GLOBAL ANALYTICAL SOLUTIONS

GERSTEL

AppNote 1/2003

Fast Analysis of Food and Beverage Products using a Mass Spectrometry Based Chemical Sensor

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Keywords

Chemometrics, ChemSensor, electronic nose, mass spectrometer (MS), headspace, SPME, HSSE, quality control, Yoghurt, Olive Oil, Coffee.

Abstract

In this study, different food and beverage samples were analysed without chromatographic separation by direct transfer of their analytes into a mass spectrometer or by disregarding chromatographic separation. Three different sample introduction techniques – Headspace, Solid Phase MicroExtraction (SPME) [1], and HeadSpace Sorptive Extraction (HSSE) – were used. Mass spectral fingerprints were compared using pattern recognition software. Multivariate statistics were used to create models that classify samples or detect spoilage and adulteration. Exploratory analysis such as principal component analysis (PCA) and hierarchical cluster analysis (HCA) indicated the viability of the data sets for classification models. Soft-independent-modelling-of-class-analogy (SIMCA) and K Nearest

Neighbours (KNN) were used to create classification models. Both SIMCA and KNN provided a quick and accurate classification of the foods and beverages with and without spoilage or adulterations.

Yoghurt, olive oil and coffee were examined under different aspects. Results indicate the successful identification of bad yoghurts lots although using different flavours. Also olive oils could be classified between degassed or not. Coffee samples could be differentiated in Robusta and Arabica as well as into there country of origin.

Introduction

Contamination, adulteration and inconsistencies in food and beverage samples should be detected fast but accurate. Chemical Sensors provide such fast measurements and are therefore ideal for these kinds of measurements. Even if throughput is crucial, precision and accuracy should never be compromised. The GERSTEL ChemSensor uses a reliable technology that is stable to changes in environmental factors like temperature and humidity.

Poor discrimination between samples cannot be compensated by building complex chemometric models. A more promising approach is to find a better sample introduction technique to improve the obtained discrimination. An appropriate technique depends not only on the characteristics of the analysed sample but also on the problem the instrument is applied for. When confronted with a wide range of problems it is essential to have an instrument that covers most common introduction techniques like the ones used in this study.

In order to illustrate the potential of this technology, three different applications have been explored. For production control of yoghurt a pass/fail screener is demanded. Discrimination of olive oils into degassed or non degassed ones is a typical quality control application. The classification of coffee is of special interest to achieve reproducible blends. All these applications are of major interest for customer acceptance. Standard samples were used to train the ChemSensor with mass spectral fingerprints.

Materials

Materials. Several lots of strawberry yoghurts were supplied by NIZO Food Research (Ede, The Netherlands). About half of the samples were aged and two types (22, 23) contained a different flavour.

Olive oil samples were provided by a customer. Five sample types were pure olive oils (Z, V, A, K, T) and 3 were degassed (W, D, R).

Coffee samples were from the Technical University of Gent (KaHo, Belgium). These were each 3 different Arabica (Brazil Santos, Java Ling Tung, Kenya) and Robusta (Grain Noir, Soft African, Vietnam) coffees.

Sample preparation.

Yoghurt: 3 g of each sample was weighed into 10 mL headspace vials and the vials were immediately sealed with crimp caps.

Olive Oil: 2 g of each sample was weighed into 10 mL headspace vials and the vials were immediately sealed with crimp caps.

Coffee: 2 g of each sample was weighed into 20 mL headspace vials. One Twister in a glass insert was added and the vials were immediately sealed with crimp caps. The vials were placed in an oven for 2 h. After that the vials were decapped and the Twister were introduced in TDS tubes. These were immediately placed in a TDS A magazine.

Instrumentation and Methods

Three different ChemSensor configurations were used in this study. GERSTEL ChemSensor Software controlled all configurations of the ChemSensor Systems. This instrument integrates chemometric software from Infometrix (Pirouette 3.11 and Instep 2.11).

