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Classification of Coffees from Different Origins by Chemical Sensor Technology

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Introduction

Digital odor characterization, such as chemical sensor technology or mass spectrometry-based electronic nose (MS-based e-nose), can be very useful for the classification of Arabica and Robusta varieties with regard to 'flexible blending' in the coffee industry.

Preliminary flavor analysis has been performed on green and roasted Arabica and Robusta coffees by simultaneous steam distillation extraction-gas chromatography-mass spectrometry (SDE-GC-MS) [1,2]. In such studies, principal component analysis (PCA) on the semi-quantitative SDE-GC-MS profiles revealed a good discrimination between Arabica and Robusta species. Furthermore, within the Arabica species some meaningful clusters were differentiated in good accordance with sensory descriptors, demonstrating a good correlation between sensory and chemical-analytical data [2]. Although the classical SDE-GC-MS approach demonstrated good classification results, it was considered time-consuming (total analysis time/coffee sample = 6 h of which 4 h are for SDE).

Objectives

The aim of this study was to explore the feasibility of chemical sensor technology for the classification of coffees from different origins. As opposed to the SDE-GC-MS approach, chemical sensor technology or mass spectrometry-based electronic nose can be considered as a fast analytical technique.

Materials and Methods

Coffee Samples

- coffee beans from 6 coffee varieties: 3 Arabicas, 3 Robustas
- standardized roasting with a Rotating Fluidized Bed (RFB) Junior roaster (Neuhaus Neotec®, Germany) (medium roast)
- packaging with CO_2 in PET metallized 15 µ/PE 80 µ packages with an external, one-way valve (Bosch®, Germany)
- grinding in a laboratory coffee grinder prior to analysis

Arabica	Robusta
Brazil	Vietnam
Java	Soft African
Kenya	Grain Noir

Static Headspace-Chemical Sensor (S-HS-ChemSensor)

- hyphenated S-HS-ChemSensor configuration:

    6890/5973N GC-MS system

    (Agilent, Palo Alto, CA)

    fully-automated MultiPurposeSampler or MPS 2 (Gerstel, Mülheim an der Ruhr, Germany)

    Pirouette® 3.02 pattern recognition software (Infometrix, Woodinville, WA, USA)

- fully-automated S-HS sampling with MPS 2 (Gerstel):

    2-g roasted and ground coffee samples (10 replicates/origin)

    10-ml vials

    incubation in agitator of MPS 2: T = 80 °C; t = 60 min

    injection volume headspace: V = 2500 µl

- ChemSensor analysis:

    injector: T = 250 °C

    column: PONA cross-linked methyl silicone (50 m x 0.2 mm I.D. x 0.5 µm film thickness); T = 250 °C

    injection mode: split (1:30)

    carrier gas: helium (1 ml/min)

    transfer line: T = 280 °C

    scan range: 40-180 m/z (70eV)

    solvent delay: t = 2.0 min

    run: t = 5.0 min

Figure 1. Gerstel Headspace ChemSensor System.

Pattern Recognition (Pirouette® 3.02)
ChemSensor data were imported into Pirouette® 3.02 software, generating a complete data matrix (60 samples x 141 variables) which can be visualized as mass fingerprints (Figure 2).

