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Discrimination of Soft Drinks using a Chemical Sensor and Principal Component Analysis

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Chemometrics, soft drinks, principal component analysis, chemical sensor, electronic nose

Abstract
A new technique that uses a chemical sensor coupled with multivariate analysis is evaluated and applied to discriminate soft drinks from different vendors. The headspace volatiles of different cola samples were analyzed using a chemical sensor that uses quadrupole mass-spectrometer technology. Analysis times per sample averaged between 3 to 4 minutes.

Soft drink samples were used to train the chemical sensor with acceptable mass spectra patterns. Small variations in the mass spectra profiles of the samples were detected using principal component analysis (PCA). In this application, 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.

Mathematical proximity of the soft drinks' mass spectra projections into the 3 dimension PC plot translates into chemical similarity since over 90% of the total variation was

captured within the first 3 PCs. In this case, samples close to each other in the principal component plot resemble each other chemically. PCs of soft drinks from the same vendors clustered together in the three dimensional PC plot validating that this chemical sensor along with multivariate analysis is capable of differentiating mass spectra patterns for the soft drink samples.

INTRODUCTION

Chemometrics refers to the application of multivariate statistical methods in chemistry. The use and popularity of chemometrics 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.

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. They are also built in such a way that each one successively account 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.

In this paper PCA is used in the headspace analysis of soft drinks using a Gerstel ChemSensor 4440 (Figure 1). This instrument integrates the advantages of multivariate analysis such as PCA with well-known technology like quadrupole mass spectrometry. It 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 soft drinks without prior chromatographic separation.

Figure 1. Gerstel ChemSensor 4440.

Experimental

Soft drinks were purchased at a local store; brands A and B were purchased in aluminum cans. Brand C was purchased in transparent plastic bottles (C-bottle) as well as aluminum cans (C-can). Eight replicas of each soft drink 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 ChemSensor 4440 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 for each sample was acquired in 0.75-minute runs in the scan mode. The carbon dioxide peak (from the air in the sample) was avoided by scanning from 46 m/z to 150 m/z range.

Brand C samples in the plastic bottle and in the aluminum can were also analyzed using a GC (6890, Agilent Technologies) with a MSD (5973). This instrument was equipped with a Thermal Desorption autosampler (TDSA, Gerstel). The samples were diluted 10 fold in water and extracted for one hour with stir bar sorptive extraction (Twister, Gerstel).

Results and Discussion

The mass spectrum of each sample can be used as a fingerprint. For example, Figure 2A shows the MS for the soft drink of Brand C from a plastic bottle. Comparison to the MS obtained for Brand C in the aluminum can (Figure 2B) indicates differences in the abundances of some ions such as 46, 69, 93, 119, etc. These differences are also present in the normalized data set (Figure 3).