Yoghurts with the Headspace ChemSensor. The Headspace ChemSensor (Figure 1) consists of a MultiPurpose Sampler MPS 2 (GERSTEL, Mülheim an der Ruhr, Germany) coupled to a Mass Spectrometer (MSD 5973, Agilent Technologies, Little Falls, DE, USA) via a ChemSensor Interface equipped with a PTV inlet (GERSTEL CIS 4 Plus). The strawberry yoghurts were incubated for 15 min at 40 °C. 2 mL of the headspace of these samples was injected into a PTV inlet (180 °C, split 10:1). The MSD was programmed to scan from 35 to 150 amu for 1 min. Samples were injected every 3.5 min. The analysis consisted of 5 replicas of each sample.

Figure 1. GERSTEL Headspace ChemSensor.

Olive Oils with the SPME ChemSensor System. The SPME ChemSensor Systems (Figure 2) consisted of a GC/MS System (6890/5973N, Agilent) equipped with a MPS 2 autosampler and PTV inlet (GERSTEL CIS 4). The samples were preincubated at 40 °C for 25 min and then extracted for 15 min using a 75 µm Carboxen/PDMS fibre. The fibre was desorbed into the PTV Inlet (280 °C, split 10:1). The GC was programmed with a fast ramp from 40 °C to 280 °C using a HP5-MS column (30 m x 0.25 mm x 0.25 µm). The MSD was programmed to scan from 35 to 200 amu for 8.72 min. The analysis consisted of 6 replicas of each sample.

Figure 2. GERSTEL SPME ChemSensor System.

Coffee with the ThermoDesorption ChemSensor System. The TDS ChemSensor Systems (Figure 3) consisted of a GC/MS System (6890/5973N, Agilent) equipped with a ThermoDesorption System (GERSTEL TDS A/TDS 2) and PTV inlet (GERSTEL CIS 4). Coffee samples were analysed by HSSE using a GERSTEL Twister (0.5 x 10 mm). Samples were incubated at 40 °C for 2 h using the Twister [2] in the headspace mode. The analytes were desorbed into a PTV at –150 °C. By increasing the inlet temperature to 280 °C the analytes were transferred to the MSD in the splitless mode. The GC was held at 250 °C for 5 min using a HP5-MS column (30 m x 0.25 mm x 0.25 µm). The MSD was programmed to scan from 40 to 180 amu. The analysis consisted of 8 replicas of each sample.

Figure 3. GERSTEL ThermoDesorption ChemSensor System.

Results and Discussion

Strawberry Yoghurts by Headspace – Mass Spectrometry. The goal of the analysis was to differentiate the samples into good (red, violet) and bad (green, blue) quality. The results show that it is possible to classify the different lots not only into fresh and aged but also which flavour has been used (Figure 4).

