



Contents lists available at ScienceDirect

LWT - Food Science and Technology

journal homepage: www.elsevier.com/locate/lwt

Identification of adulteration in ground roasted coffees using UV–Vis spectroscopy and SPA-LDA

Urijatan Teixeira de Carvalho Polari Souto ^a, Mayara Ferreira Barbosa ^a,
 Hebertty Vieira Dantas ^a, Aline Santos de Pontes ^a, Wellington da Silva Lyra ^a,
 Paulo Henrique Gonçalves Dias Diniz ^b, Mário César Ugulino de Araújo ^a,
 Edvan Cirino da Silva ^{a,*}

^a Universidade Federal da Paraíba, Departamento de Química, P.O. Box 5093, Zip Code 58051-970, João Pessoa, PB, Brazil

^b Universidade Estadual da Paraíba, Centro de Ciência e Tecnologia, Departamento de Química, Zip Code 58.429-500, Campina Grande, PB, Brazil

ARTICLE INFO

Article history:

Received 12 December 2014

Received in revised form

25 March 2015

Accepted 2 April 2015

Available online xxx

Keywords:

Ground roasted coffee

Adulteration

UV–Vis spectroscopy

Successive Projections Algorithm

Linear Discriminant Analysis

ABSTRACT

The pleasant taste and flavor of coffee are responsible for making it one of the most preferred and consumed beverages around the world. Industrial coffee plants usually roast both coffee and adulterants together, which affects directly the quality of the product, specially the sensorial characteristics of the drink. Therefore, this work aims the identification of adulterations in ground roasted coffees (due to the presence of husks and sticks) using ultraviolet–visible spectroscopy and the Successive Projections Algorithm for variable selection in association with Linear Discriminant Analysis (SPA-LDA). For this purpose, extracts of ground roasted coffees prepared in hot water alone (representing the final product as ingested by the consumers) were then analyzed. The proposed methodology obtained a 100% classification in both training and test sets, providing a simple and fast analysis of the aqueous extracts of ground roasted coffees. Moreover, it can also afford security to coffee consumers and regulatory agencies, preventing the fraudulent labeling.

© 2015 Published by Elsevier Ltd.

1. Introduction

Coffee is one of the most preferred and consumed beverages around the world due to its pleasant taste and flavor. In order to stimulate the growth in demand for coffee through the establishment of a better overall standard of quality to the global market, the International Coffee Organization (ICO) implemented in 2002 the Coffee Quality Improvement Programme (CQP), subsequently modified by Resolution No. 420 of May 2004. This Programme consists of target standards for exportable coffee, restricting exports of coffee below a minimum accepted quality level and diverting low-grade coffee to alternative uses. This improvement of coffee quality and the consequent increase in its demand took the coffee to be one of the world's top commodities, being Brazil the largest coffee-producing country (more than a third of the total world production in the crop year of 2012/2013 (Nebesny & Budryn, 2006; Van der Vossen, 2009, Souto et al., 2014; ICO, 2014)).

As the largest exporting member of ICO, the Brazilian Coffee Industry Association (ABIC) also implemented the CQP, aiming supply the highest standard of quality to its ground roasted coffees. Moreover, in 2010 the Brazilian Ministry of Agriculture, Livestock, and Food Supply (MAPA) issued the Normative Instruction No. 16, establishing a maximum limit of 1 g/100 g for a set of impurities (husks and sticks), sediments (stones, clods and sand), and foreign matter (corn, rye, sugar, barley, *açaí* seeds, etc.) in ground roasted coffees in order to avoid an illegal practice of adulteration by coffee producers (MAPA, 2010).

Nevertheless, there is an intentional or unintentional character of defrauding the ground roasted coffee by some sectors of the coffee production chain, encompassing some cooperatives and industries roasting. Industrial coffee plants usually roast both coffee and adulterants together, in increasing degrees of roasting levels (whether light, medium, medium-dark, or dark), favoring the adhesion of fine roasted coffee particles onto the surface of the adulterants due to oil absorption. Thus, the presence of these impurities affects directly the quality of the ground roasted coffee, specially the sensorial characteristics of the drink (Sano, Assad,

* Corresponding author. Tel./fax: +55 83 3216 7438.

