International Journal of Technology 11(2) 288-298 (2020)
Received June 2019 / Revised February 2020 / Accepted March 2020

International Journal of Technology

http://ijtech.eng.ui.ac.id

Mini-electronic Tongue Used to Discriminate between Coffee Samples of Different Geographical Origin

A.A. Arrieta[1*], Y.E. Núñez[2], J.M. Mendoza[3]

[1]*Department of Biology and Chemistry –University of Sucre, Carrera 28 # 5-267 Barrio Puerta Roja, P.C 700008, Sincelejo, Colombia*
[2]*Universidade Tecnológica Federal do Paraná, ua Dep. Heitor Alencar Furtado, 5000 – Campo Comprido, Curitiba – PR, 81280-340, Brazil*
[3]*Department of Mechanical Engineering, University of Cordoba, Carrera 6 No. 76-103, C.P. 14014, Montería, Colombia*

Abstract. This paper presents a mini-electronic tongue that used a polymeric sensor array made from polypyrrole to discriminate between coffee samples of different geographical origin. The electronic tongue consisted of a system with a voltammetric sensor array coupled to a multichannel measuring device (multi-potentiostat) that was controlled by a multivariable data collection and processing application. The samples analyzed comprised two types: a series of substances with different chemical and taste properties and a group of samples of coffee of the Arabica variety harvested from different geographical areas of Colombia. The electronic tongue demonstrated the ability to discriminate between solutions with different gustatory properties. In the analysis of the coffee samples, each sensor showed a particular voltammetric response to each of the samples studied. A principal component analysis was undertaken, which resulted in clear discrimination between each of the coffee samples. It was concluded that the portable electronic tongue equipped with polymer sensors is able to discriminate between samples of coffee of different geographical origin.

Keywords: Coffee; Electronic tongue; Electrochemistry; Polypyrrole; Sensors

1. Introduction

Coffee is undoubtedly one of the most popular drinks around the world, and for this reason, it has been widely studied (Mahachandra et al., 2017; Iswanto et al., 2019; Haryuni et al., 2019). Its commercialization occupies a very important place in the economies of countries like Colombia, Brazil, and Vietnam, among others. In Colombia, several dozen municipalities produce coffee; however, each producing area generates grains with different organoleptic characteristics that differentiate them from each other and from the varieties of coffee grown in other countries (Sanja et al., 2008; Athanassiou et al., 2016; Mehari et al., 2016; Thorburn-Burns et al., 2017).

Accordingly, the concept of denomination of origin was generated, which guarantees the quality and provenance of a product. In Colombia, there are more than 10 denominations of origin, and each offers a coffee with particular features and certain quality

*Corresponding author's email: alvaro.arrieta@unisucre.edu.co, Tel.: +57-3008403075
doi: 10.14716/ijtech.v11i2.3225

specifications. It is thus very important for this sector to be able to acquire technology that will allow its members to quickly and easily differentiate between and classify their products by denomination of origin. Several authors have attempted to discriminate between, classify, and determine the authenticity of coffee varieties by analyzing the chemical compounds present in the products using conventional analytical methods such as chromatography or mass spectrophotometry (Sanja et al., 2008; Mehari et al., 2016). However, more than a thousand different chemical compounds can exist in a single sample of coffee. At present, sensorial analysis is the most commonly used method to analyze the organoleptic qualities of a coffee and to determine its characteristics, among them, its geographical origin and the conditions of the crop and harvest.

These sensorial methods aim to evaluate the sensations produced by a particular coffee as a whole. Sensory analysis can be defined as the experimentation and analysis of the global characteristics of a product through the senses; such features are known as organoleptic characteristics. The senses of smell and taste are known as chemical biosensors because they respond directly to stimuli produced by molecules that cause nervous excitation. Thus, the olfactory and gustative systems serve as inspiration for the development of devices seeking in some way to mimic their ability to classify and discriminate between complex substances. These systems are known as electronic noses and electronic tongues (Parra et al., 2006; Di Rosa et al., 2017).

