Chemometrics

Application Note

Analysis of Product Quality Using Headspace Mass Spectrometry

Abstract

Many products can be characterized by evaluation of their volatile composition. Analysis of volatiles is compelling because the instruments involved in headspace analysis are simple to operate, require little maintenance and results are available with rapid turnaround. One such device frequently used for volatiles is the headspace mass spectrometer.

An early implementation of HSMS, the 4440A, was released by Hewlett Packard in the mid-1990s and was advertized as an alternative to the sensor array approach. The device was sold to Gerstel and is now marketed as the GERSTEL Headspace ChemSensor System.

The applications described in the following pages are examples of headspace analysis by the Headspace Chemical Sensor system. Each application comes with a corresponding data file that is shipped with Pirouette® as part of a demonstration kit and can be processed without a software license.

Java.dat is an example file that is used in the Headspace ChemSensor System User Guide. This file contains data collected from replicates of four Starbucks coffees: Guatemala and Sumatra, both regular and decaffeinated. Running a PCA analysis indicates that these coffees are easily distinguished by their mass spectral fingerprints.

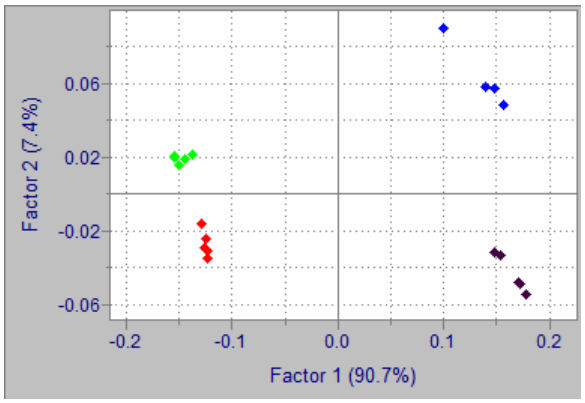

Figure 1. Four different varieties of ground and roasted coffee are easily distinguished by the Headspace ChemSensor and PCA

MoreJava.dat provides additional coffee samples, some of which are new examples of the `Java.dat` coffees, some from other parts of the world and some as aged versions of the target coffees. A Pirouette SIMCA model was made on the first set and an InStep™ method was prepared to classify samples in this set.

InStep Report

Sample	(1 - p)	Match Quality	Coffee Type
Aged DG 1	0.95	Good Match	Guatemala Decaf
Aged DG 2	0.92	Excellent Match	Guatemala Decaf
Aged DG 3	0.93	Excellent Match	Guatemala Decaf
Aged DG 4	0.93	Excellent Match	Guatemala Decaf
Aged DS 1	0.90	Excellent Match	Sumatra Decaf
Aged DS 2	0.89	Excellent Match	Sumatra Decaf
Aged DS 3	0.87	Excellent Match	Sumatra Decaf
Aged S 1	0.84	Excellent Match	Sumatra Regular
Aged S 2	0.91	Excellent Match	Sumatra Regular
Aged S 3	0.83	Excellent Match	Sumatra Regular
Aged G 1	0.98	Good Match	Guatemala Regular
Aged G 2	0.96	Good Match	Guatemala Regular
Aged G 3	0.90	Excellent Match	Guatemala Regular
Ethiopia 1	0.95	Good Match	Sumatra Regular
Ethiopia 2	0.95	Excellent Match	Sumatra Regular
Ethiopia 3	0.96	Good Match	Sumatra Regular
Ethiopia 4	0.96	Good Match	Sumatra Regular
Ethiopia 5	0.96	Good Match	Sumatra Regular
Somalia 1	0.99	No match; closest is	Guatemala Regular
Somalia 2	0.99	No match; closest is	Guatemala Regular

Figure 2. Additional coffee samples along with aged versions and new coffee types are used to show how the system can flag unacceptable batches

Another Coffee application, the **Coffee.dat** data set, includes 60 samples of 10 different Starbucks roasts. Each of the coffee types can be distinguished from one another by comparing the intensities across the mass range. A PCA scores plot illustrates clustering by region.

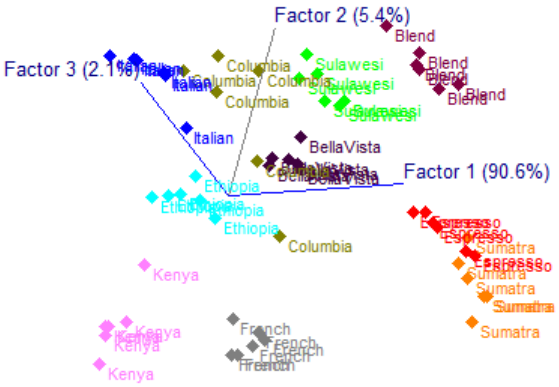

Figure 3. In a comparison of 10 varieties of Starbucks blends, the distinctiveness of each blend is still evident.

Evaluation of pure premium orange juice is possible in the **OJ.dat** data set. Even though there is no significant difference in the starting material (both Tropicana and Minute Maid use fresh-squeeze with no preservatives and no juice from concentrate) we can see distinctions based solely on the process.