E-mail address: edvan@quimica.ufpb.br (E.C. da Silva).

Cunha, Correa, & Rodrigues, 2003; Toledo, Hantao, Ho, Augusto, & Anderson, 2014).

Quality control of the drink depends on its basic attributes (aroma, flavor, body and acidity), which are traditionally evaluated by skillful tasters. However, this human sensory assessment is markedly impartial and unreliable (Murray, Delahunty, & Baxter, 2001; Sano et al., 2003; Tavares et al., 2012). To overcome these drawbacks, several analytical techniques have been applied to detect and/or quantify coffee adulteration, such as gas chromatography/mass spectrometry (Toledo et al., 2014), and high performance liquid chromatography (Pauli et al., 2014; Domingues et al., 2014), Fourier transform infrared spectroscopy (Reis, Franca, & Oliveira, 2013), near infrared spectroscopy (Ebrahimi-Najafabadi et al., 2012), mid-infrared spectroscopy (Tavares et al., 2012), and digital image processing (Sano et al., 2003; Souto et al., 2014).

A simple alternative is to develop an analytical methodology using ultraviolet–visible (UV–Vis) spectroscopy, which is one of the most common and inexpensive techniques used in routine analysis. Therefore, this work aims the identification of adulterations in ground roasted coffees (due to the presence of husks and sticks) using UV–Vis spectroscopy and the Successive Projections Algorithm for variable selection in association with Linear Discriminant Analysis (SPA-LDA). For this purpose, extracts of ground roasted coffees prepared in hot water alone (representing the final product as ingested by the consumers) were then analyzed. For comparison, others supervised pattern recognition techniques such as Soft Independent Modelling by Class Analogy (SIMCA) and Partial Least Squares Discriminant Analysis (PLS-DA) were also used. It is worth to highlight that UV–Vis spectroscopy and pattern recognition techniques were already successfully used to classify aqueous extracts of Brazilian ground roast coffee according to its type (caffeinated/decaffeinated) and conservation state (expired and non-expired shelf-life) (Souto et al., 2010).

2. Materials and methods

2.1. Sample preparation

A total of 102 ground roasted coffee samples were collected from 14 different regions of Brazil (State producers) along 6 months. They were then, certified by the Brazilian Coffee Industry Association (ABIC), and were provided by the Brazilian research laboratories *Global Center for Analysis and Research* (NUGAP), and *National Service for Industrial Training* (SENAI). The samples were distributed into two classes, being 45 non-adulterated and 57 adulterated with husks and sticks. Non-adulterated coffees are exclusively composed of ground roasted coffee beans without adulterations by husks and sticks. The adulterations in the ground roasted coffee samples were in the range of 1.04–7.63 g/100 g (4.05 ± 1.66 g/100 g) by following the Normative Instruction No. 16 of Brazilian Ministry of Agriculture, Livestock, and Food Supply (MAPA, 2010), which is based on gravimetry and optical microscopy.

An aqueous extraction procedure of the coffee samples was performed as described by Souto et al. (2010). Initially, 1.0 g of each sample was weighed and placed in a filter funnel containing a 25 μ m pore-sized quantitative filter paper (J. Prolab® white ribbon filter) coupled with an erlenmeyer. The extractions were performed by using distilled water at 90–98 °C during 25 min for each sample. After cooling process to room temperature (for 30 min), all extracts were then diluted in the proportion of 1:20 (mL:mL) with distilled water. UV–Vis spectra from the aqueous extracts were acquired according to procedure described as follows.

2.2. Instrumentation and data acquisition

UV–Vis spectra (239–405 nm) were acquired in triplicate by using a Hewlett Packard model HP 8453 UV–Vis spectrophotometer equipped with a quartz cell with optical path of 10 mm, and spectral resolution of 1 nm at a 23 ± 1 °C room temperature. Before the measurements step, blank (the same water used in extraction step) was placed inside of the sample cell to adjust the 100% transmittance signal.