Electronic tongues are used mainly to analyze substances in the liquid phase and have been applied successfully to test numerous beverages (Parra et al., 2006; Chen et al., 2008; Arrieta et al., 2010; Arrieta and Tarazona, 2014; Fuentes et al., 2017). An electronic tongue device consists of three parts: a sensor array that is responsible for sensing analytical samples, a multichannel electronic system, and a computer system equipped with multivariate statistical analysis tools. Although electronic tongues have been used in numerous applications, their use in the discrimination and classification of coffee has rarely been reported (Buratti et al., 2014; Lopetcharat et al., 2016). Indeed, to the best of our knowledge, there are no studies in which coffee samples have been classified according to their geographical origin using this new technology. Accordingly, this work explores the potential of a voltammetric electronic tongue to discriminate between coffee samples with organoleptic characteristics, which is important when validating the origin of these types of products.

The aim of this work was to evaluate the application of a mini-electronic tongue to discriminate between coffee samples from different geographic regions. The device comprised a polymeric sensor array made from polypyrrole (PPy) modified with different counterions, a multichannel electronic device based on programmable system-on-chip (PSoC) technology coupled to a computer system with multivariable analysis tools.

2. Methods

All the reagents used in this study, namely, pyrrole, potassium hexacyanidoferrate II (HCF), phosphotungstic acid (PA), sodium salt of dodecylbenzenesulfonate (DBS), sodium salt of anthraquinone-1,5-disulfonic acid (AQDS), sodium salt of p-toluenesulfonate (pTS), sulfonic acid (SF), lithium perchlorate (PC), citric acid, sucrose, vanillin, caffeine, and sodium chloride, were of analytical grade.

All the samples and solutions were prepared using Milli-Q grade ultrapure water. Coffee of the Arabica variety (*Coffea arabica*) from different geographic regions of Colombia (Cauca, Risaralda, Cesar, Quindío, and Antioquia) were used as samples. The samples were selected during the same harvest period and where similar cultivation processes had been used to allow for the highest possible study reliability. Trademarks were therefore not used since, in most cases, they use grain mixtures. The coffee samples were prepared according to NTC standard 3566 (preparation of samples for use in sensory analysis). In practice, this meant that 7 g of each sample was weighed and prepared in 100 mL of water preheated to boiling point. The infusion was allowed to decant for 5 min, then the residues were removed from the beverage surface and allowed to cool to room temperature.

A cyclic voltammetry technique was applied for the sensing of the coffee samples. This technique requires three types of electrodes: an auxiliary electrode (platinum), a reference electrode (Ag/AgCl), and working electrodes. In this case, 7 working electrodes (sensor array) were used.

The working electrodes consisted of platinum electrodes, which were modified by chronoamperometric electrodeposition (at 0.8 V) of PPy doped with 7 different counterions— HCF, PA, DBS, AQDS, pTS, SF, PC—allowing one for each sensor. Thereby, a sensor array with different properties was obtained in order to enrich the amount of information registered in each measurement. The details of the preparation of the sensor array are presented in Table 1.

The electronic tongue equipment used was developed in our laboratory and is shown in a scheme in Figure 1. The multichannel system was based on a potentiostat circuit. The equipment was developed using PSoC technology, which allowed the majority of the analog and digital blocks necessary for the electronic tongue to be configured within the same chip. The FREESOC card, which contained a PSoC5 LP chip, was programmed using the software PSoC Creator. The control functions involved the cyclic voltammetry and Bluetooth communication with the computer system, both of which were developed using PSoC Creator. Details regarding the development of the device have been published previously (Arrieta and Fuentes, 2016).

