Brazilian Journal of Analytical Chemistry
Pre-publication – Accepted after peer review
doi: 10.30744/brjac.2179-3425.AR-184-2024

BrJAC

ARTICLE

Multivariate Assessment of Ground Coffee Samples from Bahia, Brazil on the Basis of Mineral Composition

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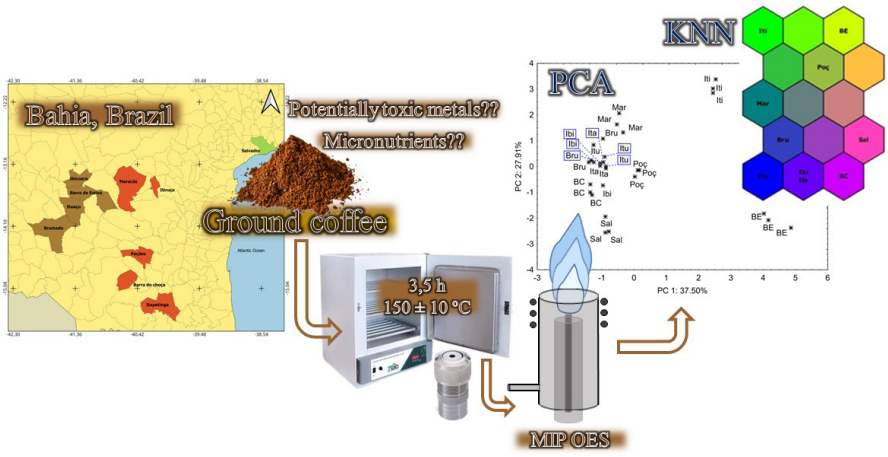

This study determined metals in ground coffee samples from different producing regions in Bahia and used Principal Component Analysis (PCA) and Kohonen neural networks as multivariate techniques to assess sample similarity based on their mineral composition. The samples were prepared using a decomposition method with dilute acid and hydrogen peroxide in a closed system under high pressure. Microwave Induced Plasma Optical Emission Spectrometry (MIP OES) was used to quantify the elements Al, Co, Cr, Cu, Fe, Mn, Ni, V and Zn. For all samples, the elements with the highest concentrations were Mn, Fe, Al, Zn and Cu; and the lowest concentrations were obtained for the elements Cr, Ni, Co and V. The results of this study provide and aggregate relevant nutritional information about coffee produced in the Southwest and Chapada Diamantina regions of Bahia.

Cite: Brandão, N. S.; da Rocha, P. C.; Amazonas, V. M.; Rocha, W. S.; Nascimento, N. A.; dos Santos, M. J. S.; Silva, A. G.; da Silva, E. G. P.; Bezerra, M. A.; Novaes, C. G. Multivariate Assessment of Ground Coffee Samples from Bahia, Brazil on the Basis of Mineral Composition. *Braz. J. Anal. Chem.* (Forthcoming). http://dx.doi.org/10.30744/brjac.2179-3425.AR-184-2024

Submitted November 27, 2024; Resubmitted April 17, 2025; Accepted August 18, 2025; Available online August 2025.

This article was submitted to the BrJAC special issue on the 21st ENQA and 9th CIAQA.

Keywords: Principal Component Analysis, Kohonen Neural Networks, Metals, Dilute acid, MIP OES

INTRODUCTION

Coffee is one of the most widely consumed beverages in the world and is produced from the roasted beans of the coffee tree. Arabica coffee (*Coffea arabica*) and conilon coffee (*Coffea canephora*) are the most widely cultivated species, and Arabica coffee is the most widely sold and consumed species, having a more appreciated aroma and flavor, while conilon, also called robusta coffee, has a more bitter flavor, containing a higher concentration of caffeine and antioxidants and a lower amount of sugar.[1]

Brazil currently occupies a prominent position as the largest coffee producer and exporter in the world.[2] The main producing regions are located in the states of Minas Gerais, Espírito Santo, São Paulo and Bahia. In the Bahia scenario, the southwest and Chapada Diamantina regions have attributes that contribute to a quality beverage, such as a mild climate, fertile soil and high altitude.[3]

Coffee seeds are rich in bioactive compounds such as chlorogenic acid, cafestol, caffeic acid and caffeine, a substance with psychostimulant properties.[4] They also have neuroprotective, antioxidant, thermogenic, anti-inflammatory, antidiabetic and antifibrotic activities. Regarding the elemental composition of coffee, this matrix contains essential macro and microelements (Ca, Mg, Fe, Co, Cu, Mn, Zn, etc.),[5] as well as potentially toxic elements (As, Cd, Hg and Pb) resulting from soil and water pollution and the uncontrolled use of inorganic fertilizers and pesticides.[6] Factors such as cultivated species, cultivation environment, production management, in addition to type of processing and storage contribute to the variation in the amount of these elements in coffee.