2.3. Chemometric procedures and software

The obtained data set was divided into training (63 samples, being 26 non-adulterated and 37 adulterated coffees) and test (39 samples, being 19 non-adulterated and 20 adulterated coffees) sets by applying the Kennard-Stone (KS) uniform sampling algorithm (Kennard & Stone, 1969). Unsupervised (Principal Component Analysis – PCA) and supervised (SIMCA, PLS-DA and SPA-LDA) pattern recognition techniques were employed. The validation step for each of the algorithms was performed using full cross-validation. The test samples were used for the final data evaluation, and for comparison of the classification models only (Soares, Gomes, Galvão Filho, Araújo, & Galvão, 2013). The classification performance of the models was evaluated for accuracy, sensitivity and specificity (Massart, Vandeginste, Buydens, Lewi, & Smeyers-Verbeke, 1998; Lavine, 2009).

The KS and SPA-LDA algorithms were performed with Matlab® 2009b (Mathworks Inc.) software. SIMCA and PLS-DA were calculated by using the Classification toolbox for Matlab® (version 2.0) released by Milano Chemometrics, and QSAR Research Group (Ballabio & Consonni, 2013).

3. Results and discussion

The quality of the coffee beans is affected by several factors coming from the stages of harvesting, processing and storage. In fact, there is a direct influence of the quality of the ground roasted coffee powder on its aqueous extracts in terms of flavor and aroma. In this sense, the main contribution is given by changes during the roasting process, in which occur relevant physicochemical reactions (such as Maillard reaction, Strecker degradation, sugars caramelizing, chlorogenic acids degradation, proteins and polysaccharides degradation) due to interactions between the various chemical compounds present in the coffee beans (proteins, carbohydrates, chlorogenic acids, caffeine, trigonelline, lipids etc.) when subjected to heat (Nicoli, Anese, Manzocco, & Lerici, 1997; Baggenstoss, Poisson, Kaegi, Perren, & Escher, 2008; Vignoli, Viegas, Bassoli, & Benassi, 2014). These differential characteristics

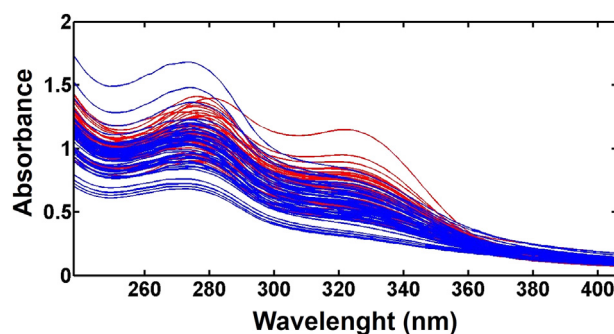


Fig. 1. UV–Vis spectra of the 102 studied roasted coffee samples: non-adulterated (in red) and adulterated (in blue) coffee samples. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

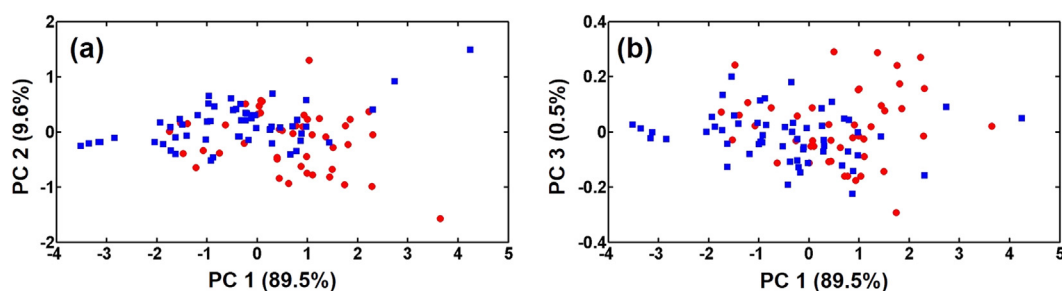


Fig. 2. Score plots for the 102 studied aqueous extracts of both non-adulterated (red circle) and adulterated (blue square) coffee samples: (a) PC1 \times PC2 and (b) PC1 \times PC3. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Table 1

Confusion matrix with accuracy, sensitivity and specificity of the classification of coffee samples by SIMCA, PLS-DA and SPA-LDA.