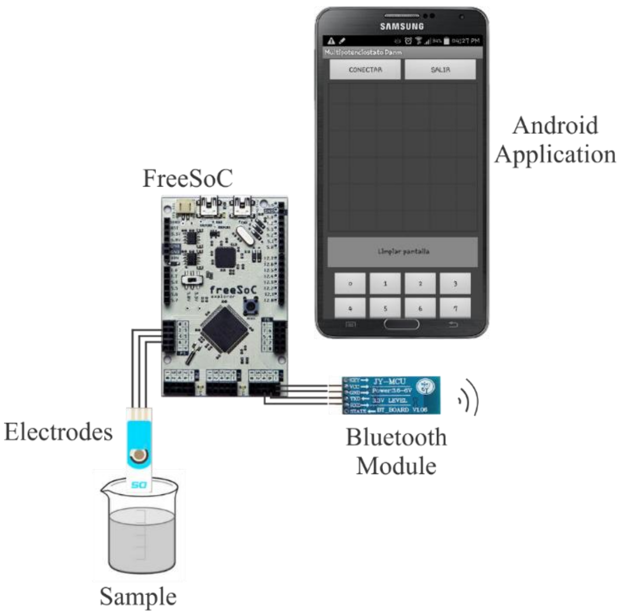


Figure 1 Scheme of the electronic tongue system

The coffee samples were measured using an electronic device developed in our laboratory. Before performing the measurements, the sensors of the polymeric sensor array were extracted from the synthesis solution and carefully washed. The data processing was done using Statistica software version 7. A principal component analysis was carried out to evaluate the discrimination capability of the electronic tongue device.

3. Results and Discussion

To test the correct operation of the electronic tongue prototype, the cyclic voltammetry technique was applied in a ferrocene 0.1 M solution using a commercial potentiostat/galvanostat PAR 273A. Similar experiments have been performed using the device (multi-potentiostat) developed in our laboratory. The applied potential range was −1 to −0.5 V over a period of 8s. Cyclic voltammetry was carried out with some of the samples using carbon working electrodes. Fifteen cycles of potential ramp in the electrochemical cell were applied in order to ensure the stability of the sensor response and the device operation. The voltammetric signals recorded by both devices were very similar, which showed that the multichannel system (multi-potentiostat) based on PSoC technology could be used for signal acquisition and in the processing stage in an electronic tongue device. The preparation conditions and counterions of the sensor array are presented in Table 1. These have been tested previously and offer stable sensors with well-defined signals (Arrieta and Tarazona, 2014).

Table 1 Polymerization conditions of the polypyrrole sensor array

Ppy/counterions	Concentration (M) Ppy/counterion	Polymerization time (s)
PPy/HCF	0.2/0.05	25
PPy/PA	0.2/0.1	50
PPy/DBS	0.2/0.1	50
PPy/AQDS	0.2/0.1	50
PPy/pTS	0.2/0.1	50
PPy/SF	0.2/0.05	25
PPy/PC	0.2/0.1	30

Determining the ability of the sensor array to discriminate between substances required preliminary testing with several simple chemical substances that had different chemical and taste properties. This is a common approach in sensor array testing (Arrieta et al., 2004; Dias et al., 2009). Thus, to evaluate the discrimination capabilities of the sensor array, the device was tested using five simple substances related to the basic flavors associated with coffee: saltiness/NaCl (0.1 M), sweetness/sucrose (0.1 M), bitterness/caffeine (0.1 M), sourness/citric acid (0.1 M), and bitterness/vanillin (0.1 M). Seven replicas of each measure were made. In terms of the voltammetric responses, a rich variety of sensor responses were observed because of the use of different electroactive materials resulting from the change in doping agent inside the Ppy sensors. Accordingly, each sensor produced a particular response to each basic taste property, thus providing a degree of cross-selectivity. Figure 2 shows the response of the PPy/AQDS sensor as an example of the responses of the sensors to the substances with different taste properties. Clearly differentiated responses can be observed for the solutions of citric acid, sucrose, and NaCl. Thus, the different registered voltammetric signals showed that each PPy sensor had demonstrated a particular response or "fingerprint" to a type of chemical substance with a specific taste property and had generated a signal based on the information received from the analyzed substance.

The information obtained from the voltammetric measurements was organized in a matrix and analyzed using a multivariate statistical method. The data were processed without previous pre-treatment using a principal component analysis method. Figure 3 shows the results obtained from the principal components analysis. It is evident that the substances with basic flavors were perfectly differentiated. The three components summarized 90.8% of the information: the first component (PC 1) with 56.7% of the information, the second component (PC 2) with 21.1%, and the third component (PC 3) with 13.0%. The spatial distribution shows that the 7 measurements in each substance formed clusters, and each cluster represented a different substance that was perfectly differentiated from the others: the NaCl/saltiness (a), citric acid/sourness (d), and sucrose/sweetness (e) clusters are located in the negative quadrant of the first component in Figure 3, and the caffeine (b) and vanillin (c) clusters that corresponded to the bitterness substances are found in the positive quadrant of the first component. This indicates an excellent discrimination capacity for these types of simple substances with their different chemical and taste characteristics.