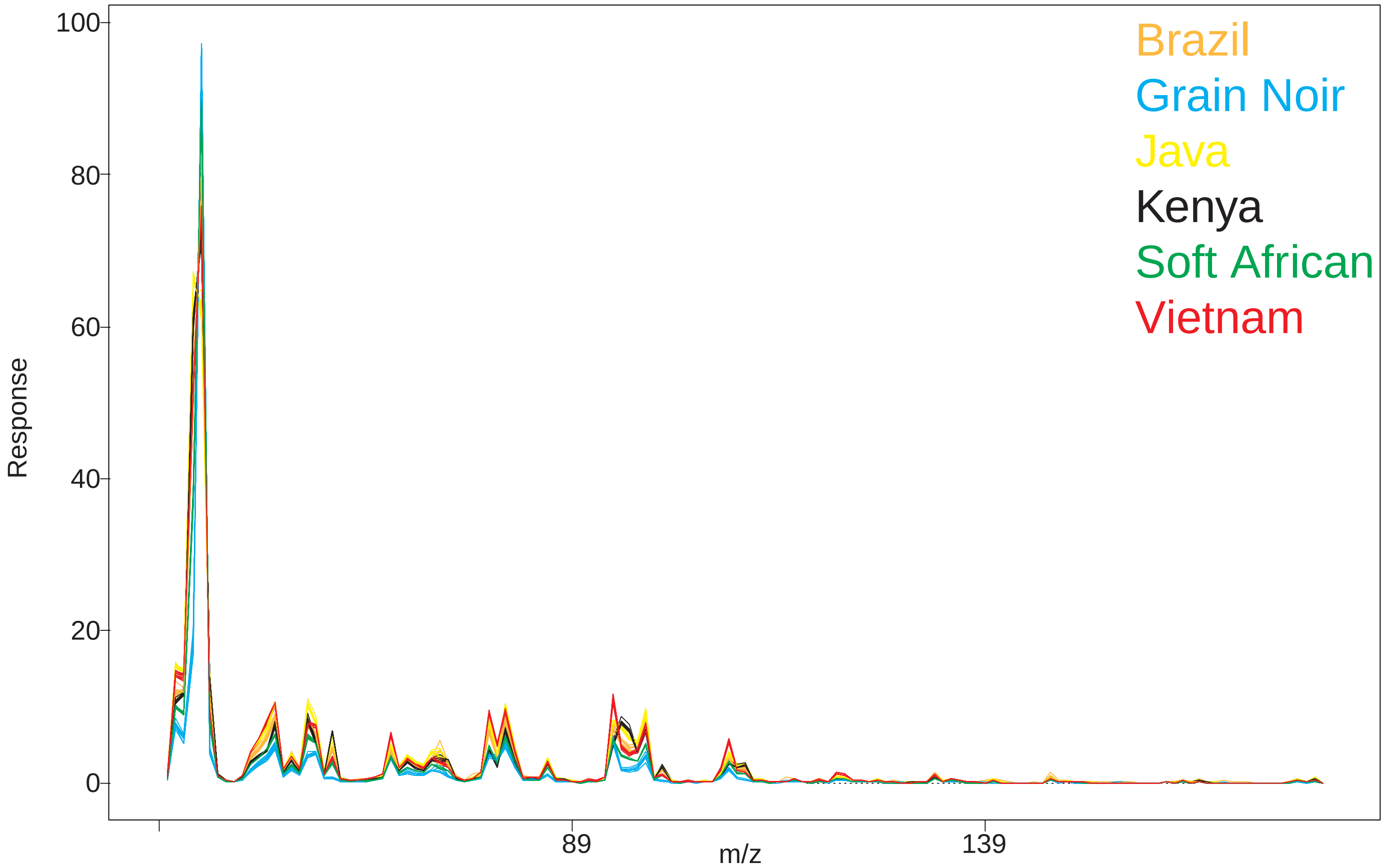

Figure 2. Mass fingerprints (10 replicates/origin) of roasted Brazil, roasted Java, roasted Kenya, roasted Grain Noir, roasted Vietnam, roasted Soft African, obtained with S-HS-ChemSensor.

During feature selection some variables were excluded from the complete data matrix: m/z 44 (CO_2), m/z 73 and 133 (column bleeding) and m/z 141 to 180 (noise: no isolation of high boiling aroma compounds with S-HS).

Algorithms used for data analysis
- Exploratory Analysis
  - Hierarchical Cluster Analysis (HCA)
  - Principal Component Analysis (PCA)
- Classification Analysis
  - Soft Independent Modeling of Class Analogy (SIMCA)
  - k-Nearest Neighbors (KNN)

Results and Discussion

For isolation of coffee aroma compounds in combination with chemical sensor technology fast automated isolation procedures are necessary. Although simultaneous steam distillation extraction (SDE) resulted in good classifications between coffees from different geographical origins [1,2], it was considered time-consuming and laborious. Commercially available electronic noses use almost exclusively static headspace (S-HS) as isolation technique. Therefore, S-HS was evaluated as a rapid isolation technique for coffee volatiles with regard to digital odor characterization. In comparison with SDE, S-HS requires shorter analysis times (1 h instead of 4 h), it also can be used on-line and fully-automated.

