



Analysis of Flavor Formulations Using a Mass Spectrometry-Based Chemical Sensor

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Several different flavor formulations were rapidly and easily compared against each other by using a mass spectrometry (MS)-based chemical sensor system. Results were validated by running the same flavor formulations with a GC-MS instrument. Overall, the fast measurement time and easy-to-interpret report generated by the chemical sensor provided advantages over conventional GC-MS analysis.

New flavors appear in a great variety of food products. For example, coffee, teas, yogurts, etc., are available in many different flavors. Individual components of different flavor formulations can be varied in composition and quantity, depending on the final product desired. Chemical analysis of these new and exotic flavors can be challenging. A traditional approach widely used in the flavor industry is the use of gas chromatography coupled with mass spectrometry (GC-MS).

Although GC-MS is a proven and reliable technique, analysis times can be long (30–60 min) and its output (a total ion chromatogram or TIC) can be difficult to compare when many samples are analyzed. In order to simplify comparison and decrease analysis times, a mass spectrometry based chemical sensor was used in this study.

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, resulting in MS analysis times of 1–3 min/sample. This produces a composite mass spectral “fingerprint” of all components in the sample rather than a TIC or discrete mass spectra of individual components. Multivariate chemometric data analysis is then applied to all of the samples’ mass spectral fingerprints, and comparison of sample profiles can be easily done with exploratory data analysis.

The same multivariate data analysis that is applied to the ChemSensor data can also be used to examine conventional 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 (intensity versus m/z) 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- μ L aliquots. The aliquots were placed in 10 mL vials which were crimped and equilibrated for 15 min at 60 °C prior to static headspace sampling. Since the Gerstel ChemSensor does not use a column for separation ahead of the mass selective detector (MSD), the entire headspace of each sample is directly introduced into the

Table 1: Interclass distances for flavor formulations. The SIMCA model was created with data acquired using static headspace

| Flavor | #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 |

MSD.

The mass spectrum of each of the eight flavor samples was acquired in 1.20 min 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 the range of 48 m/z to 160 m/z .



Figure 1: Gerstel Headspace ChemSensor.

All 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 (TDSA, Gerstel). The samples were diluted 10,000 fold and extracted for one hour using the stir bar sorptive extraction (SBSE) technique (Twister®, Gerstel).

The two data matrices were created using ChemStation DA with GERSTEL ChemSensor Macros. For multivariate data analysis, Pirouette 3.11 and InStep 2.11 were used.

Results and Discussion

Static Headspace Analysis

Headspace volatiles of each of the eight flavor samples were analyzed and a characteristic fingerprint mass spectrum was obtained for each flavor formulation. For example, Figure 2 represents the TIC and MS obtained for formulation #1. Mass fingerprints were also obtained for flavor formulations #2 through #8 (not-shown).

The mass spectral fingerprints of all eight formulations were used for developing chemometric models. Visual inspection of the mass fingerprints for all eight flavors indicated subtle differences in their

respective ion abundances. In many cases, the same ions were present in the different flavor formulations but their ratios were different.

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. [Note: the data sets were mean-centered and normalized before creating the PCA and SIMCA models].

A PCA scores plot is shown in Figure 3. 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 #8 indicate very different composition. For example, formula #8 could represent a formula with an off-odor. Inspection of Figure 4 also indicates very little differences between formulas #1 and #4.

One chemometric model was created with the above data. Classification modeling is performed using SIMCA (soft independent modeling of class analogy) algorithms. 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 on 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. 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. This suggests that formulas #1 and #4 are very similar in chemical composition.

Twister analysis

All the eight flavors were also analyzed using a Twister extraction followed by thermal desorption/GC-MS. The resulting TIC chromatograms for the eight samples indicated some differences between them. A PCA scores plot for the GC-MS flavors is shown in Figure 4. 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 3. Visual inspection of the TIC overlays for formulas #1 and #4 indicated almost no difference. These results are in agreement with the results obtained with the Gerstel ChemSensor.

The biggest advantage of using the Gerstel ChemSensor instead of the Twister TD-GC-MS analysis lies in the time savings. For example, the analysis of 50 samples required 4 h using the ChemSensor, while a single Twister GC-MS run was 30 min.

Conclusions

Differences among eight different flavor formulations were rapidly detected using a mass spectrometry based chemical sensor with static headspace introduction. Results were validated using conventional GC-MS with SBSE-TD 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.

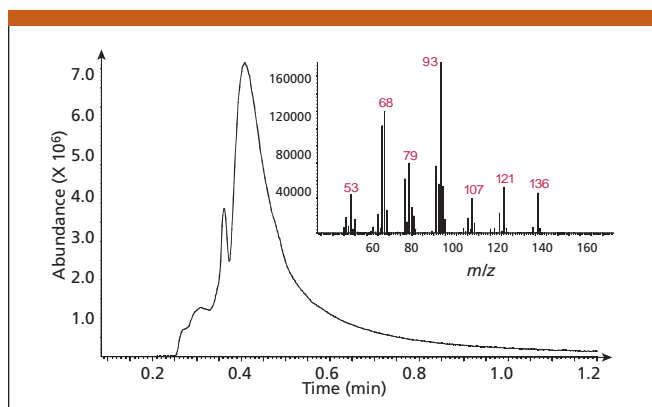


Figure 2: TIC and MS of flavor formula #1 obtained with Gerstel Headspace ChemSensor.

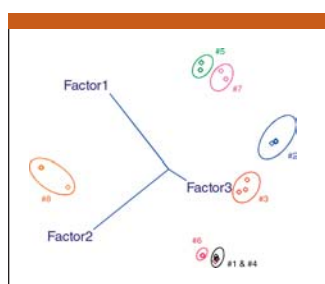


Figure 3: Projection of flavor samples into the space of the first three principal components with data acquired using the GERSTEL Headspace ChemSensor.

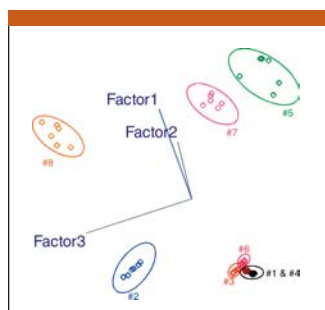


Figure 4: Projection of flavor samples into the space of the first three principal components with data acquired using Twister extraction and GC-MS.

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