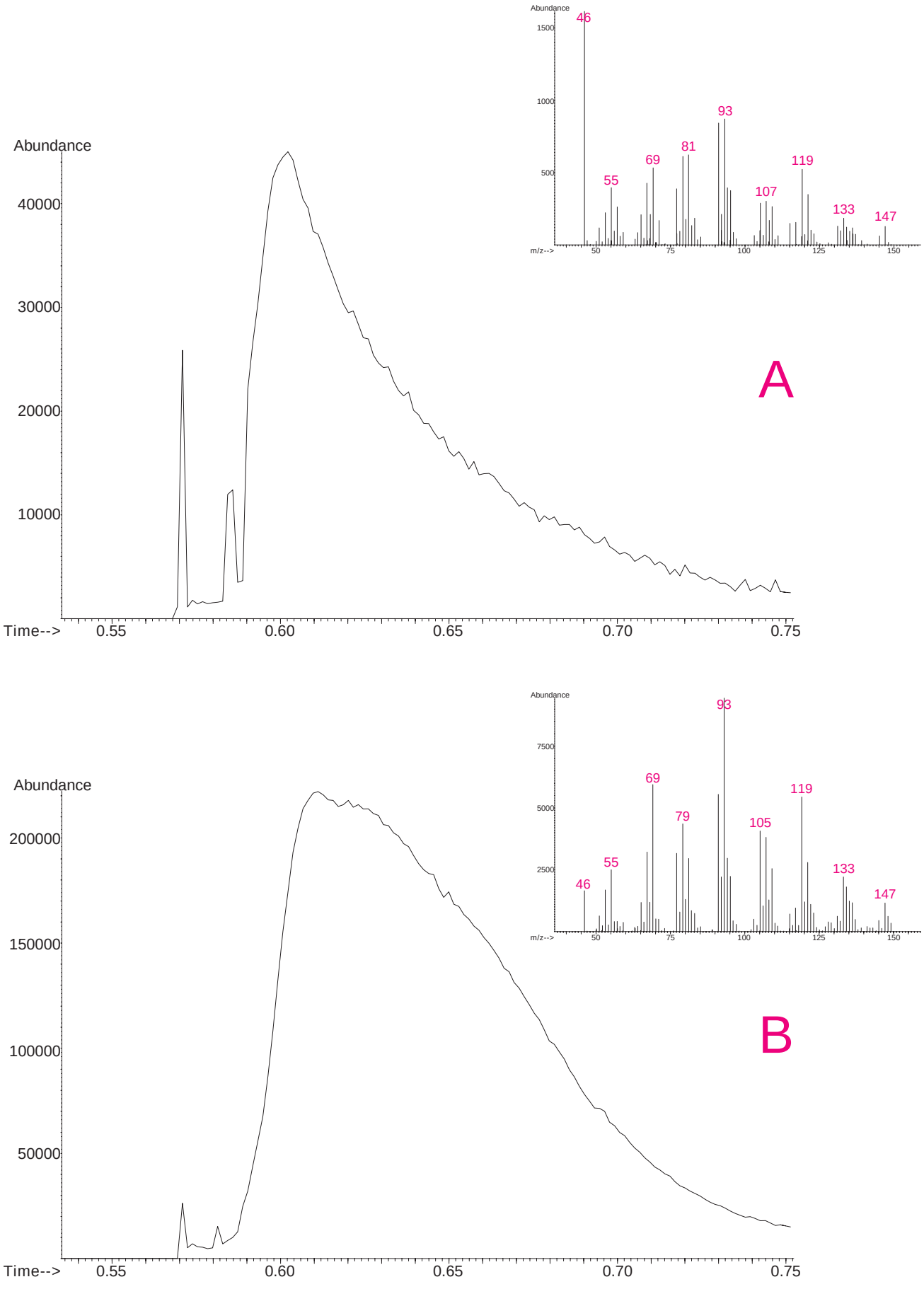

Figure 2. TIC and MS for brand C of soft drink. (A) in plastic bottle and (B) in aluminum can obtained with Gerstel ChemSensor 4440.