The basis of this now commercially available ChemSensor configuration was a GC-MS system (Agilent) with a fully-automated MultiPurposeSampler or MPS 2 (Gerstel) for on-line isolation of aroma compounds. The MPS 2 has the ability to perform two fast, fully-automated isolation techniques, such as static headspace (S-HS) and solid phase microextraction (SPME). Depending on the food matrix different fast isolation techniques can be applied with this ChemSensor configuration. This is in contrast with commercially available MS-based electronic noses, which almost exclusively use S-HS. The choice for other fast isolation methods is indispensable for highly flexible chemical sensor analysis.

Due to the high column temperature (250 °C) no chromatographic separation was performed as the aroma compounds were directly transferred to the MS. This configuration with the GC column at high temperature has the advantage of high flexibility because with the same configuration both GC-MS mode and ChemSensor mode can be applied, which is particularly useful in a R&D environment.

Hierarchical cluster analysis (HCA) on the complete data set (after feature selection and exclusion of outliers) revealed intrinsic differences between the coffee samples (Figure 3).

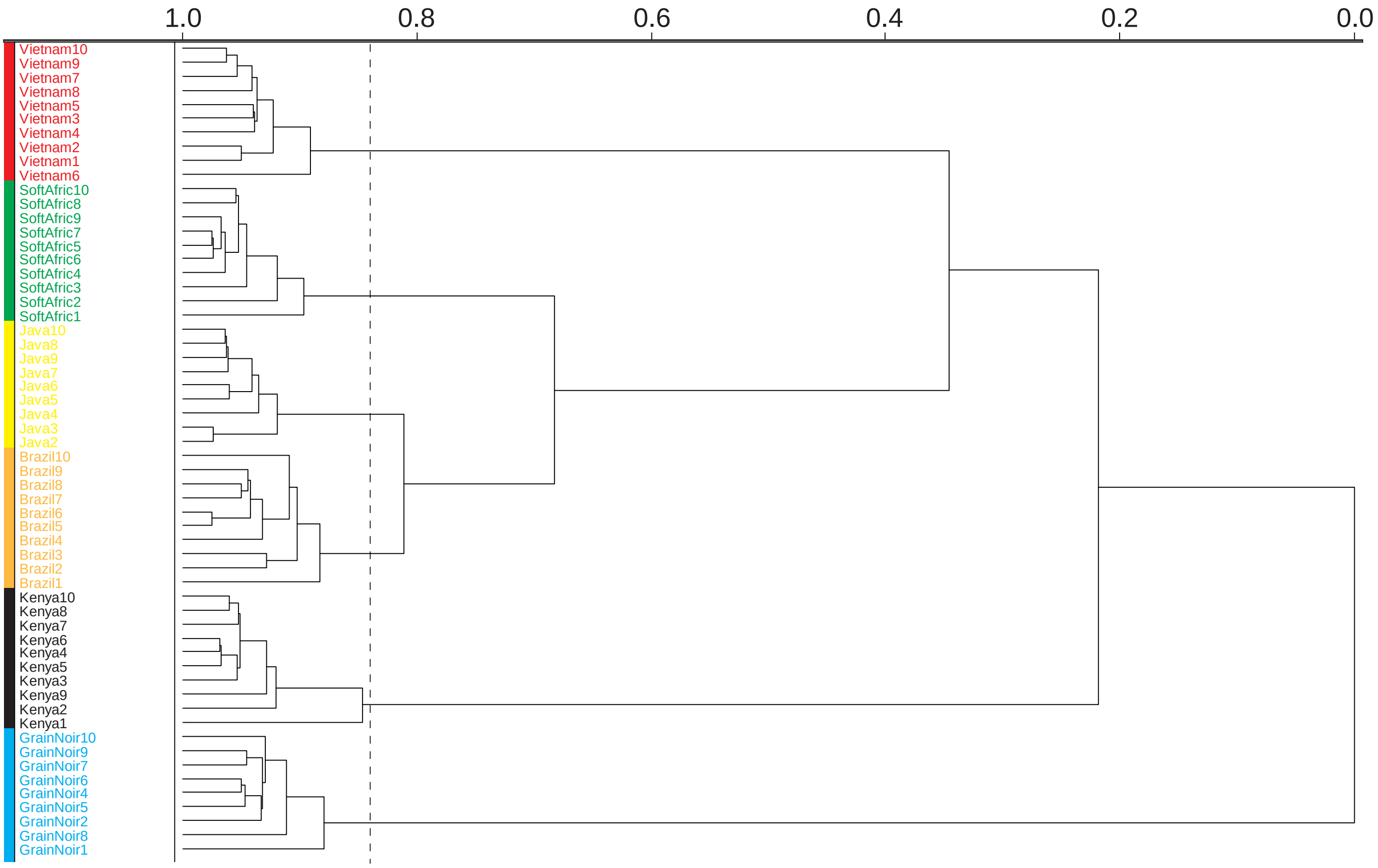

Figure 3. Hierarchical cluster analysis (HCA) dendrogram with 6 clusters at a similarity value of 0.82 (mean-center preprocessing; Euclidean distance; single linkage method).

