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ANALYSIS OF COFFEE ADULTERATED WITH ROASTED CORN AND ROASTED SOYBEAN USING VOLTAMMETRIC ELECTRONIC TONGUE

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ABSTRACT

Background. Coffee samples adulterated with roasted corn and roasted soybean were analyzed using a voltammetric electronic tongue equipped with a polypyrrole sensor array.
Materials and methods. Coffee samples were adulterated in concentrations of 2%, 5%, 10% and 20% of roasted corn and roasted soybean; 5 replicates of each were used. The discrimination capacity of a voltammetric electronic tongue elaborated with a polypyrrole sensor array, was evaluated by principal component analysis and cluster analysis, while the capacity to perform quantitative determinations was carried out by partial least squares.
Results. The results obtained by the application of principal component analysis showed an excellent ability to discriminate adulterated samples. Additionally, the classifications obtained by cluster analysis was concordant with those obtained by principal component analysis. On the other hand, the evaluation of the ability to quantitatively analyze the adulterated samples showed that the polypyrrole sensor array provides sufficient information to allow quantitative determinations by partial least squares regression.
Conclusion. It could be concluded that the voltammetric electronic tongue used in this work allows the sufficient analysis of coffee samples adulterated with roasted corn and roasted soybean.

Keywords: electronic tongue, voltammetry, polypyrrole, coffee, adulteration

INTRODUCTION

Coffee is one of the most consumed beverages worldwide and its commercialization in international markets represents the movement of millions of dollars per year (International Coffee Organization, 2017). The commercial importance of coffee and the value acquired by good quality coffee makes it the object of adulterations by some producers and marketers who want to increase their earnings. One of the most common practices in the adulteration of coffee, is the addition of toasted grain products such as soybean, rice,

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corn and sorghum, among others (Manasha and Janani, 2016; Toci et al., 2016).

Taking into account the volumes of production and the large amounts of money that are involved in this market, the detection of adulterants of this product is an analytical process of great importance. Due to the great economic impact of adulterations in the coffee market, many efforts have been made and some chemical methods have been developed to detect adulterations. Among the most outstanding and sophisticated methods are the capillary electrophoresis-tandem mass spectrometry, Laser Induced Breakdown Spectroscopy (LIBS), DNA-based method, Ultra Performance Liquid Chromatography-High Resolution Mass Spectrometry (UPLC-HRMS), electrospray ionization mass spectrometry (ESI-MS), and UV-Vis spectroscopy, among others (Daniel et al., 2018; Hong et al., 2017; Mendoza et al., 2008; Polari et al., 2015; Sezer et al., 2018).

In general, these types of chemical techniques require sophisticated and expensive instrumentation, highly qualified personnel, long processing times and, ordinarily, a large amount of solvents and pretreatment processes of the samples.

An alternative type of analysis used only in some cases is sensory analysis or tasting, which consists of evaluating the global characteristics of a product through the sense organs. Said characteristics are known as organoleptic (Gamonal et al., 2017; Sobreira et al., 2015).

The flavor of the food and the quality in terms of taste is of vital importance for the commercialization of all types of drinks, because this aspect, from the point of view of the consumer, is the main characteristic of its appreciation. The most rigorous way to achieve an appreciation of the taste of a drink is through the measurement carried out by a tasting panel, constituted by a team of experts. A tasting panel, properly prepared, can reliably assess the taste of a beverage like coffee. However, this assessment is a process that can be expensive in both time and money, because the services of expert panelists are expensive and they can only perform a certain number of analyses per day, with the necessary optimal health conditions, fatigue, etc.

The limitations of human sensory systems and the technical inconveniences of chemical methods have motivated the development of equipment that in some way emulates its operating principles. The first attempt made in 1982 by Persaud and Dodd in relation to aromas, consisted of the development of a multisensor system for the discrimination and recognition of gases (Persaud and Dodd, 1982). Since then much progress has been made at both academic and industrial levels. These systems known today as electronic noses have been and are being used in numerous applications (Loutfi et al., 2015; Majchrzak et al., 2018; Sanaeifar et al., 2017).

Due to the great success that electronic systems have had in the measurement of aromas, with the same philosophy, progress is being made in the development of a new type of equipment aimed at discriminating and recognizing flavors in liquids. These new systems are called "electronic tongues" (Vlasov et al., 2005; Winquist, 2008).