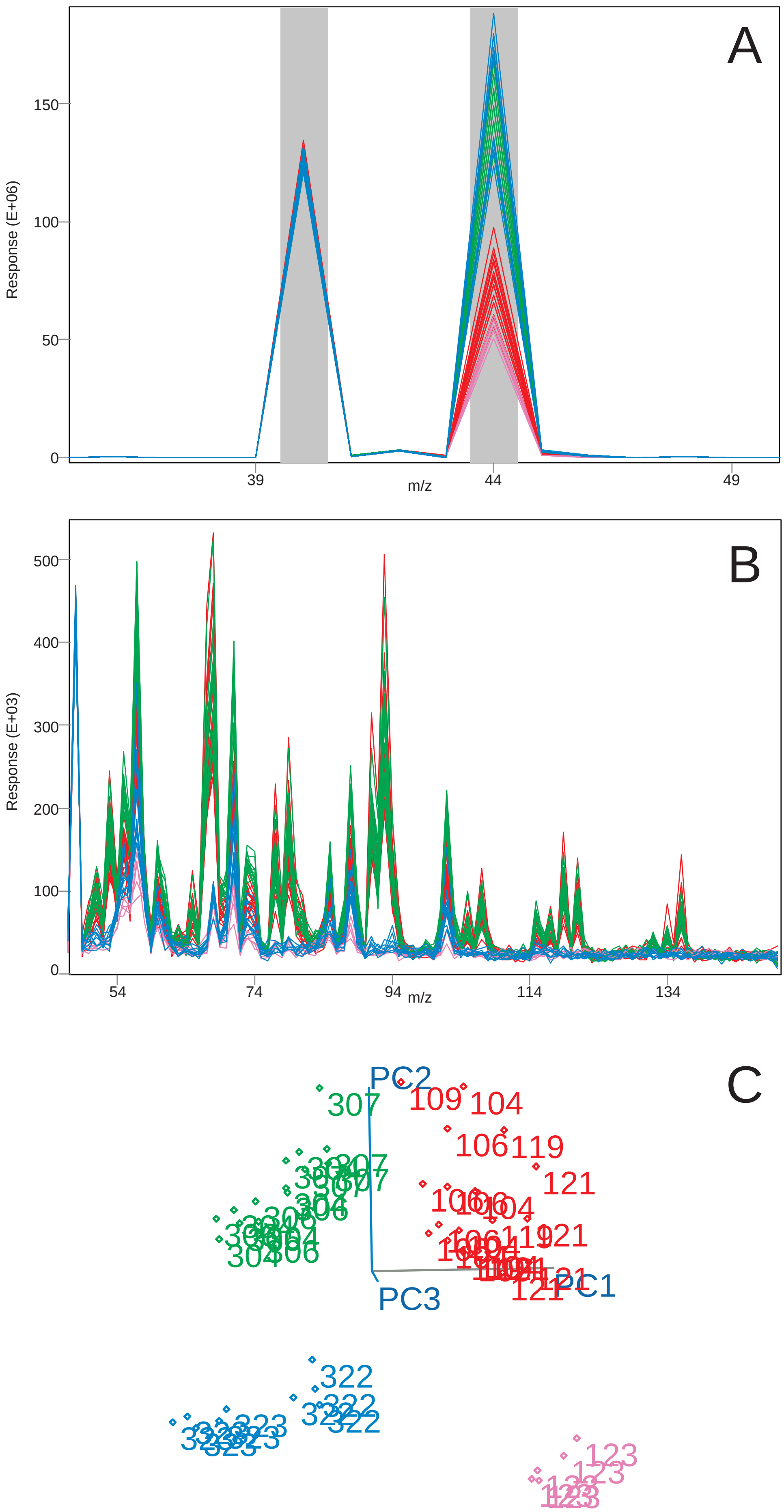

Figure 4. Lineplot 35 – 50 amu (A) and 50 – 150 amu (B). SIMCA 3D plot (C) of strawberry yoghurt as obtained by Headspace-Mass Spectrometry.

The first part of the lineplot (Figure 4A) shows that good and bad qualities can be discriminated mainly basing on m/z 44 (acetaldehyde) while the second part (Figure 4B) shows that the difference in the utilised flavour only affects the higher masses. As can be seen from the SIMCA 3D plot good (fresh) and bad (aged) strawberry yoghurts can be clearly discriminated. Fresh samples have positive values on the factor 1 axis while aged samples have negative values. Factor 2 discriminates between the different flavours used.

Olive Oils by SPME – Mass Spectrometry. For quality control it is important to classify if olive oils are pure (red) or degassed (green). The SIMCA algorithm was able to model these differences easily. Further more the SPME technique distinguishes the five types of pure olive oils (Figure 5). For the degassed samples no discrimination within the types was obtained due to the low content of volatile compounds that leads to low signal (Figure 5A).