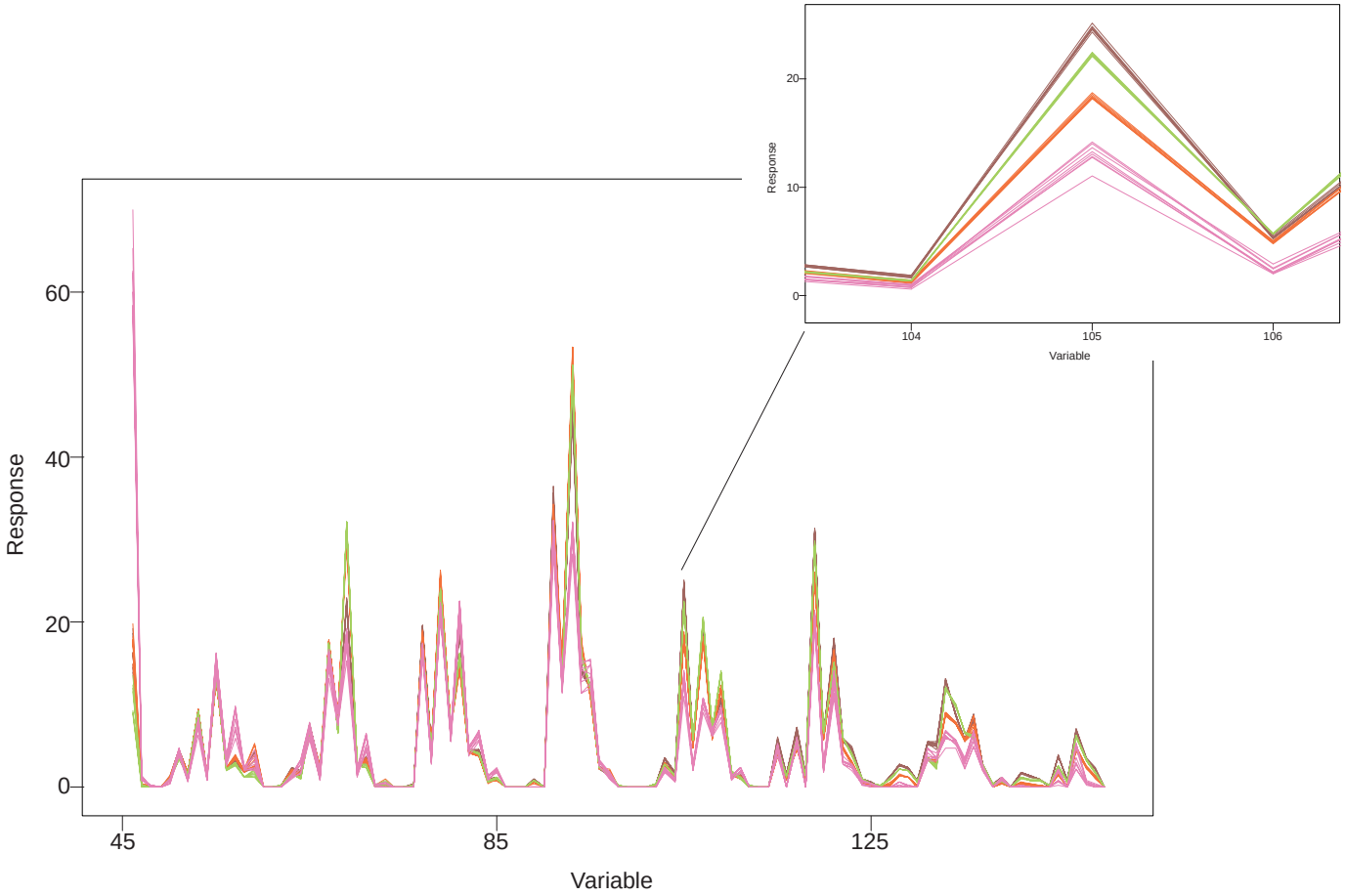

Figure 3. Normalized MS data of sodas.

Projection of the mass spectra of the four soft drinks into the space of the first three (Figure 4A) and two (Figure 4B) principal components shows good clustering between replicas. Since over 90% of the variance was captured within the first 3 PCs, we can be confident that differences in the samples scores are differences in the soft drinks headspace. The first PC (horizontal axis in Figure 4B) explains the difference between brand C in the plastic bottle and the rest of the samples. This indicates that the headspace of brand C in the bottle is very different than the headspace from the other sodas. The second PC (vertical axis of Figure 4B) indicates differences between brands B to A.

