Chemometric Discrimination of Philippine Civet Coffee Using Electronic Nose and Gas Chromatography Mass Spectrometry

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Abstract

This study presents a practical and promising approach to profile the headspace aroma attributes of Philippine civet coffee using electronic nose (E-nose) and gas chromatography mass spectrometry (GCMS). Chemometric pattern method was applied to enhance the discrimination of civet coffee against its control coffee beans (not eaten by civet animal). E-nose analysis revealed that aroma characteristic is one of the most important quality indicators of civet coffee. The result was supported by GCMS analysis. The chromatographic fingerprints indicated that civet coffee differed with their control beans in terms of composition and concentration of individual volatile constituents. Chemometric discrimination of E-nose and GCMS data demonstrated a clearly separated civet from their control coffees indicating that cultivar and geographic origins dictate the aroma and volatiles variations in coffee.

Keywords: civet coffee; electronic nose; gas chromatography mass spectrometry; chemometric discrimination

1. Introduction

Civet coffee is the top most expensive coffee in the world [1]. It is made from coffee cherries, which have been eaten and passed through the digestive tract of Asian palm civet (Paradoxurus
Civets naturally select and consume the ripest and sweetest coffee cherries whereby the undigested inner beans are excreted. The unique aroma and flavor quality of civet coffee has been associated to the breaking down of proteins during civet digestion [2]. The increasing popularity and appreciation of civet coffee and its limited annual supply could possibly lead to the occurrence of adulterated and fraudulent civet coffee beans in the market. It is therefore important to discriminate civet coffee from non-civet coffee. At present, there is no internationally accepted method of verifying whether a bean is civet coffee. Traditionally, coffee aroma has been used to characterize coffee quality. The volatile compounds in coffee contribute greatly to its overall aroma quality [3].

Sensory panel evaluation is commonly used to assess the aroma profile of coffee. However, this technique has some drawbacks such as the difficulty to train the panel effectively in order to limit subjectivity of human response to odors and the variability between individuals [4]. The emergence of an electronic nose (E-nose) for the discrimination of odors has become attractive and useful to the food industry because of its ease of use, versatility, and broad range of applications [5]. Similarly, the application of GCMS in coffee analysis has proven to be a valuable technique to characterize the volatile compounds responsible for the aroma quality of coffee [6]. In this work, E-nose and GCMS analysis of Philippine civet coffee were carried out for the first time to determine the potential of the instruments to discriminate civet coffees with their control coffee beans (not eaten by civet). Chemometric analysis was applied to visually display the similarities and distinction between civet and control coffee beans.

2. Experimental

2.1 Coffee Samples and Instruments

Four different commercial brands of Philippine coffees were analyzed. Three coffees (civet and control) were taken from Northern part of Luzon (Kalinga, Asipulo, and Cordillera) and one from southern part of the Philippines (Matutum, South Cotabato). The coffee samples were Arabica (Cordillera and Matutum) and Robusta (Asipulo and Kalinga) varieties.

The Electronic Olfactory System, EOS835 was manufactured by Sacmi Imola scarl, Italy [7]. E-nose analysis was carried out using six metal oxide (MOX) sensors whose characteristics and fabrication parameters are shown in Table 1. Headspace generation was held at 40 °C for 10 min with 1 min shaking. Then, 2 ml volume was extracted and injected into carrier line at 50 °C with injection speed of 4 ml/min.

<table>
<thead>
<tr>
<th>No.</th>
<th>Sensing layer</th>
<th>Thickness (nm)</th>
<th>Catalyst</th>
<th>Operating T (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>SnO2-RGTOa</td>
<td>300</td>
<td>Ag</td>
<td>400-500</td>
</tr>
<tr>
<td>2</td>
<td>SnO2-RGTOa</td>
<td>300</td>
<td>Au</td>
<td>400-500</td>
</tr>
<tr>
<td>3</td>
<td>SnO2-RGTOa</td>
<td>300</td>
<td>Mo</td>
<td>400-500</td>
</tr>
<tr>
<td>4</td>
<td>WO3b</td>
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</tr>
<tr>
<td>5</td>
<td>SnO2-In2O3c</td>
<td>300</td>
<td>none</td>
<td>350-500</td>
</tr>
<tr>
<td>6</td>
<td>SnO2-In2O3c</td>
<td>350</td>
<td>none</td>
<td>400-500</td>
</tr>
</tbody>
</table>

a Tin Oxide-Rheotaxial Growth and Thermal Oxidation technique
b Tungsten Oxide
c Tin-Indium Oxide

GCMS analysis was performed using Hewlett Packard GCMS model HP6890/5973 (Hewlett Packard, CA, USA equipped with crossbond carbowax capillary column (Restek 11023). Headspace was generated at 70 °C for 10 min and volatiles extraction at 70 °C for 20 min.
3. Results and Discussion

The responses of the MOX sensors to the coffee samples varied greatly. A comprehensive view of the PCA score plot of the E-nose data is illustrated in Figure 1 and the dendrogram graph is shown in Figure 2. Chemometric analysis through principal component analysis (PCA) and cluster analysis reveals groupings that differentiate civet and non-civet (control) coffee. The discrimination indicates that the headspace vapor, and therefore the aroma of each civet coffee is different from their corresponding control coffee beans. The distinct data structure of the individual civet coffee shows that the passage of the beans through the digestive tract of civet affects the aroma attributes of coffee [2].

Data obtained from gas chromatography-mass spectroscopy (GCMS) indicates the presence of at least 47 major components (Figure 3) in the headspace of civet and non-civet (control) coffees. It was observed that the composition of volatile compounds in civet coffee is almost similar to their controls but of different concentrations. PCA plot (Figure 4) of prominent coffee volatiles exhibits a good classification between civet and control coffee beans. The separation in the GCMS-PCA plot between civet and control coffees is complementary with the E-nose results. Chemometric discrimination of civet from non-civet coffee reveals that the aroma characteristic is one of the most important quality indicators of civet coffee.

The integration of E-nose and GCMS data of the PCA plot shown in Figure 5 reveals a good correlation between aroma quality and coffee volatiles of civet coffee considering that individual civet
coffee was successfully discriminated with its control beans. Cluster separation among civet coffees suggested that the aroma quality of civet coffee is region-specific. Results provide proof that E-nose is a promising and practical tool in evaluating the authenticity of civet coffee.

Fig. 5. PCA plot of E-nose and GCMS data for civet and control coffee beans.

5. Conclusion

E-nose (EOS835) has proven to be useful in discriminating the aroma quality of Philippine civet coffee. The finding was supported by the differences between the relative GCMS traces of the different coffees. Chemometric analysis through PCA and cluster analysis demonstrated groupings that differentiate civet and non-civet coffee. Results revealed that aroma characteristic is one of the most important quality indicators of civet coffee. The unique aroma quality of civet coffee can be attributed to the intestinal digestive process of civet. The cluster separation among civet coffee samples indicated that varietal and geographical origins dictate the aroma variations in coffee. Thus, it can be concluded that the aroma characteristics of civet coffee is varietal and region-specific. This remarkable performance provides proof that E-nose can be used in discriminating the authentic aroma quality of civet coffee.

Acknowledgements

This research work was funded by the Philippine Council for Industry, Energy and Emerging Technology Research and Development (PCIEERD), Department of Science and Technology (DOST), Philippines, the University of Modena and Reggio Emilia and the University of Brescia, Italy. One of the authors (E.O) gratefully acknowledges the sandwich thesis grant provided to her by DOST-PCIEERD.

References