The electronic systems for the measurement of flavors, or electronic tongues, are one of the most promising methods for developing a fast, cheap and objective method for the evaluation of the flavor of a food. In addition, this method does not require pretreatment of samples, does not use solvents and can be portable because the instrumentation is simple.

Since the first prototype was developed in 1990 by Toko (1990), a certain number of research groups have focused their efforts on the improvement of those systems through the use of various measurement strategies and techniques, potentiometry and voltammetry, being the techniques most widely used. In this sense, it is important to note that voltammetry offers some advantages when compared to potentiometry, among the most outstanding of which is that voltammetric measurements can be performed on ionic and non-ionic analytes, while potentiometry requires an ionic medium for its realization; the instrumentation used in voltammetry is more robust and less susceptible to electronic noise; and with voltammetry, it is possible to use different measurement techniques such as cyclic voltammetry, wavelength and pulsing, among others. In addition, with potentiometry, a single piece of data of the analyzed sample is considered (potential), while with voltammetry a curve or signal is obtained which contains much more information of the sample analyzed (Arrieta et al., 2018a; Rodríguez-Méndez et al., 2010; Wei and Wang, 2014, Wei et al., 2018).

Voltammetric electronic tongues have shown their potential in a large number of applications (Di Rosa et al., 2017; Escuder-Gilabert and Peris, 2010; Winquist, 2008). In addition, this type of device permits the possibility of using metal electrodes and chemically modified electrodes. The use of modified electrodes allows the collection of more information-rich signals because voltammetric signals are products of the interaction of the different substances present in the sample and the chemical compound used as a modifier. This strategy has been used successfully through modification made with polypyrrole and has been tested in samples such as coffee, milk, beer and wine, among others (Antunes et al., 2005; Arrieta et al., 2018a; González-Calabuig and Del Valle, 2018; Rodríguez-Méndez et al., 2010).

The electronic tongue has been used to analyze samples of coffee adulterated with grains of different coffee varieties (Barroso et al., 2019). However, it has not been used in the detection of adulterations with roasted soybean and roasted corn in coffee samples. Therefore, the aim of this work was to explore the detection capacity of roasted soybean and roasted corn in coffee of a voltammetric electronic tongue, elaborated with a sensor array modified with polypyrrole and a multichannel measuring device developed with PSoC (Programable System on Chip) technology.

MATERIALS AND METHODS

The reagents employed were of analytical quality. The chemical solutions and samples were prepared by using milli-Q quality ultrapure water. The coffee samples analyzed consisted of 45 samples; 5 samples of pure Arabica coffee (unadulterated), 20 samples of roasted Arabica coffee adulterated with roasted corn and 20 samples of roasted Arabica coffee adulterated with roasted soybean. With both adulterants (roasted corn and roasted soybean) four concentrations were used (2%, 5%, 10% and 20%) and 5 samples (replicates) were used for each concentration.

The samples were prepared according to NTC 3566 (Colombian Technical Rule for sample preparation to use in sensory analysis); 7 grams of coffee sample was weighed and added to 100 ml of water. The water was heated in the heater up to boiling point. The infusion was decanted for 5 min, then the remains were eliminated from the solution's surface and the coffee solution was cooled to room temperature.

The voltammetric electronic tongue device was made in our laboratory. This device has three fundamental parts; a cross-sensitivity sensor array, a portable multi-channel potentiostat (multipotentiostat) electronic system and a control program and data acquisition.

The sensor array consisted of seven polypyrrole sensors which were obtained by electropolymerization of pyrrole with various doping agents on platinum electrodes. The doping agents used were sodium sulphate (SO4), sodium dodecylbenzenesulfonate (DBS), ammonium persulphate (SF), potassium ferrocyanide (FCN), lithium perchlorate (PC), p-toluenesulfonic acid (TSA), anthraquinone-2,6-disulfonic acid disodium salt (AQDS).

The sensor array had a circular configuration and they were prepared on a commercial card AC9C of BVT Technologies. For the elaboration of each one of the sensors, a 0.1 $mol \cdot L^{-1}$ polypyrrole solution and 0.8 V of polymerization potential was used in all cases. The particular parameters used in the elaboration of the sensors are presented in Table 1. The details of the optimization of this process have previously been published (Arrieta et al., 2018b).

