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Geographical origin classification of Argentinean honeys using a digital image-based flow-batch system

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ABSTRACT

In this paper a geographic origin classification of honey samples from Argentina was proposed. For this reason, a conventional flow-batch system with a simple webcam to capture digital images was employed. In this methodology, analytical information is generated from color histograms obtained from the digital images employing different color models (RGB (red–green–blue), HSB (hue–saturation–brightness) and Grayscale). Three chemometric tools were employed for geographic origin classification (SPA-LDA (successive projections algorithm-linear discriminant analysis), SIMCA (soft independent modeling for class analogy), and PLS-DA (partial least squares-discriminant analysis)). The proposed method is a good option to be used in quality control laboratories for the classification of honey samples according to their geographical origin.

1. Introduction

During the last decade, Argentina was positioned as one of the first honey producers in the world, being simultaneously the principal exporter of bulk honey. Due to the diversity of climates, Argentina has a wide variety of floral resources that allows these activities to be carried out in most of the territory. However, the province of Buenos Aires concentrates more than 50% of national production. The southwest of the province of Buenos Aires is located in the south of the Pampean region and presents different natural regions: mountain range, valleys, plains and forest. These environments are related to the climatic conditions and vegetal species valuable for beekeeping. The organoleptic characteristics of honey are strongly associated with the botanical origin, depending on geographical area in which bees collect pollen. Then, the honey produced in Argentina is internationally appreciated by physicochemical, microbiological and sensory (flavor and color) attributes and it is positioned at the top of the global preferences [1–3].

Currently, the honey market tends to classify them according to their geographical or botanical origin. Baroni et al. [4] evaluate the floral origin of honey determining its volatile organic compounds by using headspace solid-phase microextraction and gas chromatography coupled to mass spectrometry and chemometric techniques. On the other hand, the classification of floral origin of honeys was carried out by chemical and physical characteristics combined with chemometrics [5]. The determinations of 14 trace elements applying Instrumental Neutronic Activation Analysis (INAA) allowed the differentiation of multifloral honeys from Argentine Pampas in combination with chemometric techniques [6]. Escriche et al. show a method to differentiate two types of citrus honey that comes from two different botanical origins by determining the content of flavonoids, phenolic acids and volatile compounds and statistical data evaluation techniques [7]. Classification of honeys according to their botanical and geographical origin by using only seven elements and chemometric techniques was carried out [8]. Cometto et al. determined free amino acid composition of honey samples by reversed-phase high-performance liquid chromatography and statistical analyses [9]. Honeys produced in the regions of the province of Córdoba (Argentina), were classificated by geographical origin using chemometrics and chemical properties and mineral profile [10].

Some of these methods have been developed based on palynological studies, sensory characterization, mineral analysis, flavonoid contents, etc. The palynological studies have the disadvantages of being slow, tedious and require trained analysts [11]. Within sensory characterization, color determination is relevant. The international reference techniques for defining honey color are based on Pfund method which is based on optical comparison. These color units are obtained using subjective visual assessment that can lead to differences in the reported values between users and does not distinguish between small variations of color. On the other hand, the determination of this parameter is laborious, time consuming and requires large amounts of sample [12]. Moreover, some determinations involve time-consuming and laborious procedures, for example to evaluate mineral honey composition a muffle furnace at a temperature of 550 °C over night should be used [13].

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In some cases, are necessary purification steps, for example to determine flavonoids as reported by Bogdanov et al. [14].

In order to overcome these drawbacks, digital images as a potential tool for qualitative and quantitative analysis, have been used in the recent years [15–18]. Color digital image processing involves the use of color models in order to provide specification of colors by using some standard. In essence, a color model is a specification of a three-dimensional coordinate system and a subspace within the system where each color component is represented by a single point.

There are many models used to measure and describe color, including RGB (red–green–blue), HSB (hue–saturation–brightness) and Grayscale. The RGB color model is based on the theory that all visible colors can be created using the primary additive colors red, green and blue. These colors are known as primary additives because when combined other colors are produced. The HSB model defines a color space in terms of three constituent components: Hue (color type), Saturation (intensity of color) and Brightness (brightness of color). Finally, grayscale is a range of shades of gray without apparent color [19–21].