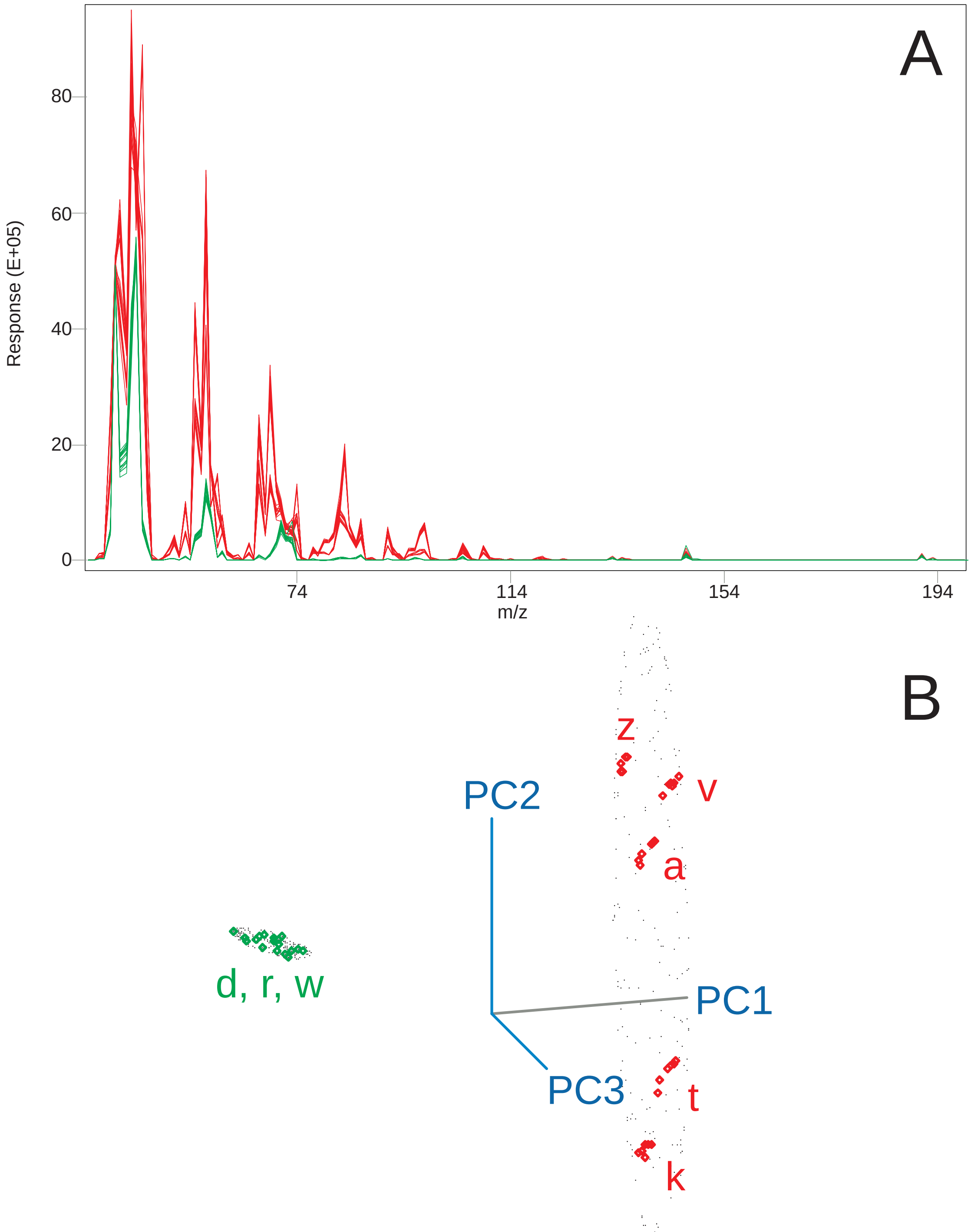

Figure 5. Lineplot (A) and SIMCA 3D plot (B) of degassed (negative PC1) and pure olive oils (positive PC1) as obtained by SPME-Mass Spectrometry.

Coffee by HSSE TDS – Mass Spectrometry. For coffee classification into Robusta and Arabica as well as their country of origin was demanded [3, 4, 5]. A SIMCA model was created after excluding the ions caused by column bleed (73, 133, 147 and 177), Twister material (75, 173) and phthalates (149). Figure 6 shows a clear discrimination between the Arabica and Robusta coffees.