The electronic measurement system was elaborated with a FREESOC card which has a programmable microchip PSoC 5LP. The programming was made with the PSoC creator software. The device was capable of carrying out cyclic voltammetry through 7 channels

Table 1. Elaboration conditions of the polypyrrole sensor array by electrochemical polymerization

Sensor	Acronym	Counterion concentration $mol \cdot L^{-1}$	Time s
S1	PPy/SO4	0.05	60
S2	PPy/DBS	0.1	45
S3	PPy/SF	0.05	70
S4	PPy/FCN	0.1	50
S5	PPy/PC	0.1	60
S6	PPy/TSA	0.1	60
S7	PPy/AQDS	0.05	70

simultaneously and transmitted the data via Bluetooth to a smartphone with an android application specially created for this device. The android application was developed to allow control of the electronic device and the storage of data. The details of the elaboration of the electronic device and the control android application have been reported in previous publications (Arrieta et al., 2015; 2018b).

All measurements were made in triplicate and at room temperature in 10 mL of sample. The voltammetry was carried out in a potential range of –1.0 V to 0.5 V, with a sweep speed of 0.1 $V \cdot s^{-1}$. The android application organized the data currents (I) registered in the voltammograms and ordered them as a matrix, each column being a current value. Each sensor yielded a voltammogram of 100 current data, therefore 700 columns were generated (7 sensors with 100 data each). The data obtained was analyzed by principal component analysis (PCA), cluster analysis (CA) and partial least squares (PLS). The Minitab V18 software was used to carry out the statistical analysis.

RESULTS AND DISCUSSION

The initial measurements were aimed at exploring the electrochemical behavior of the polypyrrole sensor array in the studied coffee samples. For this, measurements were made with the sensor array in samples adulterated with roasted corn and roasted soybean at 2% and 10%, and an unadulterated sample of coffee. The objective of this first study was to determine if the sensor array used presented cross-sensitivity to the group of samples. That is, if the sensors respond differently to different samples and if each of the sensors offers a different response that contributes to the discrimination by registering a voltammetric fingerprint of the samples (Vlasov et al., 2005).

Figure 1 shows the voltammograms recorded with the PPy/SF sensor versus the unadulterated coffee samples and those adulterated with roasted corn and roasted soybean at 2% and 10%. It can be observed that the oxidation and reduction potentials of the voltammograms were different in each curve, and the shape of the curves is slightly different in each sample. The oxidation potential for the unadulterated sample was 0.04 V and the reduction potential –0.31 V. The oxidation and reduction potentials in the samples

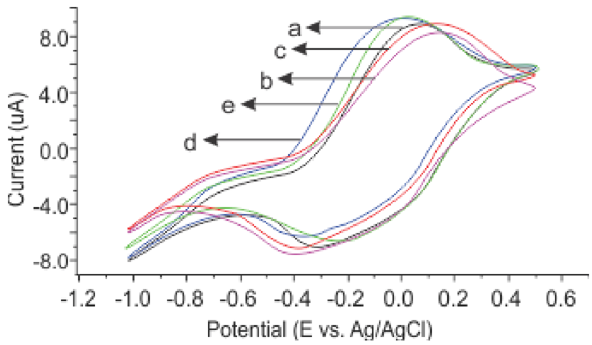

Fig. 1. Voltammetric response of PPy/SF sensor in coffee samples: a – unadulterated, b – adulterated with 2% of roasted corn, c – adulterated with 10% of roasted corn, d – adulterated with 2% of roasted soybean, e – adulterated with 10% of roasted soybean

adulterated with roasted corn were 0.16 V and –0.41 V for the adulteration at 2%, and 0.12 V and –0.39 V for the 10% adulteration. The adulterated sample with roasted soybean at 2% showed oxidation and reduction potentials at 0.00 V and –0.37 V respectively, while in the case of the sample with 10% adulteration potentials of 0.02 V for oxidation and –0.21 V for the reduction were shown.