In order to obtain the digital images, it would be appropriate to implement an automatic system that includes a web cam. Among the automatic methods, Flow–Batch methodology (FB) is a good option since it combines the intrinsic favorable features of the flow and batch techniques. Therefore, they can be considered as a multipurpose analytical accessory. These systems are characterized by the use of a chamber and threeway solenoid valves fully computer-controlled. One of the advantages of the FB is that it is considered as a universal purpose accessory tool easily attached to any conventional equipment for instrumental analysis. Flow–Batch systems allow high sampling frequencies, low cost per analysis, less consumption of reagent and sample, and less chemical waste than classical methods, principles considered in green analytical chemistry [22–25].

The aim of this work was to carry out a digital image-based flow-batch system for geographic origin classification of honey samples from southwest of the province of Buenos Aires, Argentina. For this purpose, a Flow–Batch system which includes a simple webcam to capture digital images was employed. Data treatment involved the use of a suitable variable selection technique, the successive projections algorithm (SPA) [26], associated to the linear discriminant analysis (LDA) to improve the classification results. Alongside of SPA-LDA, SIMCA (soft independent modeling for class analogy), and PLS-DA (partial least squares-discriminant analysis) were used for comparison.

2. Material and methods

2.1. Samples preparation

A set of 210 representative honey samples from southwest of the province of Buenos Aires, Argentina, were collected from supermarkets and local producers. Samples from three differing geographical origins were selected: 75 from the mountain region called the Sierra de la Ventana, 70 from the north and 65 from the south of this mountain region. In Fig. 1, the samples that were collected can be seen in the three regions. Samples were kept in a cool dry place until analysis. For image acquisition, a 50% (w/v) solution of each honey sample was prepared in ultra pure water (18 M Ω Barnstead).

2.2. Apparatus and software

In order to obtain digital images, a Philips Webcam SPC900NC VGA with a CCD sensor was used. LabView 7.1 (National Instruments) software used to control the Flow–Batch system was used. The digital images obtained were processed with the ImageJ program (a free internet download). Chemometric data treatment was implemented with The Unscrambler_ 9.7 (CAMO S/A), and Matlab_ 2009b (Mathworks Inc.) software.

2.3. Flow–Batch system

A schematic diagram of the proposed Flow–Batch system is shown in Fig. 2. This system was composed of a lab-made detection cell (DC) built in PTFE which has an inner volume of 5 mL, a quartz circular window and the corresponding holes which allow the entry and exit of the honey solutions. Three three-way solenoid valves (model 137 161T031, Nresearch) were used as follows: VH valve allows the admission of honey sample solution to the DC; VW valve allows the access of

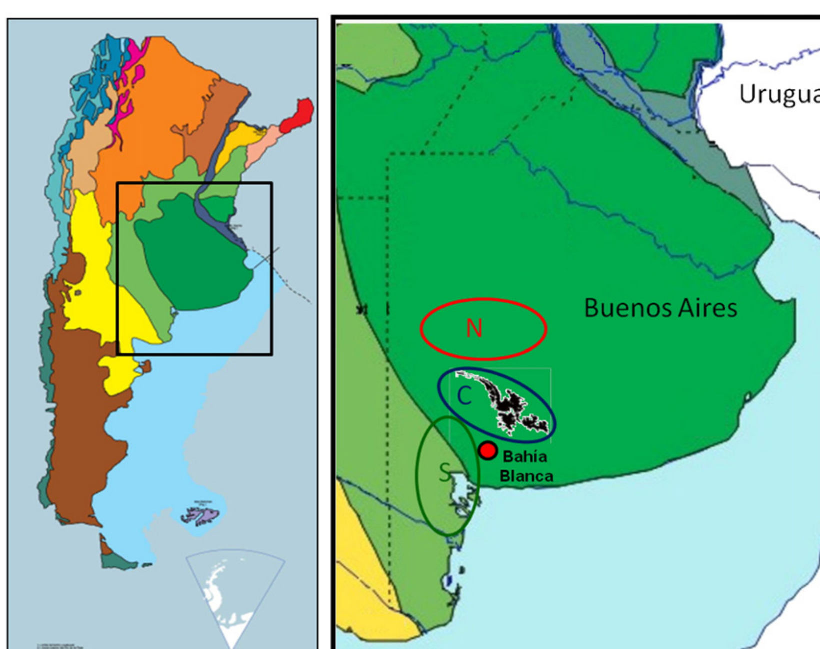

Fig. 1. Geographical location of the studied honey samples. N: north, S: south, and C: Sierra de la Ventana.