		Training set		Test set	
		Class A	Class N	Class A	Class N
Assigned by SIMCA	Class A (6 PCs) ^a	23	14	13	7
	Class N (3 PCs) ^a	3	23	1	18
SIMCA metrics	Accuracy (%)	73.0		79.5	
	Sensitivity (%)	62.2		65.0	
	Specificity (%)	88.5		94.7	
Assigned by PLS-DA (11 latent variables) ^b	Class A	36	1	20	0
	Class N	1	25	1	18
PLS-DA metrics	Accuracy (%)	96.8		97.4	
	Sensitivity (%)	97.3		100	
	Specificity (%)	96.1		94.7	
Assigned by SPA-LDA	Class A	37	0	20	0
	Class N	0	26	0	19
SPA-LDA metrics	Accuracy (%)	100		100	
	Sensitivity (%)	100		100	
	Specificity (%)	100		100	

A = adulterated and N = non-adulterated coffee samples.

^a Optimal number of PCs for each class is indicated in parenthesis.

^b Optimal number of latent variables is indicated in parenthesis.

of aqueous extracts of ground roasted coffees are therefore reflected in their respective spectra of molecular absorption in the UV–Vis region, as discussed in the next Section.

3.1. Exploratory analysis of the data

Fig. 1 shows the absorbance spectra of all aqueous extracts of coffee samples in the range of 239–405 nm. As can be seen, the most informative portion of the spectra is related to the useful $n \rightarrow \pi^*$ transition of the C=O chromophore, which is present in the molecules of trigonelline, caffeine, caffeic acid and melanoidins (Moores, McDermott, & Wood, 1948; Kogan, DiCarlo, & Maynard, 1953; Bicchi, Binello, Legovich, Pellegrino, & Vanni, 1993; De

Maria, Trugo, Moreira, & Petracco, 1995; Murray et al., 2001; Bekedam, Loots, Schols, Van Boekel, & Smit, 2008; Fujioka & Shibamoto, 2008; Moreira, Scheel, Hatumura, & Scarminio, 2014). However, differences between this chromophore and conjugated olefinic bonds, besides of intermolecular interactions with the polar solvent (water) used in the extractions, cause displacement on the maxima electronic absorptions of trigonelline from 272 nm to 275 nm, caffeine from 276 nm to 280 nm, caffeic acid from 320 nm to 325 nm, and melanoidins from 400 to 405 nm (Moreira, Nunes, Domingues, & Coimbra, 2012; De Maria et al., 1995; Fujioka & Shibamoto, 2008; López-Martínez, López-de-Alba, García-Campos, & De León-Rodríguez, 2003; Bekedam, Schols, Van Boekel, & Smit, 2006).

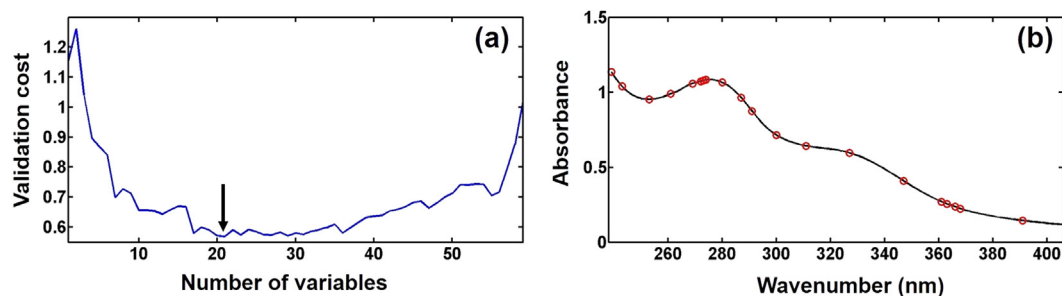


Fig. 3. (a) Graph of the cost function value versus the number of selected variables in SPA-LDA. (b) Mean spectra of the 102 studied aqueous extracts of ground roasted coffee samples with the variables selected by SPA. The arrow in (a) indicates the optimum number of variables selected by SPA. The red circles in (b) indicate the 21 wavelengths selected by SPA. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