This allowed it to be established that the polypyrrole sensor array had a good cross sensitivity in the coffee samples under study. Additionally, it was observed that each of the sensors provided a different signal, which reflects a diversity and variability in the information obtained. These results allowed it to be established that the sensor array provided a voltammetric fingerprint of each of the samples and therefore sufficient information for their analysis and discrimination.

In order to evaluate the discrimination capacity of the electronic tongue against the adulterated coffee samples, the measurements were made in each of the samples and all the data was organized in a matrix with the current data recorded by the sensor array, the rows being the samples under analysis. The discrimination capacity was carried out through a principal component analysis. The results obtained with this statistical treatment are presented in Figure 2, in which the scores of the first three components are presented and summarize 93.45% of the variance (48.21% in the

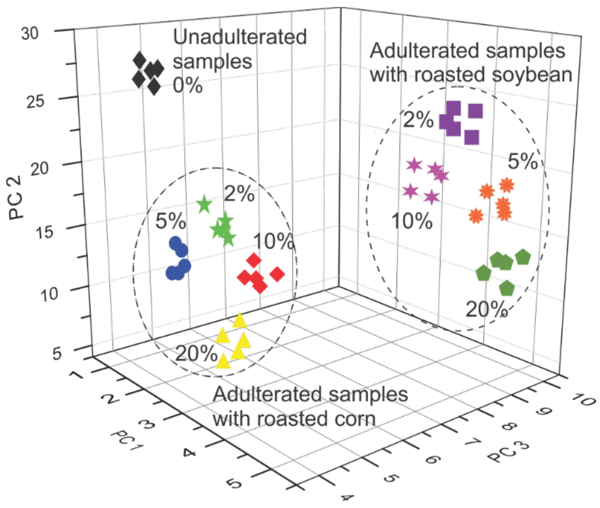

Fig. 2. 3D PCA plot analysis for unadulterated and adulterated coffee samples by using electronic tongue device

first component, 32.59% in the second component and 12.65% in the third component). It can be observed that the samples were clearly discriminated.

The samples of unadulterated coffee were markedly distant from the adulterated samples. In addition, the samples were grouped into two large groups (macro groups), one corresponding to the samples adulterated with roasted corn and the other with samples adulterated with roasted soybean, showing that, in addition to discriminating the adulterated samples, it was possible to differentiate the type of adulterant. Within the groups of each adulterant, samples with different concentrations of adulterants were also differentiated into subgroups.

In order to validate the excellent discrimination capacity shown by the electronic tongue in the principal component analysis, a cluster analysis was carried out. The coefficient of similarity and Euclidian distance were used to group the cases in clusters.

Figure 3 shows the dendogram obtained from the cluster analysis. The discrimination of the samples in groups can be clearly appreciated. As in the principal component analysis, the unadulterated sample is separated from the others, while the samples adulterated with roasted corn and roasted soybean are separated into two macro groups, which contain subgroups of the adulterated samples in different concentrations well differentiated from each other.

The possibility of using the electronic tongue to make quantitative determinations of the amount of adulterant was explored through the application of partial least squares analysis (PLS). The PLS regression analysis was carried out with cross validation for checking the model and five latent variables were used. The Figure 4 shows the PLS graphs in which real concentrations of adulterant vs. predicted concentrations by an electronic tongue are shown by fitting the experimental points to a linear model.

