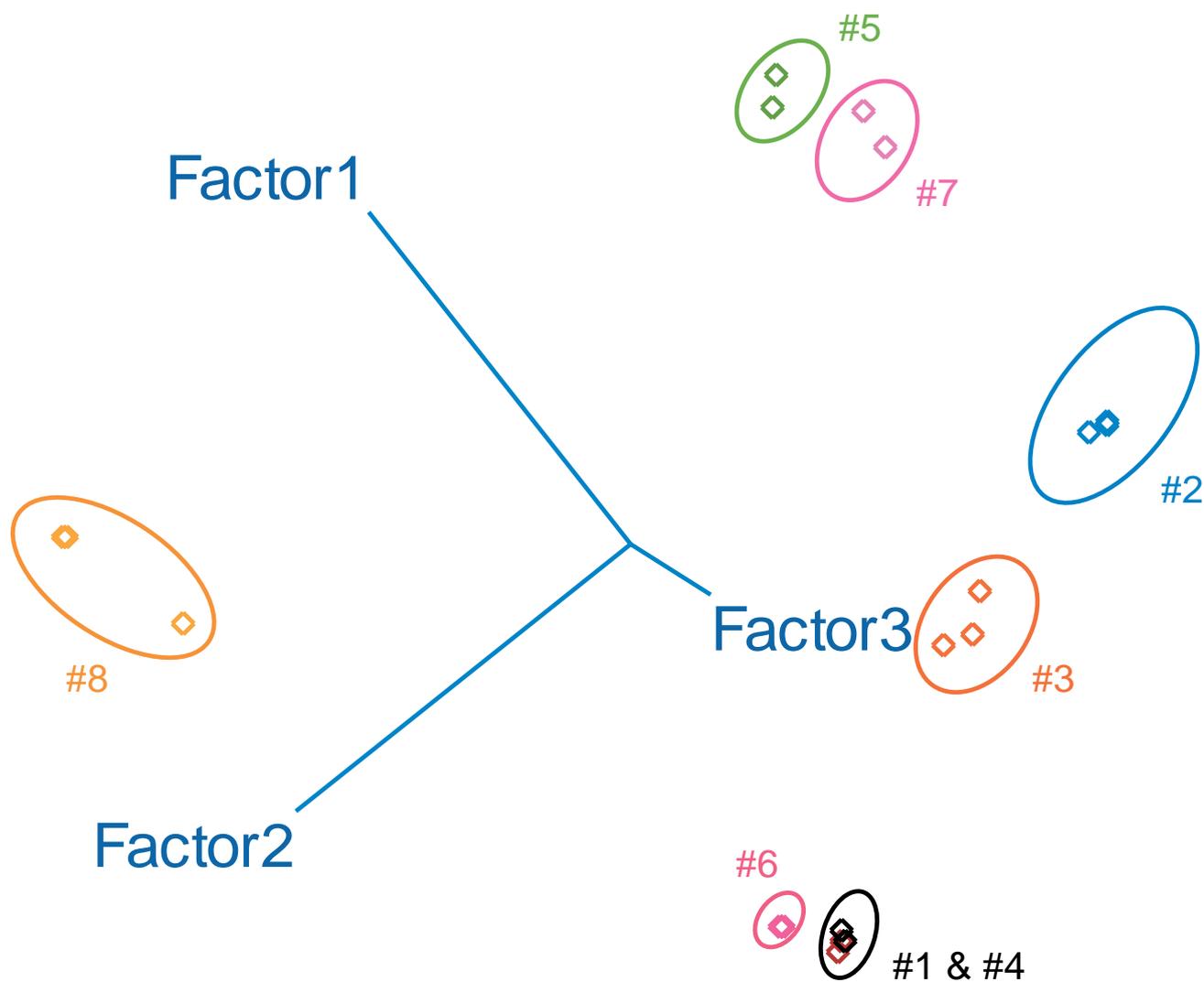
One chemometric model was created with the above data. Soft-independent-modeling-class-analogy (SIMCA) uses PCA to model the shape and position of the samples. An acceptance region is then created for each different type of class. SIMCA models also provide interclass distances between samples, these distances are reported in Table 1.

The larger the interclass distance between two groups, the better separated the groups. As a rule of thumb, interclass distance of 3 or greater indicates good separation between the samples. Interclass distance of less than 3 indicates small differences between the samples. For this analysis, it can be seen that the smallest interclass distance is between flavors #1 and #4 with a value of only 6.4.

