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A new approach to evaluate vinegars quality: application of Small Sensor System (S3) device coupled with enfleurage

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Abstract

In this work is illustrated the application of S3 (Small Sensor System) device, equipped with an array of six metal oxide semiconductor (MOX) gas sensors, coupled with enfleurage as new approach to characterize the aromatic profile of Balsamic Vinegars (BVs). Thanks to the enfleurage in fact, the lipophilic volatile compounds are extracted from balsamic vinegar while acetic acid and its derivatives whose high concentration negatively influences MOX sensors sensitivity are not involved in the process. The obtained results show the huge potentiality of this new approach to evaluate BVs quality. All the samples were analyzed in parallel by GC-MS (Gas Chromatography-Mass Spectrometry) with SPME (Solid Phase Micro-Extraction).

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Keywords: MOX gas sensors; GC-MS with SPME; Balsamic Vinegars; Enfleurage.

1. Introduction

Vinegar production is a process that uses relatively low-cost raw materials, such as grapes, apples, pears, honey, syrups, cereals, hydrolyzed starches, beer and wine, to obtain products with a relatively high price [1]. Italian balsamic vinegars produced from regional foodstuffs according to well-established methods are one of the product groups that mainly take advantage of the use of “poor” raw materials.

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The entire production of BVs is concentrated in the Emilia Romagna region: Balsamic Vinegar of Modena (BVM) with PGI (Protected Geographical Indication) status and Traditional Balsamic Vinegar with PDO (Protected Denomination of Origin) status [2]. BVM and TBV have a high content of volatile compounds (VCs) that contribute to determine an unmistakable and worldwide-appreciated aroma. Therefore, the characterization of the aromatic profile of BVs is one of the most important factors in quality control and authenticity assessment of the product.

The aim of this work was to establish a new approach to permit the application of S3 device in the evaluation of BVM and TBVs quality and authenticity. S3 device in fact is a very easy-to-use, fast, accurate, low power consumption, cost-effective and portable tool that can become a valuable alternative for classical expensive methods of aromatic profile characterization such as chemical analysis and sensory analysis. Since the MOX gas sensors are sensitive to a high concentration of acids, such as acetic acid that is widely present in BVs, before the analysis of VCs it was carried out the enfleurage, an ancient technique based on the ability of solid fats at room temperature to absorb, dissolve and bind the aromatic compounds [3].

2. Materials and methods

2.1. Samples

Balsamic vinegars, with different residence time, were kindly provided by Acetaia Giudici (Reggio Emilia, Italy). Before each analysis, the pH of the samples has been adapted adding solid $NaHCO_3$. To understand the best way to conduct the enfleurage, six types of fats with different origin (animal, vegetable and synthetic) were selected: lard, butter, PSFA (Palmitic Saturated Fatty Acid), margarine, paraffin and vaseline.

2.2. Enfleurage

Enfleurage was carried out under cold and hot conditions, as shown in Table 1.

Table 1. Comparison between the processes of cold and hot enfleurage.

Cold Enfleurage	Hot Enfleurage
• The fat was heated to its melting point and poured into a Petri dish (9 cm x 1.5 cm) in order to obtain a 3 mm-thick layer.	• Balsamic vinegar was directly added into the melted fat.
• After the melted fat has cooled down at room temperature, 20 ml of balsamic vinegar, corresponding to a 3 mm-thick, was added to fat layer.	• The blend was repeated using 1:2, 1:1 and 2:1 ratios of fat and balsamic vinegar.
• The Petri dishes were closed and placed in an incubator at 25°C for 1-8h.	• The mixture was warmed at 40, 50 and 60 °C and stirred at 300rpm for 30, 60 and 90 min.
• The saturated fat was physically separated from the supernatant liquid and subjected to low-temperature centrifugal separation.	• After a centrifugal separation carried out at low temperature, the saturated fat was physically removed from the supernatant liquid.