In preliminary flavor analysis SDE-GC-MS profiles revealed a significant difference between Arabica and Robusta species at the level of the phenolic aroma compounds (phenol, guaiacol, 4-ethylguaiacol, 4-vinylguaiacol). It was found that Robusta coffees showed between 4 to 5-fold higher concentration of phenolic aroma compounds compared to Arabica coffees [3]. S-HS-GC-MS analysis of the coffee varieties revealed that no high boiling aroma compounds were isolated. HCA obtained no discrimination between Arabica and Robusta species on the basis of low-volatile phenolic aroma compounds, which are crucial character impact flavor compounds, as they were not isolated by S-HS.

Principal component analysis (PCA) provided graphical displays of variability and patterns of association in the S-HS-ChemSensor multivariate data set and identification of outliers. Figure 4 shows a 2D PCA scores plot of the complete data set after exclusion of outliers, explaining 96.6% of the total variance (PC1 91.7%, PC2 4.9%). The scores plot (PC2 versus PC1) shows discrimination between Arabica and Robusta on the first PC. Robustas tend to have positive PC1 scores, whereas Arabicas tend to have negative PC1 scores. In the loading plot the direction of Kenya was characterized by m/z 60 (acetic acid, 3-methyl butanoic acid). This is in accordance with the dominant acid/sour character of this Arabica variety. The direction of Java and Kenya was dominated by m/z 95 (1-(2-furyl)ethanon). Features m/z 53, 80 and 108 contributed highly to the Robusta direction.

Classification analysis with k-nearest neighbors (KNN) was performed on the complete data matrix after feature selection. No misclassifications were diagnosed with 1-NN classification.