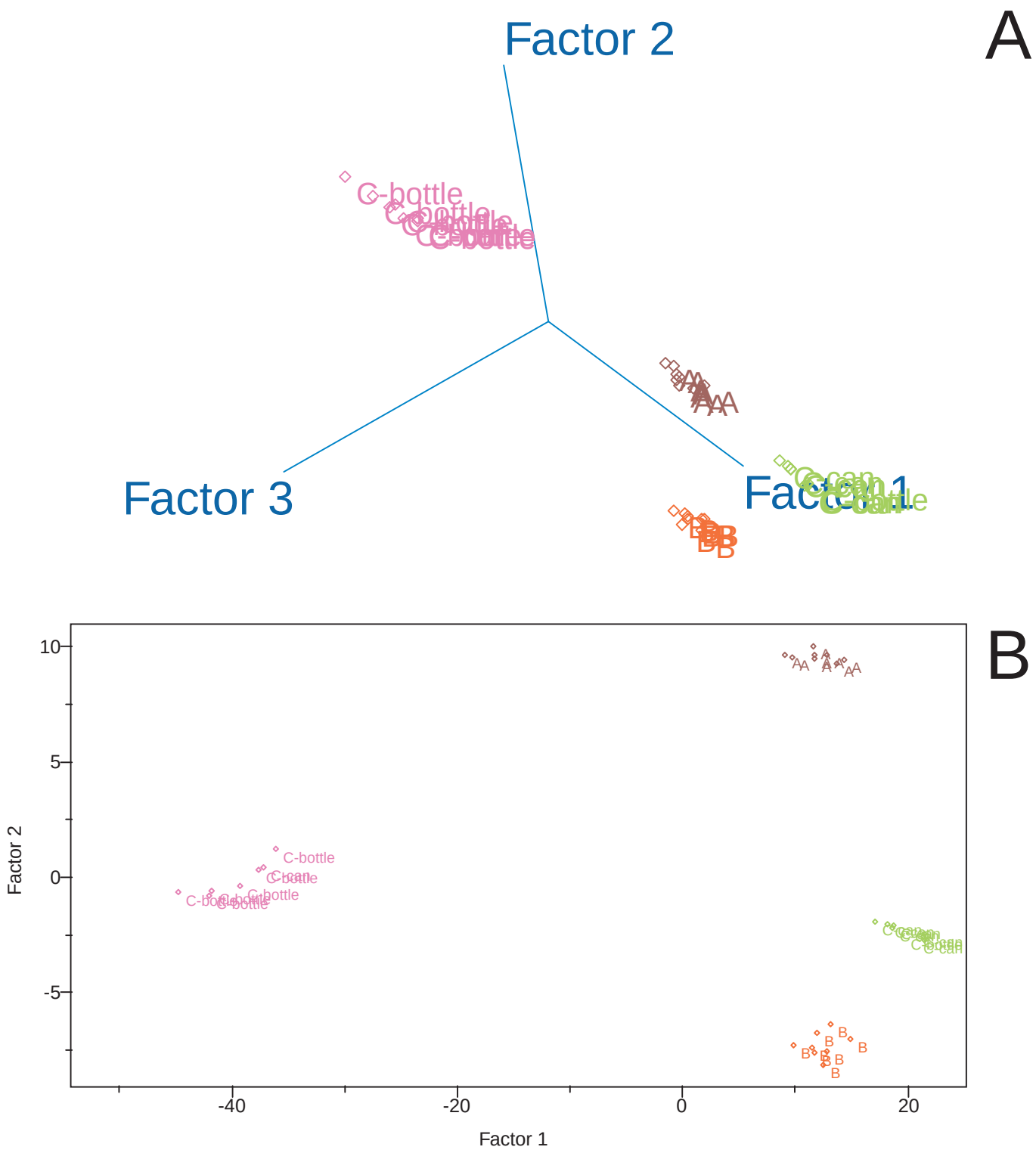

Figure 4. Projection of the sodas mass spectra into the space of the first three (A) and two (B) principal components.

Figure 5 shows the output of cluster analysis using the Euclidean distance and single linkage method. These results are in agreement with the results obtained with PCA. The first cluster is Brand C-bottle indicating a very different sample. Four different clusters can be distinguished in this dendrogram confirming the differences in the headspace of the samples.