2.3. GC-MS with SPME

GC-MS analysis was performed using a Shimadzu Gas Chromatograph GC2010 PLUS (Kyoto, KYT, Japan) equipped with a Shimadzu single quadrupole Mass Spectrometer MSQP2010 (Kyoto, KYT, Japan) ultra and a HT280T auto-sampler (HTA S.r.l., Brescia, Italy) that permitted SPME analysis. The vials were incubated in an oven thermostatically regulated at 40ºC for 15 minutes due to create the headspace equilibrium. In order to extract the volatile compounds of the samples was used a DVB/CAR/PDMS (50/30µm) (Supelco Co., Bellefonte, PA, USA) SPME fiber. To provide the adsorption of volatile compounds, the SPME fiber was exposed to the headspace of the vials for 15 minutes at 40°C. For desorption of the compounds, the fiber was placed in the injector of the heated GC for 6 min at 220°C. Volatile compounds were separated using an analytical capillary column (DB-WAX capillary column, 30m x 0.25 mm x 0.25µm, Agilent Technologies, Santa Clara, CA, USA) and the carrier gas was ultrapure helium (99.99%) at a constant flow rate of 1.5 ml/min. The temperature program for the GC was

performed in the following way: 40 °C for 3 min, increased to 220 °C at a rate of 4.5°C/min, with a 1 min of holding time. For each SPME analysis, 1 g of fat, saturated or clean, was placed in a 20 ml chromatographic vial. The determination of aromatic profile of BVs was carried out placing 2 ml of sample in a 20 ml chromatographic vial.

2.4. S3 device

S3 device used has been created in the SENSOR Lab, CNR INO Brescia in Italy (http://sensor.ing.unibs.it). The sensor array located into the tool is constituted of three RGTO thin film technology sensors [4] and three nanowires sensors [5, 6] and it is inside a thermally controlled sensor chamber. Two of the three nanowires are zinc oxides sensor but with different operating temperatures and the third one is a tin oxide sensor. The nanowires manifest a very high length-to-width ratio, creating a 3D network exposed to the gas. In this way, the adsorption surface is increased, enhancing the response of the instrument and decreasing the threshold. Tin and zinc oxide nanowires also have a high degree of crystallinity. This characteristic results in an enhanced performance and in a long-term stability for sustained operations. The tool was also provided with the auto-sampler headspace system HT280 (HTA S.r.l., Brescia, Italy), supporting a 40 loading sites carousel and a shaking oven to equilibrate the sample headspace. To carry out the analysis, 1 g of saturated fat was placed in a 20 ml chromatographic vial; control samples were also performed using clean fat. All the vials were cover with silicon-PTFE septum, crimped with an aluminium crimp and placed in a randomized mode into the carousel. Each vial was incubated at 40°C for 10 min into the auto-sampler oven, by shaking it during all the incubation. The sample headspace was then extracted from the vial in static headspace path and injected into the carried flow (speed 4 ml/min) through a properly modified gas chromatography injector (kept at 40°C to prevent any condensation). The sensor baseline was performed by using synthetic chromatographic air with a continuous flow rate of 10 ml/min and the recovery time was 28 min.

The data analysis was run by means of Principal Component Analysis (PCA). Data were processed by EDA software, a home written software developed in MATLAB® at Sensor Laboratory, to observe the clusters separation of the samples.

3. Results and discussion

3.1. GC-MS with SPME results

Thanks to the GC-MS with SPME analysis, it has been possible to evaluate the volatile profile of fats and their ability to extract the aromatic compounds from balsamic vinegars. In accord to the tradition, the results indicated that lard has the best intrinsic characteristics to conduct the enfleurage. In particular, in cold enfleurage the extraction of VCs has been slowly progressive up to 4h of exposure time while in hot enfleurage better experimental response was obtained as follow: 2:1 ratio fat/BV, 60°C, 60’ (Figure 1).