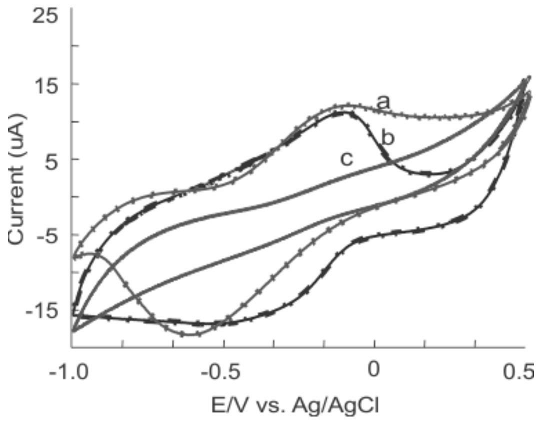


Figure 2 Voltammetric signals from PPy/AQDS obtained from: (a) citric acid (sourness); (b) sucrose (sweetness); and (c) NaCl (saltiness)

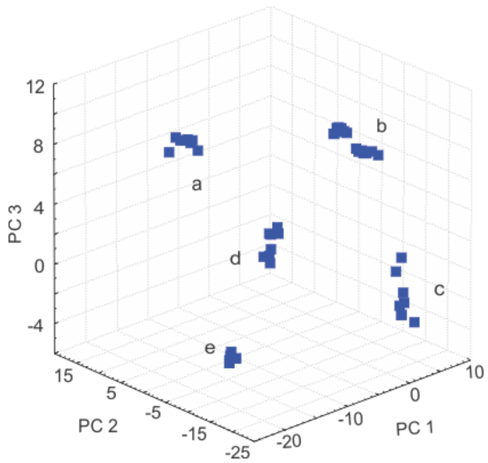


Figure 3 Plot of the principal component analysis obtained using the signal matrix of the simple substances with basic taste properties: (a) NaCl (saltiness); (b) caffeine (bitterness); (c) vanillin (bitterness); (d) citric acid (sourness); and (e) sucrose (sweetness)

Although the PPy sensor array had been tested previously to discriminate between coffee samples from different commercial brands (Arrieta and Tarazona, 2014), discriminating between samples from different geographic locations is more complex due to the high similarity of the characteristics of the samples; they tend to be coincident in terms of grain variety, toasting, vintage, and preparation processes. In this study, once the ability of the device to discriminate between simple substances had been demonstrated, measures were taken of samples of coffee from different geographic regions in order to test the discrimination capacity of the device in a substance as complex as coffee, which has more than 1000 chemical compounds.

Figure 4 shows the results obtained from the principal component analysis using the signal matrix and represents the five coffee samples from the different geographic regions of Colombia (i.e., Cauca, Risaralda, Cesar, Quindío and Antioquia). As can be seen, the polymeric sensor array was able to discriminate perfectly between the five coffee samples. The three principal components represented reflect a variance of 87.71%. The first component collected the most information at 41.01%. The second component also collected a significant amount of information at 26.92%, while the third component collected 19.78%.

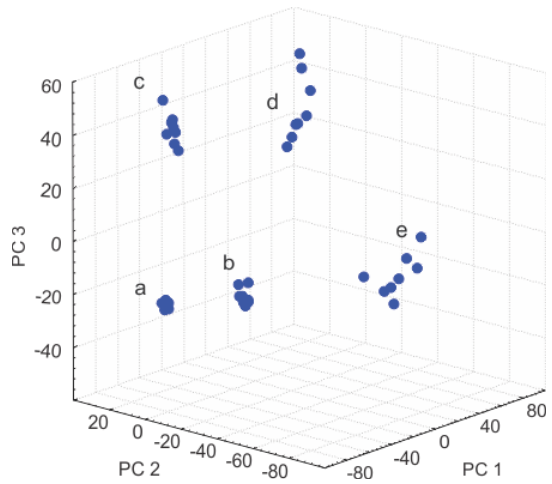


Figure 4 Principal component analysis results obtained using the signal matrix of five coffee samples from the geographic regions of: (a) Quindio; (b) Risaralda; (c) Caldas; (d) Antioquia; and (e) Cesar