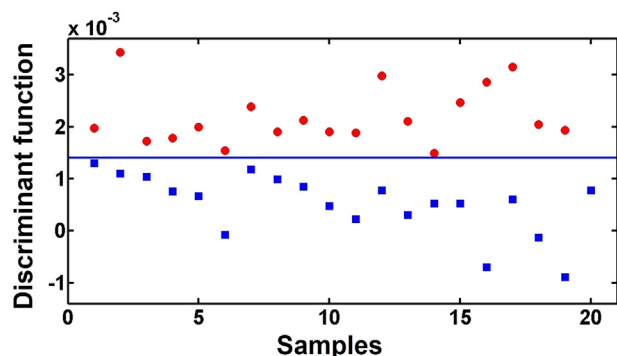


Fig. 4. Fisher's discriminant function for the 39 studied aqueous extracts of ground roasted coffee samples in the test set using the 21 wavelengths selected by SPA.

In order to evaluate the discriminating ability of the UV–Vis spectra of the aqueous extracts of both non-adulterated and adulterated coffees, a principal component analysis was performed. Fig. 2 shows the score plots in the three first PCs (PC1 \times PC2 and PC1 \times PC3) resulting from the application of PCA to the UV–Vis spectra of all samples. Although Fig. 2 shows a tendency of separation, a slight overlap between the two studied classes is observed, which can be related to their similarities in chemical composition. Therefore, it can be verified that the use of supervised pattern recognition techniques can lead to a more appropriate classification of the studied coffee samples, as presented in Section 3.2.

3.2. Classification

The construction of the multivariate classification models was performed using a training set (63 samples), and followed by validation using the leave-one-out cross-validation technique. A test set (39 samples) was then used for final data evaluation and comparison to the classification models. Table 1 presents the confusion matrix, with the accuracy, sensitivity and specificity of the coffee samples classifications using SIMCA, PLS-DA and SPA-LDA models.

Although PLS-DA results were satisfactory (superior to 94%) for the accuracy, sensitivity and specificity rates, the SPA-LDA model obtained 100% classification (also in terms of accuracy, sensitivity and specificity rates) for all samples used in the training and test sets. The optimal SPA-LDA model was determined for a minimum validation G cost value of 0.5693 (Fig. 3a) obtained by using 21 variables alone (Fig. 3a). This means that the selected wavelengths contribute better to the prediction ability of the SPA-LDA model to discriminate non-adulterated and adulterated (by husks and sticks) coffee samples, instead of full spectrum-based SIMCA and PLS-DA models. For illustration, Fig. 4 shows the Fisher's discriminant function for the 39 studied aqueous extracts of ground roasted coffee samples in the test set using the 21 wavelengths selected by SPA.

4. Conclusion

This paper demonstrates a new methodology to identify adulteration of ground roasted coffees for husks and sticks using molecular absorption spectroscopy in the UV–Vis region and supervised pattern recognition techniques. In this sense, the use of UV–Vis spectroscopy and variable selection taken by SPA associated with linear discriminant analysis was the most appropriate approach for classification of the 102 studied aqueous extracts of ground roasted coffee samples.

This approach presents intrinsic advantages because it provides a simple and fast analysis of the extracts of ground roasted coffees prepared in hot water alone, which represent the final product as ingested by the consumers. Moreover, it can also afford security to coffee consumers and regulatory agencies, preventing the fraudulent labeling. However, a larger and more varied testing of other adulterants that uses more coffee samples must be implemented to generalize the proposed methodology.

Compliance with ethics requirements

Urijatan Teixeira de Carvalho Polari Souto declares that he has no conflict of interest.

Mayara Ferreira Barbosa declares that he has no conflict of interest.

Hebertty Vieira Dantas declares that he has no conflict of interest.

Aline Santos de Pontes declares that he has no conflict of interest.

Wellington da Silva Lyra declares that he has no conflict of interest.

Paulo Henrique Gonçalves Dias Diniz declares that he has no conflict of interest.

Edvan Cirino da Silva declares that he has no conflict of interest. Mário César Ugulino de Araújo declares that he has no conflict of interest.

This article does not contain any studies with human or animal subjects.