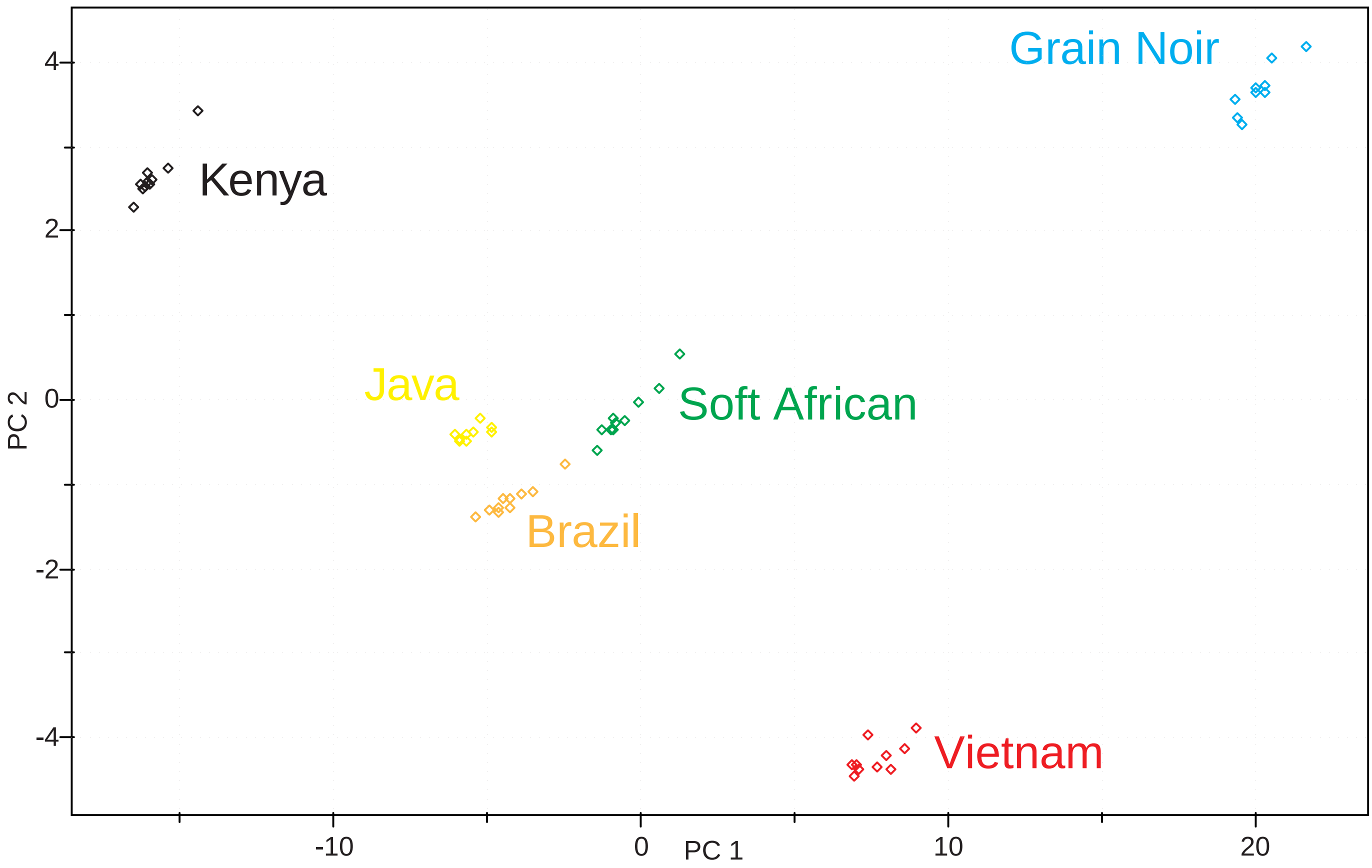

Figure 4. Projection of coffees mass spectra into the first two principal components space. Roasted Brazil (10)†, roasted Java (9), roasted Kenya (10), roasted Grain Noir (9), roasted Vietnam (10), roasted Soft African (10); mean-center preprocessing; normalization: 100.00; exclusion of outliers: Java1, GrainNoir3. †: number of replicates.

After feature selection and exclusion of outliers soft independent modeling of class analogy (SIMCA) was performed on the complete data set (Figure 5). The SIMCA plot with small ellipses for the confidence intervals (0.95) revealed good reproducibility of the S-HS-ChemSensor data. No misclassifications were found and interclass distances varied between 8.43 and 86.01 (Brazil-Java (8.43); Brazil-Soft African (12.03)). Since with KNN and SIMCA no misclassifications were observed, S-HS-ChemSensor analysis was capable to correctly identify the 6 geographical origins from the coffees in the training set.