The geometric distribution of the samples in the main component graph was somewhat related to the distribution of the geographic areas of the samples. For example, in Figure 5, the sample corresponding to Cesar is located a distance from the group of the other four samples (Quindio, Risaralda, Caldas, and Antioquia), which corresponds to the nearest and similar areas in terms of their geographical features. This may be because, with an average altitude of 50 m, the Cesar region is agroclimatically different from the other coffee-producing regions in this study. On the other hand, it is important to note that the samples from Quindio and Risaralda are closer to each other on the graph. This may be because the two regions share many similarities in terms of weather conditions, temperature, soil type, and altitude (1458 m and 1516 m, respectively), which gives them similar humidity. It was therefore expected that the samples from these two regions would be more similar to each other than to the other regions. The samples from Caldas and Antioquia also showed a certain closeness, which may be attributed to similarities in their agroclimatic conditions. The map in Figure 5 clearly shows the areas of origin of the samples and their geographical distribution. This result confirms that the electronic tongue sensor array was able to register sufficient information in its signals to discriminate between coffee samples of the same variety that were processed in similar ways and whose main difference was their geographical location (i.e., origin denomination).

Figure 5 Map of the geographic regions of the coffee samples under study: (a) Quindio; (b) Risaralda; (c) Caldas; (d) Antioquia; and (e) Cesar

4. Conclusions

In this study, an electronic tongue device with PSoC technology that was integrated with a polymeric sensor array with PPy modified using different counterions was shown to be capable of discriminating between simple substances with distinct chemistry and gustatory properties: NaCl (saltiness), sucrose (sweetness), caffeine (bitterness), citric acid (sourness), and vanillin (bitterness). Each sensor presented a different signal for each analyzed sample, demonstrating cross-selectivity, and this allowed the sensor to generate a fingerprint of the sample. This information was then extracted through principal component analysis, enabling the sensor to discriminate between each substance. The mini-electronic tongue device was able to discriminate between samples of coffee harvested from different geographical areas (although the samples were of the same varieties and processed similarly). In this study, it was concluded that the information provided by the sensor array could collect and supply sufficient information to discriminate between the coffee samples from different origin denominations. Additionally, the results showed that this discrimination was related to the geographical similarities of the areas of origin of the samples. This type of study opens the possibility of applying the electronic tongue not only in the coffee sector, but also for use with other products where the designations of origin are synonymous with quality and have a significant impact on the price of, and market for, the products.

Acknowledgements

The authors acknowledge the financial support provided by the Administrative Department of Science, Technology and Innovation (Colciencias) and the University of Sucre.

References

Arrieta, A.A., Apetrei, C., Rodríguez-Méndez, M.L., De Saja, J.A., 2004. Voltammetric Sensor Array based on Conducting Polymer-modified Electrodes for the Discrimination of Liquids. *Electrochimica Acta*, Volume 49(26), pp. 4543–4551

Arrieta, A.A., Fuentes, O., 2016. Electronic Tongue: New Tool for Food Analysis Based a PSoC (Programmable System-on-Chip) Technology. *Advance Journal of Food Science and Technology*, Volume 12(11), pp. 603–608

Arrieta, A.A., Rodríguez-Méndez, M.L., De Saja, J.A., Blanco, C.A., Nimubona, D., 2010. Prediction of Bitterness and Alcoholic Strength in Beer using an Electronic Tongue. *Food Chemistry*, Volume 123(3), pp. 642–646

Arrieta, A.A., Tarazona, R., 2014. Electronic Tongue and Neural Networks, Biologically Inspired Systems Applied to Classifying Coffee Samples. *American Journal of Analytical Chemistry*, Volume 5(4), pp. 266–274

Athanassiou, C.G., Chiou, A., Rumbos, C.I., Karagiannis, A., Nikolidaki, E.K., Panagopoulou, E.A., Kouvelas, A., Karathanos, V.T., 2016. Effects of Electric Infrared Heating with Light Source Penetration on Microbial and Entomological Loads of Dried Currants and Their Organoleptic Characteristics. *Journal of Pest Science*, Volume 89(4), pp. 931–943

Buratti, S., Sinelli, N., Bertone, E., Venturello, A., Casiraghi, E., Geobaldo, F., 2014. Discrimination between Washed Arabica, Natural Arabica and Robusta Coffees by using Near Infrared Spectroscopy, Electronic Nose and Electronic Tongue Analysis. *Journal of the Science of Food and Agriculture*, Volume 95(11), pp. 2192–2200