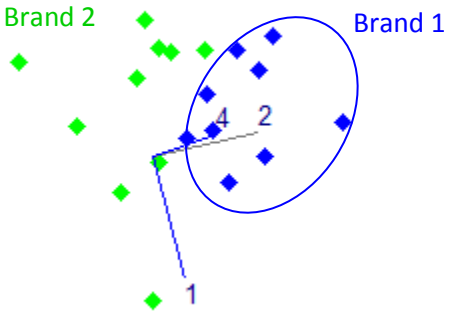

Figure 4. Although the distinction is much less than for many of the food samples shown here, there is still enough discriminating power in the Headspace ChemSensor to distinguish premium orange juices

A comparison of soft drinks by headspace is available in the **Cola.dat** file. Approximately 4 mL of the product was poured into a headspace vial and heated at 80°C to release the volatiles. Note that the presence of CO_2 does not affect the analysis. PCA shows that it is possible to easily distinguish these beverages.

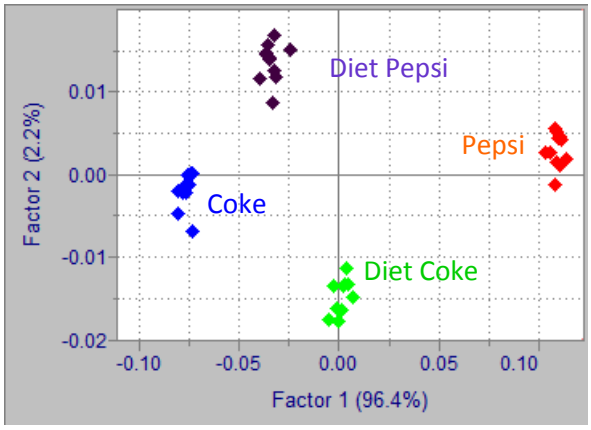

Figure 5. Coca-Cola and Pepsi (both diet and regular) can be easily differentiated using the Headspace ChemSensor ; this is a PCA scores plot showing the distinctiveness

OliveOil.dat contains data on pure virgin olive oils from Spain and Greece plus pure hazelnut oil (a common adulterant). There are also some 5% and 10% hazelnut in Greek olive oil mixtures in this data. Use SIMCA to identify and exclude the Spanish oils, then do a regression analysis to assess level of adulteration.

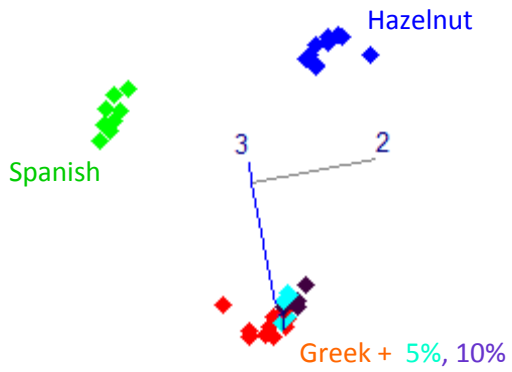

Figure 6. The level of adulteration of olive oil can be tracked using the headspace mass spectrometry system

In the **Butter.dat** set, we utilize the Headspace ChemSensor as a replacement for direct measurement of the peroxide value (PV) in order to monitor the freshness of the butter. The higher the PV number, the more rancid the butter.

data courtesy of Dr. Vincent Shiers, Leatherhead.

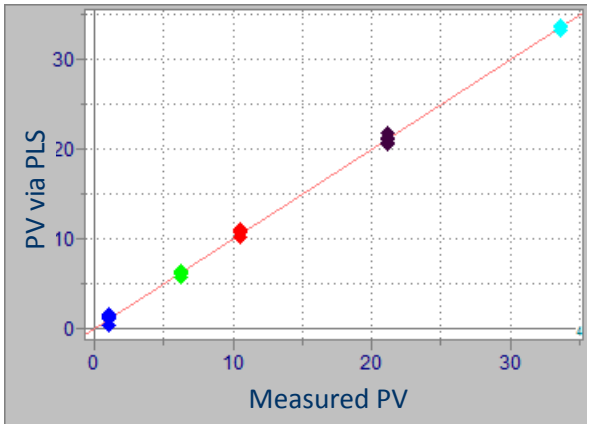

Figure 7. Measuring the peroxide value of butter is time consuming and is replaced with a five minute analysis (with no sample preparation) and a PLS calibration

The **Diesel.dat** file evaluates the kerosene content in diesel fuel. Both are complex mixtures of paraffinic and naphthenic hydrocarbons of approximately the same molecular weight range. This is a quality issue, providing a check on the back-blending that is common in refineries. In addition, there is a safety concern; a high kerosene content increases the risk of automotive fires during accidents.

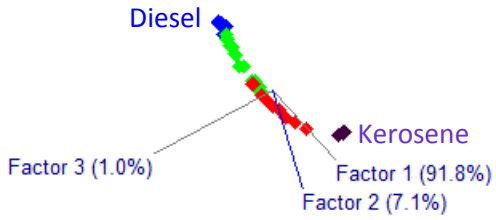

Figure 8. Diesel is a complex mixture of hydrocarbons, but various amounts of diesel in kerosene (a similar mixture of hydrocarbons) can be monitored easily with a regression method such as PLS