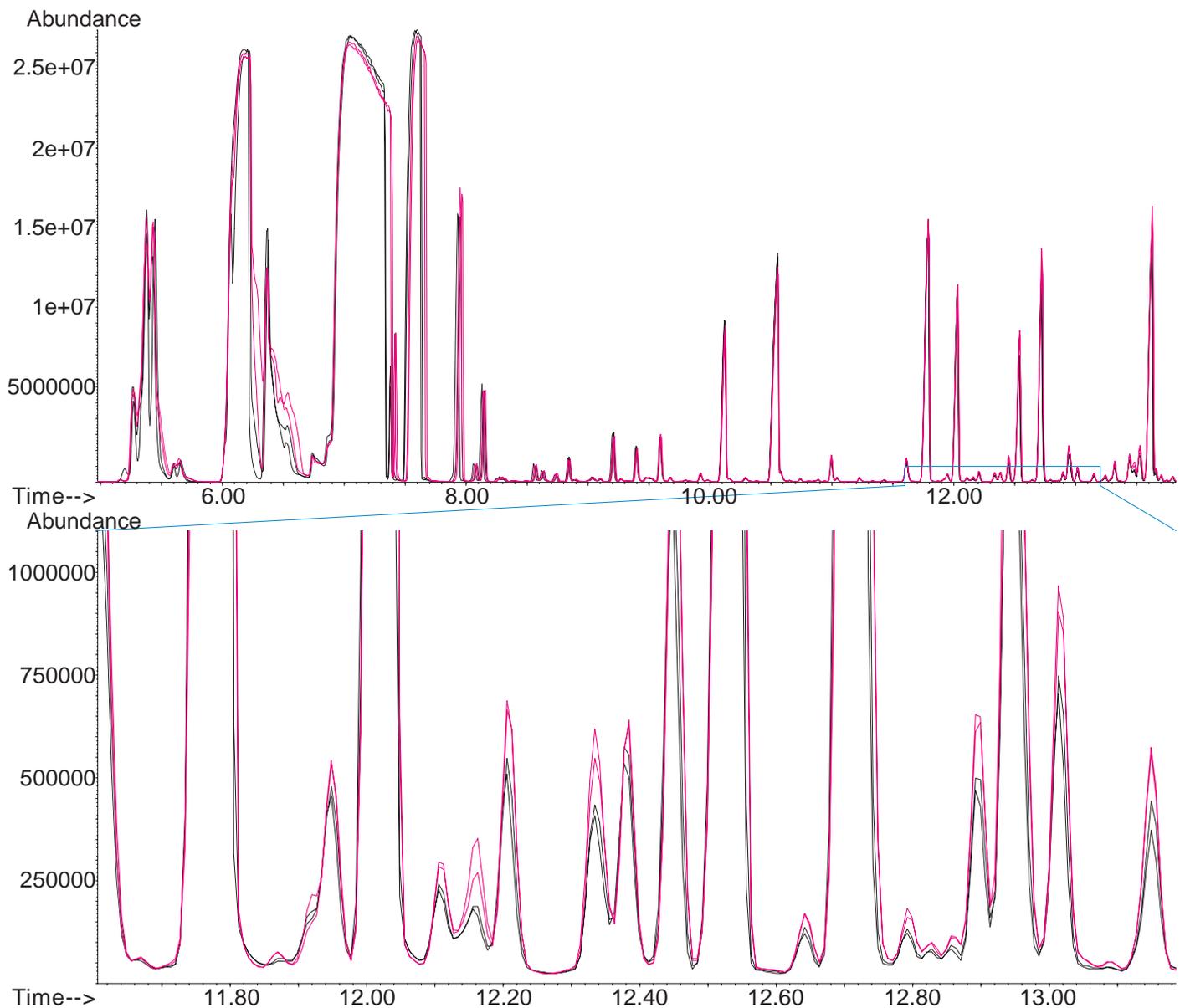
**Table 1.** Interclass distances.

	#1	#3	#4	#6
#1	0.0	24.6	6.4	7.2
#3	24.6	0.0	34.2	24.3
#4	6.4	34.2	0.0	11.3
#6	7.2	24.3	11.3	0.0

*Twister analysis.* All the eight flavors were also analyzed using Twister extraction. The resulting chromatograms for the eight samples indicated some differences between them. A PCA scores plot for the GC/MS flavors is shown in Figure 6. It can be seen in this figure that the clustering is similar to the one obtained with static HS. For example, formulas #1 and #4 cluster very tight, which can also be seen in Figure 5. Figure 7 contains a TIC overlay of formulas #1 and #4, both in replicas. It can be seen from Figure 7 that the chromatograms for formulas #1 and #4 match very closely. These results are in agreement with the results obtained with the GERSTEL ChemSensor.



**Figure 6.** Projection of flavor samples into the space of the first three principal components with data acquired using Twister extraction and GC/MS.

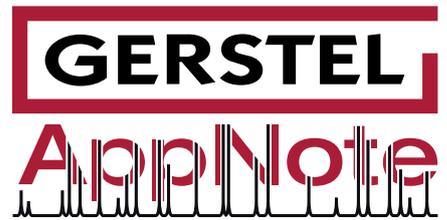


**Figure 7.** Overlay chromatograms of flavor #1 and flavor #4 acquired using Twister extraction and GC/MS.

The biggest advantage of using the GERSTEL ChemSensor instead of the Twister GC/MS analysis lies in the time savings. For example, the analysis of 50 samples required 4 hours using the Chemsensor, while a single Twister GC/MS run was 30 minutes.

## CONCLUSIONS

Differences between 8 different formulations were detected using a mass spectral based chemical sensor with static headspace introduction. Results were validated using traditional GC/MS with SBSE-Thermal Desorption introduction. Advantages of using the chemical sensor include fast sample throughput and easy to interpret results. For this particular application, flavor formula #1 was found to be very similar to flavor formula #4. This result was also confirmed by the flavor supplier.



### 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 Toritsu-dai 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

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