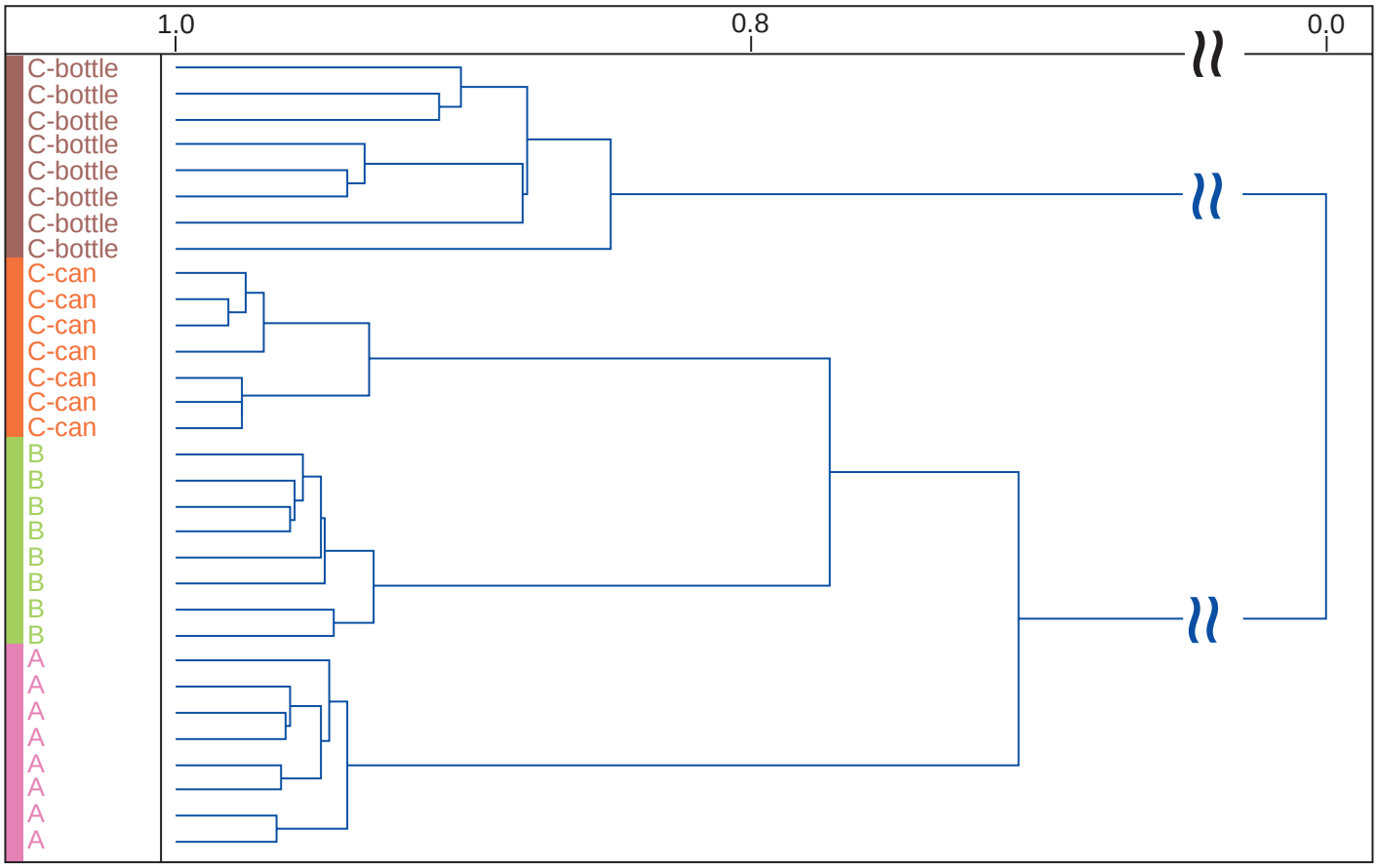

Figure 5. Cluster analysis using the Euclidean distance and the single linkage method.

A total ion chromatogram (Figure 6) obtained with Twister extraction for brand C in the can and bottle show differences in the abundance of some compounds. Table 1 lists some of these compounds with the tentative identification based on MS library matches. Some of these compounds may be light sensitive and therefore have lower area counts in the plastic bottle. For example, ion 119 is the base peak of p-Cymene which area is 77% higher in the Brand C-can than Brand C-bottle.