Chen, Q., Zhao, J., Vittayapadung, S., 2008. Identification of the Green Tea Grade Level using Electronic Tongue and Pattern Recognition. *Food Research International*, Volume 41(5), pp. 500–504

Di Rosa, A.R., Leone, F., Cheli, F., Chiofalo, V., 2017. Fusion of Electronic Nose, Electronic Tongue and Computer Vision for Animal Source Food Authentication and Quality Assessment – A Review. *Journal of Food Engineering*, Volume 210, pp. 62–75

Dias, L.A., Peres, A.M., Veloso, A.C., Reis, F.S., Vilas-Boas, M., Machado, A.A., 2009. An Electronic Tongue Taste Evaluation: Identification of Goat Milk Adulteration with Bovine Milk. *Sensors and Actuators B: Chemical*, Volume 136(1), pp. 209–217

Fuentes, E., Alcañiz, M., Contat, L., Baldeón, E., Barat, J.M., Grau, R., 2017. Influence of Potential Pulses Amplitude Sequence in a Voltammetric Electronic Tongue (VET) Applied to Assess Antioxidant Capacity in Aliso. *Food Chemistry*, Volume 224(1), pp. 233–241

Haryuni, Dewi, T.S.K., Suprapti, E., Rahman, S.F., Gozan, M., 2019. The Effect of *Beauveria bassiana* on the Effectiveness of *Nicotiana tabacum* Extract as Biopesticide against *Hypothenemus hampei* to Robusta Coffee. *International Journal of Technology*, Volume 10(1), pp. 159–166

Iswanto, T., Hendrianie, N., Shovitri, M., Altway, A., Widjaja, T., 2019. The Effect of Mixed Biological Pretreatment and PEG 4000 on Reducing Sugar Production from Coffee Pulp Waste. *International Journal of Technology*, Volume 10(3), pp. 453–462

Lopetcharat, K., Kulapichitr, F., Suppavorasatit, I., Chodjarusawad, T., Phatthara-aneksin, A., Pratontep, S., Borompichaichartkul, C., 2016. Relationship between Overall Difference Decision and Electronic Tongue: Discrimination of Civet Coffee. *Journal of Food Engineering*, Volume 180, pp. 60–68

Mahachandra, M., Munzayanah, S., Yassierli, 2017. The Efficacy of One-time and Intermittent Intake of Coffee as a Countermeasure to Sleepiness on Partially Sleep-deprived Drivers. *International Journal of Technology*, Volume 8(2), pp. 300–310

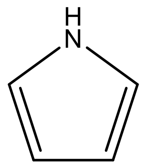
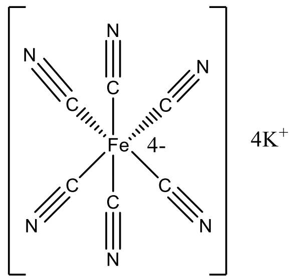
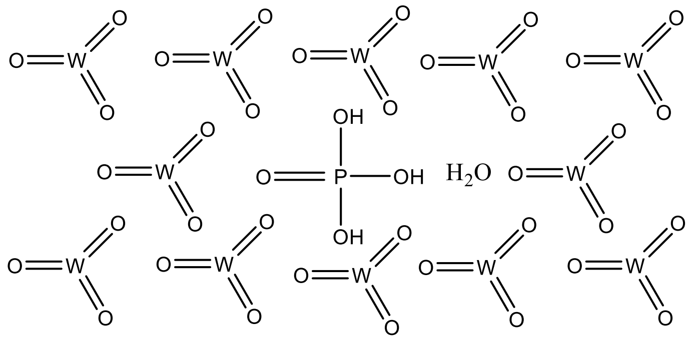
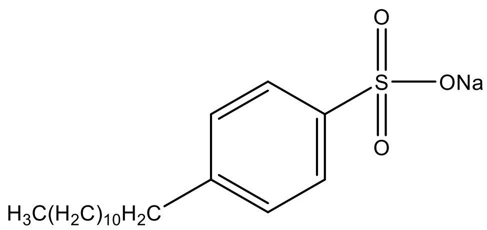
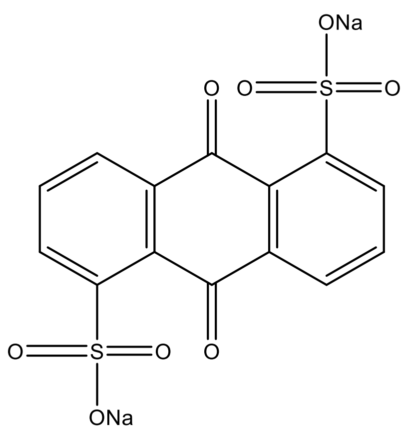
Mehari, B., Redi-Abshiro, M., Chandravanshi, B.S., Combrinck, S., Atlabachew, M., McCrindle, R., 2016. Profiling of Phenolic Compounds using UPLC-MS for Determining the Geographical Origin of Green Coffee Beans from Ethiopia. *Journal of Food Composition and Analysis*, Volume 45, pp. 16–25