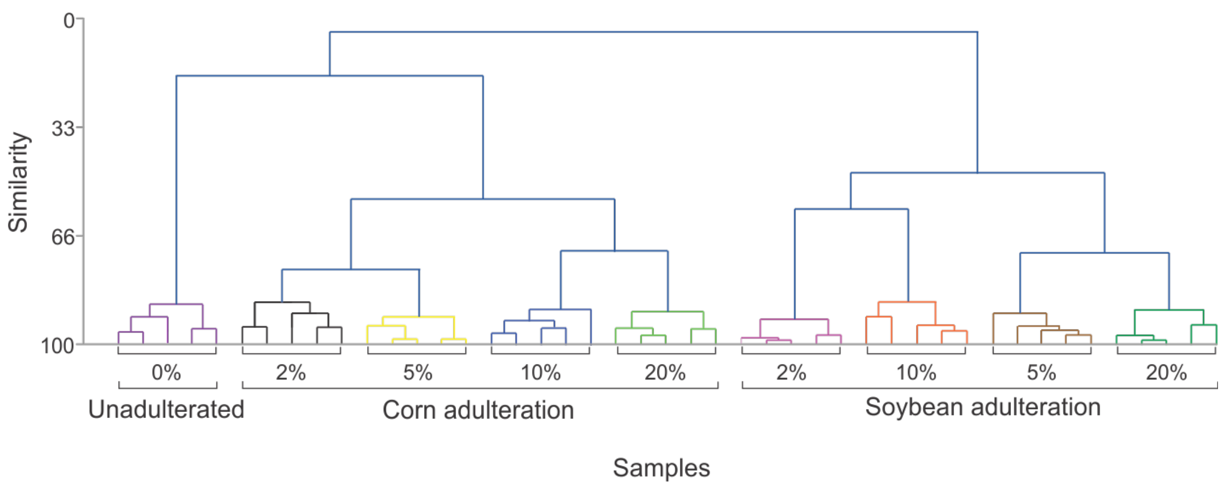

Fig. 3. Dendogram from cluster analysis for adulterated coffee with roasted soybean and roasted corn

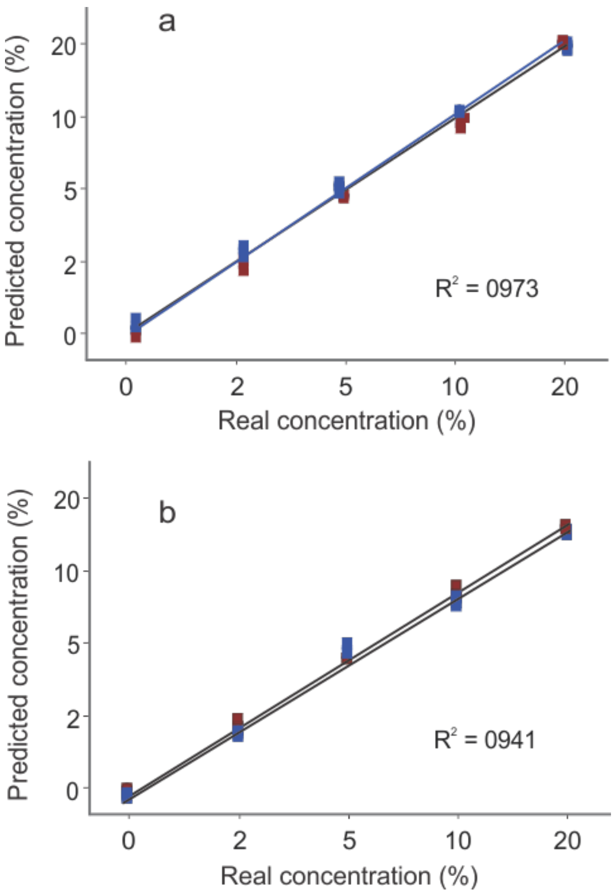

Fig. 4. Real concentration vs. predicted concentration by electronic tongue obtained by PLS models of adulterated samples with: a – roasted corn, b – roasted soybean

It can be observed that with the models it was possible to establish a good correlation, with R2 values of 0.973 for the prediction model of samples adulterated with roasted corn and 0.941 for the model of the samples adulterated with roasted soybean. The predicted concentration values obtained using PLS technique, by correlating the reals concentrations and the electronic tongue responses, showed a good correlation among them. These results show that the electronic tongue used in this study could be successfully applied as an alternative analytical method for quantification of roasted corn and roasted soybean used as adulterants in coffee.

CONCLUSIONS

Through the use of a voltammetric electronic tongue equipped with a polypyrrole sensor array, it was possible to discriminate samples of coffee adulterated with roasted corn and roasted soybean in different concentrations. The discrimination was carried out by principal component analysis and the results showed an excellent capacity for discrimination.

The discrimination capacity was also evaluated and corroborated through the application of cluster analysis. The results were consistent with those obtained by principal component analysis, which allows a good level of certainty of the classification made with the application of the developed electronic tongue.

The ability to perform quantitative determinations was carried out through the application of partial least squares. The results of this study showed that the information provided by the sensor array contains quantitative information that can be used to predict the concentration of adulterants in coffee samples using regression models.

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