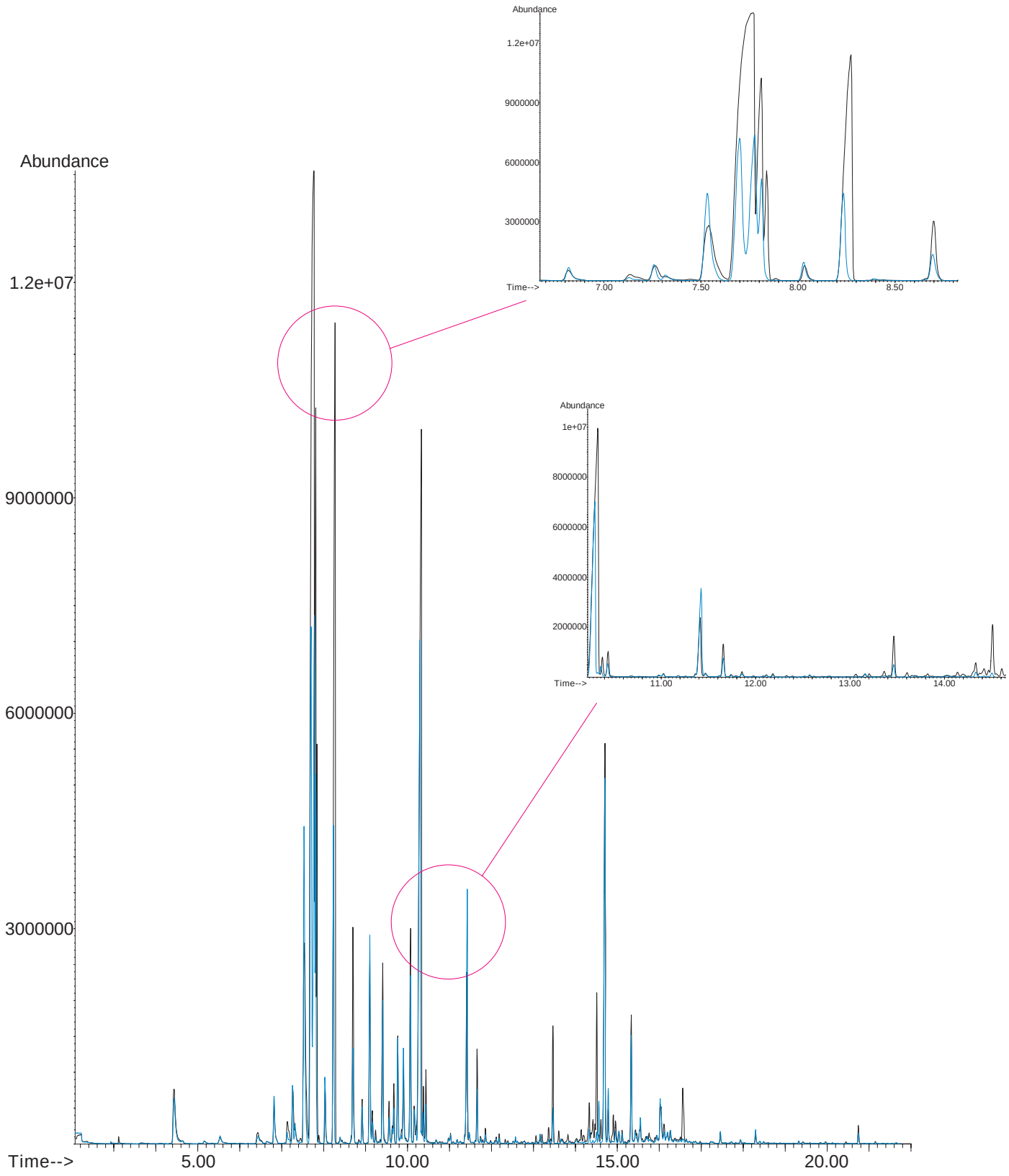

Figure 6. Overlay TIC of brand C soda in plastic and aluminum cans obtained with a GC/MS and Twister extraction.

Table 1. Compounds tentatively identified for brand C in bottle and can.

RT	Compound	CAS-No.	Area Can	Area Bottle
7,54	Isocineole	470-67-7	102069924	103656698
7,70	p-Cymene	99-87-6	746888596	173051194
7,78	dl-Limonene	138-86-3	175379717	166193590
8,27	γ-Terpinene	99-85-4	302596655	72725154
8,70	α-Terpinolene	586-62-9	54000986	25362445
9,10	D-Fenchyl alcohol	1632-73-1	45167850	50816577
10,30	1-α-Terpineol	10482-56-1	354477580	170103762
11,41	Cinnamic aldehyde	104-55-2	40553827	69866792
13,47	Carophyllan-2,6-α-oxide	60269-11-6	24889057	7432300
14,30	β-Maaliene	489-29-2	11638866	3238485
14,50	β-Bisabolene	495-61-4	32557454	2631935
14,78	o-Methoxycinnamic aldehyde	1504-74-1	7232474	10709627
15,96	Benzophenone	119-61-9	np	trace
16,57	α-Bisabolol	72691-24-8	16891946	np

Conclusions

The fast and accurate classification of samples using an instrument that integrates multivariate statistics with mass spectrometry technology is now possible. Principal component analysis of the soft drinks indicates differences in the chemical composition of their headspace. These results are also in agreement with cluster analysis.

It has been shown how the results obtained with the Gerstel ChemSensor 4440 also relate to the results obtained with Twister extraction. Using both techniques together, it is possible to both quickly classify samples and identify the components responsible for the differences.

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