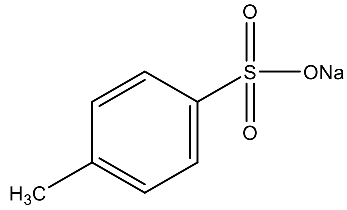
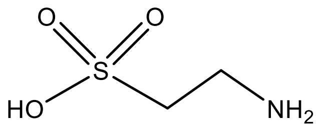
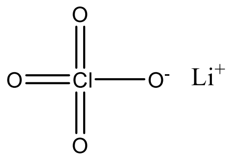
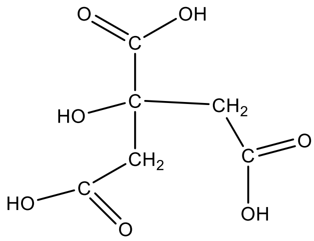
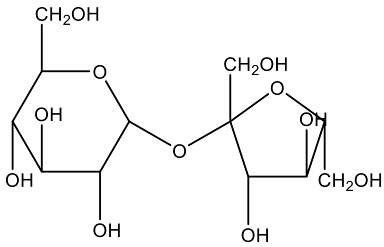
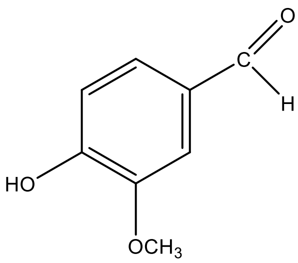
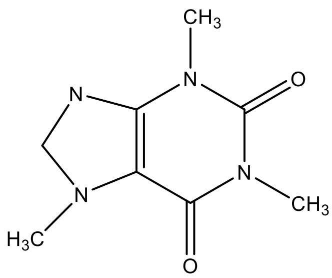
Parra, V., Arrieta, A.A., Fernández-Escudero, J., Rodríguez-Méndez, M.L., De Saja, J.A., 2006. Electronic Tongue based on Chemically Modified Electrodes and Voltammetry for the Detection of Adulterations in Wines. *Sensors and Actuators B*, Volume 118(1-2), pp. 448–453

Sanja, R.A., Carasekb, E., Janusz, P., 2008. Headspace Solid-phase Microextraction–gas Chromatographic–Time-of-Flight Mass Pectrometric Methodology for Geographical Origin Verification of Coffee. *Analytica Chimica Acta*, Volume 617(1-2), pp. 72–84

Thorburn-Burns, D., Tweed, L., Walker, M.J., 2017. Ground Roast Coffee: Review of Analytical Strategies to Estimate Geographic Origin, Species Authenticity and Adulteration by Dilution. *Food Analytical Methods*, Volume 10(7), pp. 2302–2310

ADDITIONAL INFORMATION
Structure of the chemical compounds used in the work

Chemical compounds	Structure
Pyrrole	
Potassium hexacyanidoferrate II	
Phosphotungstic acid	
sodium salt of dodecylbenzenesulfonate	
Sodium salt of anthraquinone-1,5-disulfonic acid	

Sodium salt of p-toluenesulfonate	
Sulfonic acid	
Lithium perchlorate	
Citric acid	
Sucrose	
Vanillin	
Caffeine	
Sodium chloride	Na^{+} Cl^{-}