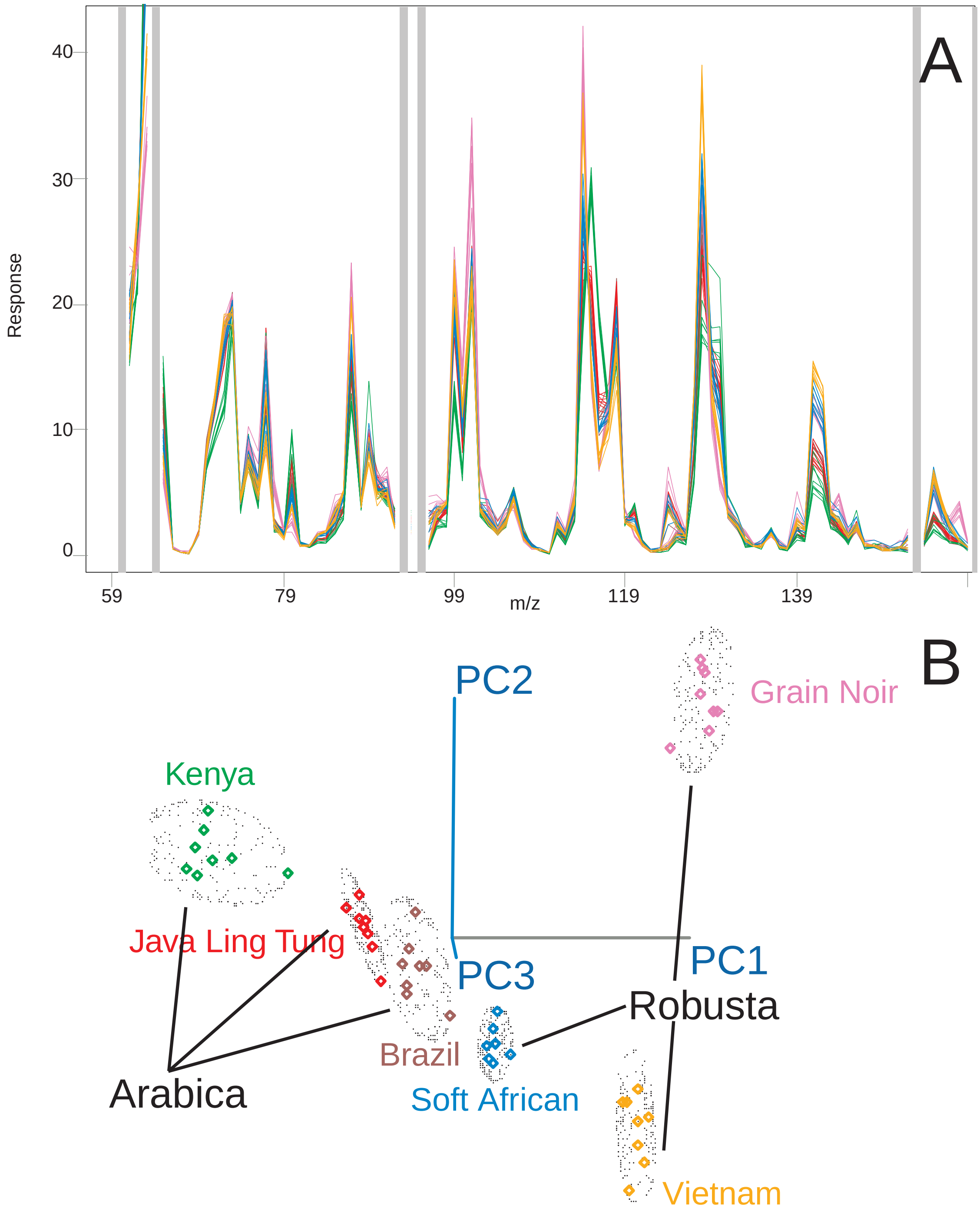

Figure 6. Lineplot (A) and SIMCA 3D plot (B) of Robusta and Arabica coffees as obtained by HSSE TDS-Mass Spectrometry.

Note that Robusta coffees have positive values of Principal Component (PC) 1 while Arabica coffees show negative values. Within the group of Arabica and Robusta coffees clear discrimination into regions can be found. Even coffee types Brazil Santos (brown) and Java Ling Tung (red) can be discriminated (the multidimensional plot is misleading).

Comparing Sample Introduction Techniques. All sample types were analysed using the chemometrics approach with all three different sample introduction techniques. It is not always straightforward to decide which sample introduction technique is the most useful. In general all sample introduction techniques lead to different results because a different compound range is amenable by the sample introduction technologies. The best technique depends on the criteria the user sets for his product to be most important for the quality.

Conclusion

In all cases, testing sets were correctly classified. Overall, the positive and fast identification of spoilage and adulteration demonstrates the usefulness of the MS chemical sensor detecting samples with close chemical composition. More results about the classification of food and beverages have been published [6, 7].

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