Acknowledgments

The authors gratefully acknowledge Capes and CNPq Brazil scholarships and research fellowships. The authors also thank the Brazilian research laboratories *Núcleo Global de Análise e Pesquisa* (NUGAP), and the *Serviço Nacional de Aprendizagem Industrial* (SENAI) for providing the samples. Paulo Henrique Gonçalves Dias Diniz thanks the Fundação de Apoio à Pesquisa do Estado da Paraíba – FAPESQ-PB (Grant no. 022/13).

References

- Baggenstoss, J., Poisson, L., Kaegi, R., Perren, R., & Escher, F. (2008). Coffee roasting and aroma formation: application of different time-temperature conditions. *Journal of Agricultural and Food Chemistry*, 56, 5836–5846.
- Ballabio, D., & Consonni, V. (2013). Classification tools in chemistry. Part 1: linear models. PLS-DA. *Analytical Methods*, 5, 3790–3798.
- Bekedam, E. K., Loots, M. J., Schols, H. A., Van Boekel, M. A. J. S., & Smit, G. (2008). Roasting effects on formation mechanisms of coffee brew melanoidins. *Journal of Agricultural and Food Chemistry*, 56, 7138–7145.
- Bekedam, E. K., Schols, H. A., Van Boekel, M. A. J. S., & Smit, G. (2006). High molecular weight melanoidins from coffee brew. *Journal of Agricultural and Food Chemistry*, 54, 7658–7666.
- Bicchi, C. P., Binello, A. E., Legovich, M. M., Pellegrino, G. M., & Vanni, A. C. (1993). Characterization of roasted coffee by S-HSGC and HPLC-UV and principal component analysis. *Journal of Agricultural and Food Chemistry*, 41, 2324–2328.
- De Maria, C. A. B., Trugo, L. C., Moreira, R. F. A., & Petracco, M. (1995). Simultaneous determination of total chlorogenic acid, trigonelline and caffeine in green coffee samples by high performance gel filtration chromatography. *Food Chemistry*, 52, 447–449.
- Domingues, D. S., Pauli, E. D., Abreu, J. E. M., Massura, F. W., Cristiano, V., Santos, M. J., et al. (2014). Detection of roasted and ground coffee adulteration by HPLC by amperometric and by post-column derivatization UV–Vis detection. *Food Chemistry*, 146, 353–362.
- Ebrahimi-Najafabadi, H., Leardi, R., Oliveri, P., Casolino, M. C., Jalali-Heravi, M., & Lanteri, S. (2012). Detection of addition of barley to coffee using near infrared spectroscopy and chemometric techniques. *Talanta*, 99, 175–179.
- Fujioka, K., & Shibamoto, T. (2008). Chlorogenic acid and caffeine contents in various commercial brewed coffees. *Food Chemistry*, 106, 217–221.
- International Coffee Organization. (2014). *Improving quality*. http://www.ico.org/improving_quality.asp?section=What_We_Do Accessed 11.02.14.
- Kennard, R. W., & Stone, L. A. (1969). Computer aided design of experiments. *Technometrics*, 11, 137–148.

