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Original Research Article

Characterization of Mexican coffee according to mineral contents by means of multilayer perceptrons artificial neural networks

Roberto Muñiz-Valencia [a,*], José M. Jurado [b], Silvia G. Ceballos-Magaña [c], Ángela Alcázar [b], Julio Hernández-Díaz [a]

[a] Facultad de Ciencias Químicas, Universidad de Colima, Carretera Colima-Coquimatlán km 9, 28400, Coquimatlán, Colima, Mexico
[b] Department of Analytical Chemistry, Faculty of Chemistry, University of Seville, c/ Profesor García González 1, 41012 Seville, Spain
[c] Facultad de Ciencias, Universidad de Colima, c/ Bernal Díaz del Castillo 340, 28045 Colima, Mexico

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ABSTRACT

The content of Ca, Cu, Fe, K, Mg, Mn, Na and Zn has been determined in Mexican roasted coffee beans from four producing states by means of inductively coupled plasma optical emission spectrometry (ICP-OES). The concentrations of these elements were used to differentiate the coffee growing area. Kruskal–Wallis test highlighted significant differences between metals in samples from the four origins. Principal component analysis was used to visualize the natural trends of data distribution for the considered groups. Forward stepwise linear discriminant analysis (LDA) was used to differentiate coffee origins as well as to find out the best chemical descriptors (Ca, K, Mn, Mg, Na and Zn). The overall sensitivity and specificity of LDA were 81% and 94%, respectively. These results were improved when a multilayer perceptron artificial neural networks model was applied, allowing the differentiation of Mexican roasted coffees with 93% prediction ability and 98% specificity.

1. Introduction

World coffee consumption has seen strong growth over the last ten years, reaching an estimated 137.9 million bags in 2011 (ICO-a, 2012). Consequently, geographical characterization of coffee is an interesting topic due to the economical importance for producing countries, the establishment of products with certified origins or agricultural practices, and the preference of consumers for certain products with differentiating characteristics (Barham and Weber, 2012).

There are two commercially used coffee species, namely *Coffea arabica* L. and *Coffea canephora*, known as arabica and robusta, respectively (Carrera et al., 1998). Mexico is the worlds' 5th largest arabica coffee producer, with Chiapas, Colima, Oaxaca and Veracruz as the main growing states (Historia del cafe, 2012). The arabica coffees beans command higher prices (by >200%) than the respective robusta coffee beans. Nevertheless, the price also depends on the geographic origin (ICO-b, 2012). Taking into account this fact, several works have focused on the discrimination of coffee species. The composition also depends on environmental factors and it is becoming more important to differentiate among coffee origins to assess coffee quality (Choi et al., 2010).

Chemical composition can be used to differentiate between coffee varieties and geographical origin by means of pattern recognition techniques. Most of the literature on this topic has been carried out with the aim of differentiating between arabica and robusta species, as the literature about coffee origin discrimination is very scarce. Major growing regions have been differentiated using the contents of mineral elements (Anderson and Smith, 2002; Akamine et al., 2010), phenolic and methylxanthine (Alonso-Salces et al., 2009), metabolomic profiles (Choi et al., 2010), volatile composition (Risticevic et al., 2008), fatty and chlorogenic acids (Bertrand et al., 2008) and elemental profiles and stable isotopes (Santato et al., 2012).

The purpose of this study was to use inductively coupled plasma optical emission spectrometry (ICP-OES) multi-element analysis combined with chemometrics for differentiating the geographical origin of Mexican coffee beans from the states of Chiapas, Colima, Oaxaca and Veracruz (Fig. 1). The presented work gives important identity information about the coffee produced in Mexico contributing to the development of the Mexican agribusiness. In addition, there is no reported methodology for differentiating Mexican coffee

* Corresponding author. Tel.: +52 3123161163; fax: +52 3123161163.
E-mail address: robemuva@yahoo.com (R. Muñiz-Valencia).

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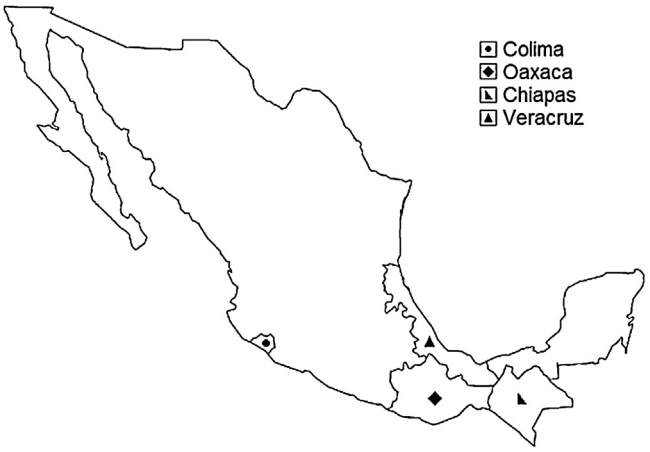

Fig. 1. Studied Mexican coffee production areas.

beans. The proposed method consists of: (i) the mineralization of coffee samples using a microwave digestion system; (ii) the determination of, Ca, Cu, Fe, K, Mg, Mn, Na and Zn by means of ICP-OES; (iii) the application of Pattern recognition techniques, such as linear discriminant analysis (LDA) and multilayer perceptron artificial neural networks (MLP-ANN) in order to differentiate their geographical origin.