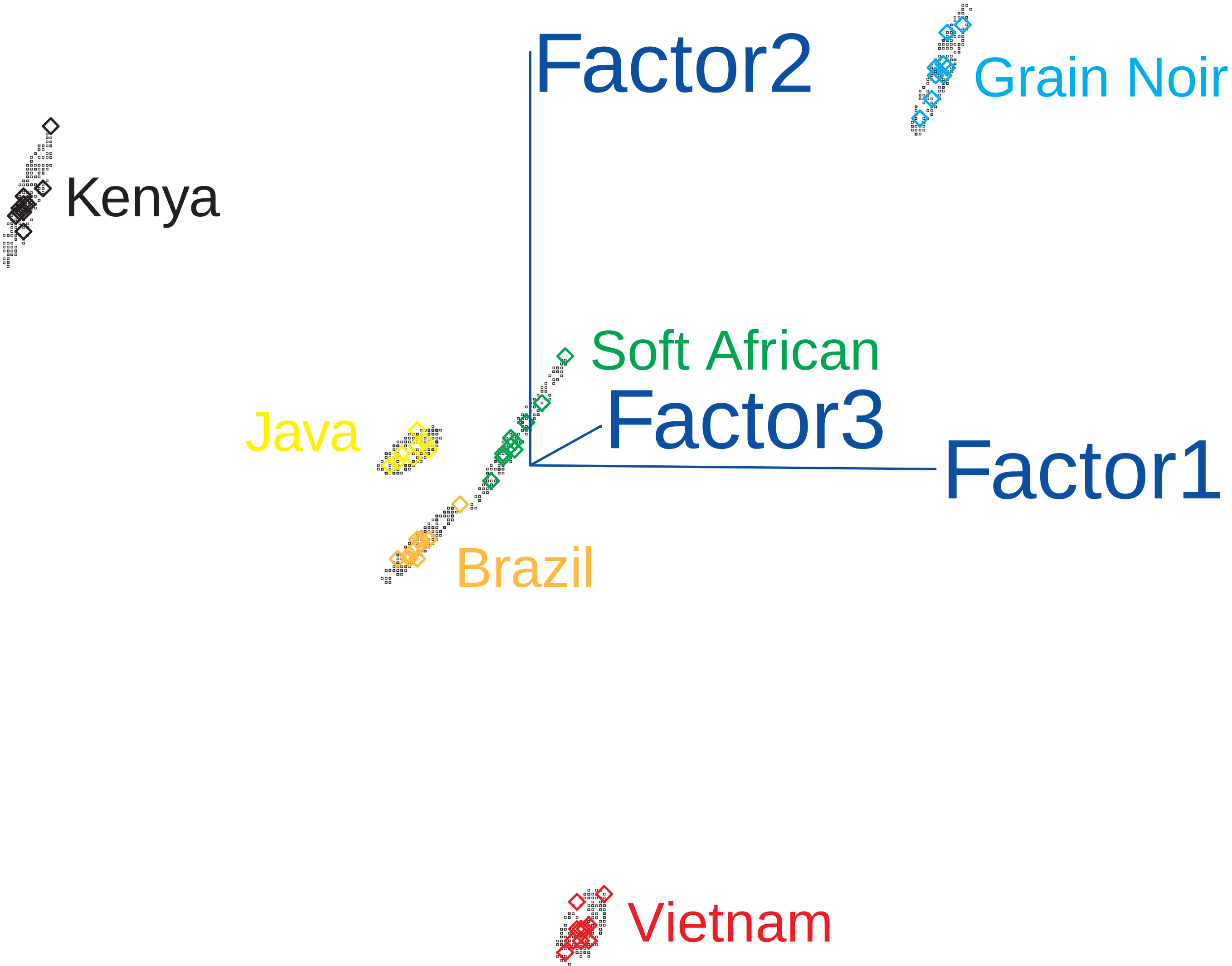

Figure 5. 3D SIMCA plot (class projections) of roasted Brazil (10)†, roasted Java (9), roasted Kenya (10), roasted Grain Noir (9), roasted Vietnam (10), roasted Soft African (10); mean-center preprocessing; normalization: 100.00; exclusion of outliers: Java1, GrainNoir3; probability threshold: 0.950. †: number of replicates. The small dots around the sample data points normalize the confidence intervals (0.95).

Previous studies indicated that classification between Arabica and Robusta species can be achieved on the basis of phenolic aroma compounds [2,3]. In this study using static headspace sampling classification of coffee varieties from different origins could not be achieved on the basis of character impact phenolic aroma compounds. This implies that coffee varieties with low 'phenolic' Robusta character may not be selected for production of low-cost, high-quality commercial coffee blends using S-HS-ChemSensor technology. However, we were able to discriminate all coffee varieties under consideration in this study on the basis of high-volatile aroma compounds.

Conclusions

The hyphenated configuration of static headspace sampling with quadrupole mass spectrometry (MS) as a sensing system (S-HS-ChemSensor) in combination with pattern recognition software was successfully used for the classification of coffee varieties from different origins. Using the S-HS-ChemSensor classifications were performed with shorter analysis times in comparison with the classical SDE-GC-MS approach.

Acknowledgements

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