- Kogan, L., DiCarlo, F. J., & Maynard, W. E. (1953). Determination of caffeine and trigonelline in coffee by paper chromatography. *Analytical Chemistry*, 25, 1118–1120.
- Lavine, B. K. (2009). Validation of classifiers. In B. Walczak, R. Tauler, & S. Brown (Eds.), *Comprehensive chemometrics* (Vol. 3, pp. 587–599). Oxford: Elsevier.
- López-Martínez, L., López-de-Alba, P. L., García-Campos, R., & De León-Rodríguez, L. M. (2003). Simultaneous determination of methylxanthines in coffees and teas by UV–Vis spectrophotometry and partial least squares. *Analytica Chimica Acta*, 493, 83–94.
- Massart, D. L., Vandeginste, B. G. M., Buydens, S. J., Lewi, P. J., & Smeyers-Verbeke, J. (1998). *Handbook of chemometrics and qualimetrics, Part A*. Amsterdam: Elsevier.
- Ministério da Agricultura, Pecuária e Abastecimento. (2010). *Regulamento técnico para o café torrado em grão e para o café torrado e moído*. Instrução Normativa Nº 16, de 24 de Maio de 2010.
- Moore, R. G., McDermott, D. L., & Wood, T. R. (1948). Determination of chlorogenic acid in coffee. *Analytical Chemistry*, 20, 620–624.
- Moreira, A. S. P., Nunes, F. M., Domingues, M. R., & Coimbra, M. A. (2012). Coffee melanoidins: structures, mechanisms of formation and potential health impacts. *Food & Function*, 3, 903–915.
- Moreira, I., Scheel, G. L., Hatumura, P. H., & Scarminio, I. S. (2014). Solvent effects on extraction of chlorogenic acids, caffeine and trigonelline in *Coffea arabica*. *Química Nova*, 37, 39–43.
- Murray, J. M., Delahunty, C. M., & Baxter, I. A. (2001). Descriptive sensory analysis: past, present and future. *Food Research International*, 34, 461–471.
- Nebesny, E., & Budryn, G. (2006). Evaluation of sensory attributes of coffee brews from robusta coffee roasted under different conditions. *European Food Research and Technology*, 224, 159–165.
- Nicoli, M. C., Anese, M., Manzocco, L., & Lerici, C. R. (1997). Antioxidant properties of coffee brews in relation to the roasting degree. *LWT—Food Science and Technology*, 30, 292–297.
- Pauli, E. D., Barbieri, F., Garcia, P. S., Madeira, T. B., Acquaro, V. R., Jr., Scarminio, I. S., et al. (2014). Detection of ground roasted coffee adulteration with roasted soybean and wheat. *Food Research International*, 61, 112–119.
- Reis, N., Franca, A. S., & Oliveira, L. S. (2013). Performance of diffuse reflectance infrared Fourier transform spectroscopy and chemometrics for detection of multiple adulterants in roasted and ground coffee. *LWT—Food Science and Technology*, 53, 395–401.
- Sano, E. E., Assad, E. D., Cunha, S. A. R., Correa, T. B. S., & Rodrigues, H. R. (2003). Quantifying adulteration in roast coffee powders by digital image processing. *Journal of Food Quality*, 26, 123–134.
- Soares, S. F. C., Gomes, A. A., Galvão Filho, A. R., Araújo, M. C. U., & Galvão, R. K. H. (2013). The successive projections algorithm. *Trends in Analytical Chemistry*, 42, 84–98.
- Souto, U. T. C. P., Barbosa, M. F., Dantas, H. V., Pontes, A. S., Lyra, W. S., Diniz, P. H. G. D., et al. (2014). Screening for coffee adulteration using digital images and SPA-LDA. *Food Analytical Methods*. <http://dx.doi.org/10.1007/s12161-014-0020-7> (in press).
- Souto, U. T. C. P., Pontes, M. J. C., Silva, E. C., Galvão, R. K. H., Araújo, M. C. U., Sanches, F. A. C., et al. (2010). UV–Vis spectrometric classification of coffees by SPA-LDA. *Food Chemistry*, 119, 368–371.
- Tavares, K. M., Pereira, R. G. F. A., Nunes, C. A., Pinheiro, A. C. M., Rodarte, M. P., & Guerreiro, M. C. (2012). Mid-infrared spectroscopy and chemometrics were used to identify adulteration in roasted and ground coffee by addition of coffee husks. *Química Nova*, 35, 1164–1168.
- Toledo, B. R., Hantao, L. W., Ho, T. D., Augusto, F., & Anderson, J. L. (2014). A chemometric approach toward the detection and quantification of coffee adulteration by solid-phase microextraction using polymeric ionic liquid sorbent coatings. *Journal of Chromatography A*, 1346, 1–7.
- Van der Vossen, H. A. M. (2009). The cup quality of disease-resistant cultivars of arabica coffee (*Coffea arabica*). *Experimental Agriculture*, 45, 323–332.
- Vignoli, J. A., Viegas, M. C., Bassoli, D. G., & Benassi, M. T. (2014). Roasting process affects differently the bioactive compounds and the antioxidant activity of arabica and robusta coffees. *Food Research International*, 61, 279–285.