2. Materials and methods

2.1. Chemicals and reagents

Water (HPLC grade) from Fermont (Nuevo Leon, Mexico), trace metal grade 70% nitric acid from J.T. Baker (Estado de Mexico, Mexico), 30% hydrogen peroxide and 1000 mg/L elemental stock standard solutions of K, Ca, Fe, Na, Mg, Mn, Cu and Zn purchased from Sigma–Aldrich (St. Louis, MO, USA) were used. A single or a mixture of these elements was prepared daily by diluting the stock solution with ultrapure water in 5% (v:v) nitric acid. Prior to use, all glassware and polypropylene flasks were washed with 10% (v:v) nitric acid and rinsed with ultrapure water.

3. Coffee samples

All samples used for this study were roasted coffee beans belonging to *C. arabica* L. variety. A total of 51 commercial samples of coffee from states of Mexico (Fig. 1): Chiapas ($n = 12$), Colima ($n = 24$), Oaxaca ($n = 6$) and Veracruz ($n = 9$) were purchased from local producers. Samples were 100% arabica and their geographical authenticity was established according to the information given by the local suppliers.

3.1. Samples analysis

Prior to the determination of Ca, Cu, Fe, Na, K, Mg, Mn and Zn, coffee samples were dried at 103 °C for determination of their moisture (International Organization of Standardization, 1994). An Optima 7000 ICP-OES spectrometer with dual view configuration (Perkin Elmer, Waltham, Ma, USA) and the WinLab32 software package was used for determining metal content. The operational parameters are shown in Table 1. The mineralization of coffee samples was accomplished using a QLab 6000 closed vessel microwave digestion system (Questron Technologies, Mississauga, ON, Canada) equipped with 200 mL Teflon PFA vessels. The used protocol was adapted from that proposed by Fernandes et al. (2005). Briefly, a 250 mg milled sample (from an agate mortar) was weighed in a PTFE digestion vessel and mixed with 1 mL of 30% H_2O_2 and 3 mL of 70% HNO_3. Subsequently, the vessel was placed on the microwave turntable to digest the coffee sample. The microwave oven temperature program consists of increasing from ambient temperature to 160 °C in 10 min, holding at 160 °C for 10 min before cooling to ambient temperature. The resulting solution was diluted to 25 mL with ultrapure water before the ICP-OES determination in triplicate.

Table 1
ICP-OES operating conditions.

Parameter	Condition
Power	1450 kW
Plasma flow	17 L/min
Auxiliary flow	0.20 L/min
Nebulizer flow	0.55 L/min
Replicates	3
Spray chamber	Cyclonic
Nebulizer	Meinhard
Emission lines (nm)	K 766.490, Mg 285.213, Ca 317.933, Fe 238.204, Na 589.592, Mn 257.610, Cu 327.393, Zn 206.200

3.2. Data analysis

A data matrix with eight columns (determined elements) and fifty one rows (analyzed samples) was built for chemometric calculations. Kruskal–Wallis test was used to highlight potential discriminant variables according to the statistical differences found between coffee origins. Principal component analysis (PCA) was used to previsualize data trends. Linear and non-linear pattern recognition techniques, such as LDA and MLP-ANN, respectively, were applied to carry out the classification of coffee samples according to their geographical origin. Data processing was made by using the statistical package Statistica 8.0 (Stafsoft™, Tulsa, OK, USA). Auto scaled data were used in all calculations.

4. Results and discussion

4.1. Method performance

The performance characteristics of the method, such as trueness, linearity on the calibration range, limit of detection (LOD) and quantification (LOQ), and precision (repeatability and intermediate precision) were assessed.

The trueness of the method was evaluated by means of recovery assays. A control sample was fortified in n levels ($n = 3$) corresponding to a low, medium and high level of concentration, covering the 80%, 100% and 120% of the mean expected value (González et al., 2005). Each level was analyzed in triplicate. The global recoveries (R) for each element with their expanded uncertainties (U) were calculated (Jurado et al., 2007) and the results are shown in Table 2. As can be seen, recoveries do not

Table 2
Recovery, linearity (% L), sensitivity (LOD and LOQ), repeatability and intermediate precision and obtained for the analyzed elements.

Element	R (%)	% L	LOD (mg/kg)	LOQ (mg/kg)	RSD_{repeat} (%)	RSD_{IP} (%)
Ca	100 ± 2	99.5	0.2	0.8	2.0	7.5
Cu	99 ± 3	98.7	0.2	0.7	1.5	6.2
Fe	99 ± 2	99.2	0.1	0.4	1.6	4.8
K	98 ± 3	99.0	0.3	0.9	2.4	5.2
Mg	100 ± 6	98.8	0.4	1.5	1.0	3.4
Mn	101 ± 3	99.7	0.2	0.3	2.1	6.8
Na	104 ± 4	99.8	0.5	1.7	1.0	3.5
Zn	101 ± 7	98.9	0.1	0.2	0.8	4.4

R (%), mean recovery ± expanded uncertainty; % L, linearity; LOD, limit of detection; LOQ, limit of quantification; RSD_{repeat}, repeatability; RSD_{IP}, intermediate precision; Each sample was analyzed in triplicate.