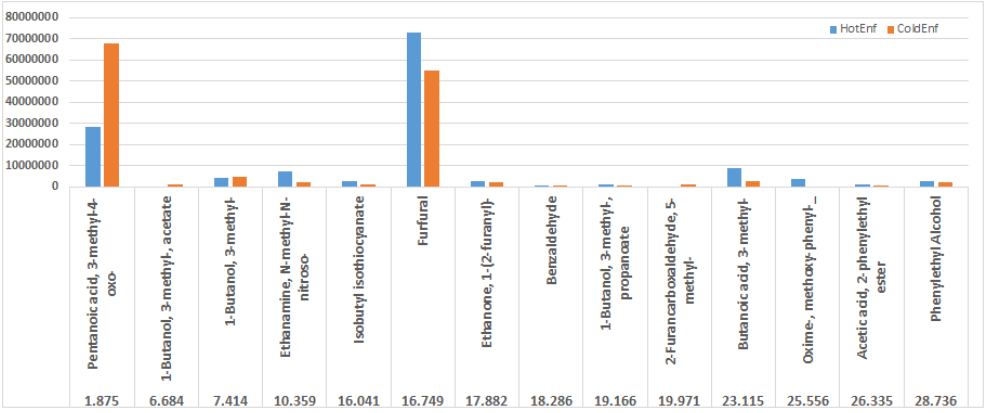

Fig. 1. Histogram of the GC-MS with SPME analysis for better experimental response of hot enfleurage (HotEnf) and for cold enfleurage after an exposure time of 1h (ColdEnf).

3.2. S3 device results

The PCA score plot in Figure 2 shows four well-separated clusters. The first one is the cluster formed by saturated lard samples after an exposure time to BV of 1h (black dots) while the second one is the cluster formed by saturated lard after hot enfleurage carried out at better experimental condition (blue dots). The other two clusters refer to the control samples (respectively green dots and red dots). The first two principal components were kept because they accounted for 97.20% of the variance in the data set. The results suggest that the instrument is able not only to identify the saturated samples (along PC1) but also to separate the two different types of enfleurage (along PC2).

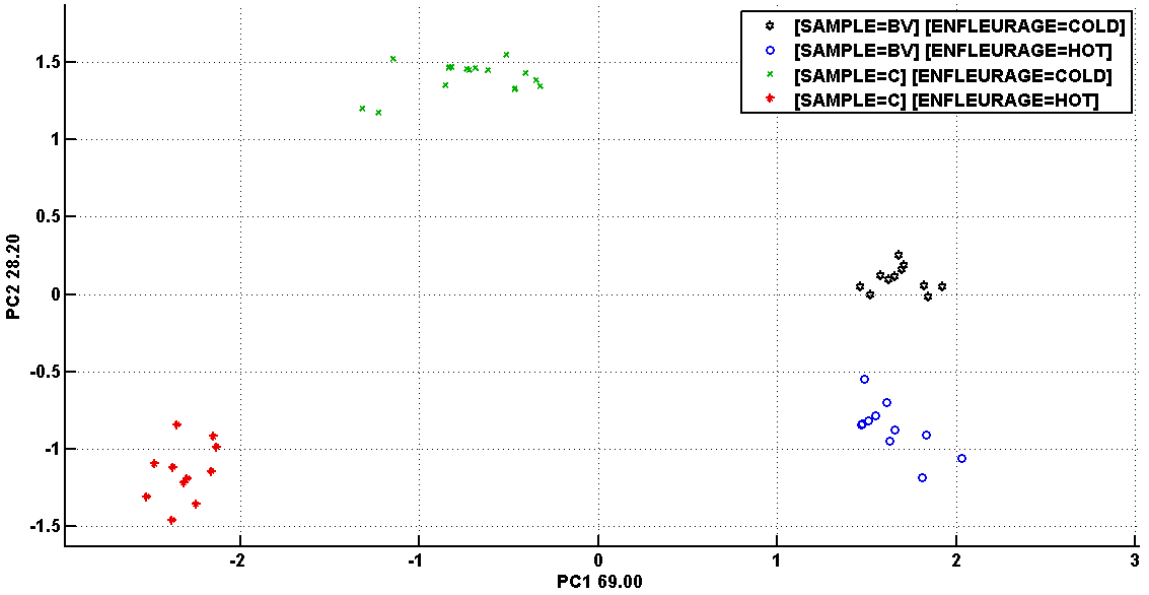

Fig. 2. PCA score PLOT showing four different clusters corresponding to the four tested samples. In addition, it shows a PC1 value of 69.00% and a PC2 value of 28.20%.

4. Conclusions

The achieved results support the ability of the S3 coupled with enfleurage to evaluate BVs quality and authenticity. This new approach in fact is able to provide a fast and versatile response to be use in the continuous monitoring of the balsamic vinegar production and in the identification of adulteration. The use of S3 coupled with enfleurage and a suitable chemometric analysis, may also represent a powerful methodology to assess the maturation and ageing degree of BVs of undeclared age.

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