Essential micronutrients naturally present in coffee may present a potentially toxic character depending on their concentration levels. Copper is an important component of enzymes involved in the metabolism of amino acids, glucose, and cholesterol. On the other hand, several studies associate Wilson's disease with excessive copper accumulation in the body.[7] Zinc plays a crucial role in the development and functioning of the immune system. Conversely, chronic ingestion of zinc can increase levels of low-density lipoprotein (LDL) and decrease levels of high-density lipoprotein (HDL). The absorption of Zn can be influenced by the presence of Cu and Fe.[8] Iron is also an important essential element, necessary in the synthesis of hemoglobin, while the excess is stored as hemosiderin and ferritin proteins in the liver.[9]

Manganese is a micronutrient required for bone growth and acts in the regular metabolism of carbohydrates, proteins, and lipids. A dysfunction known as manganism, characterized by cognitive disabilities and motor disturbances, is caused by the excess of this element in the brain.[10] Cobalt is an essential element for forming vitamin B12, whereas other cobalt compounds present carcinogenic properties for the human body following excessive exposure.[11]

Aluminium is not essential for human metabolism; adversely, its toxicity disrupts hepatic energy metabolism and can be associated with Parkinson's and Alzheimer's diseases.[12] The essentiality of the element vanadium in human physiology has been a subject of great discussion. On the other hand, its excess can affect important cellular functions such as cell cycle, signaling pathways as well as cell survival mechanisms.[13] Chromium presents itself as a special case among the elements. In the human body, Cr(III) is essential for the metabolism of proteins, lipids, and glucose. In contrast, Cr(VI) is a potent carcinogen, with no recognized biological function.[14] Nickel is an essential trace element for several animal species, plants and micro-organisms. However, a deficiency state in humans is not very well established. The chronic exposure to nickel and its compounds can cause lung fibrosis, cardiovascular disease and cancer of the respiratory tract.[15]

Given the high global consumption and nutritional value of coffee, the study of the elemental composition of this matrix becomes important and necessary. To meet this demand, several analytical techniques have been used for quantification, such as atomic absorption spectrometry (AAS), direct mercury analyzer (DMA), inductively coupled plasma optical emission spectrometry (ICP OES), inductively coupled plasma mass spectrometry (ICP-MS), microwave induced plasma optical emission spectrometry (MIP OES), in addition to electroanalytical methods.[16]

Among the aforementioned techniques, MIP OES emerges as an interesting alternative for multielement analysis, since the instrument sensitivity is suitable for quantification in various food samples. Furthermore, the plasma generated in MIP OES is sustained by nitrogen taken from atmospheric air, which significantly reduces analysis costs.[17,18] However, this technique requires that the sample be in solution, a condition that can be achieved with the use of strong acids, a mixture of acids or a mixture of an acid and another auxiliary reagent. In this context, our study applied a previously validated decomposition procedure based on the application of diluted nitric acid and hydrogen peroxide, reducing the amount of reagents in the experiments, in accordance with the principles of green chemistry.[19]

Multielement techniques such as MIP OES, ICP OES and ICP-MS normally require multivariate data processing due to the large volume of information generated in the analyses, which can be obtained by applying Principal Component Analysis (PCA), an unsupervised technique based on a linear transformation that reduces the dimensionality of the original dataset while preserving the maximum possible variance. This reduction is achieved by generating new orthogonal variables, known as principal components (PCs), which retain most of the original information and allow the identification of patterns and similarities among samples. However, PCA is inherently limited to identifying linear correlations and may fail to reveal more complex, non-linear structures within the dataset. As an alternative, Artificial Neural Networks (ANN), particularly the Kohonen Self-Organizing Map (KSOM), have been increasingly applied for exploratory multivariate analysis. KSOM is an unsupervised, non-linear method capable of preserving the topological relationships of the input data, providing an intuitive and detailed visualization of sample similarities and variable contribution, and enabling the detection of subtle patterns that may not be identified by linear techniques such as PCA.[20,21]

This paper presents a current study on the concentrations of essential and potentially toxic elements in ground coffee samples grown in different producing regions of Bahia. KSOM and PCA were used as multivariate tools to assess the similarity of the samples based on the mineral composition quantified by MIP OES. The study also aimed to verify whether the levels of metals present in coffee are in accordance with those found in the literature. Our study is the first to determine the concentrations of metals in ground coffee from the vast majority of cities evaluated.

MATERIALS AND METHODS

Instrumentation

Multielement determination was performed using an MIP OES (4210, Agilent Technologies, Melbourne, Australia) axial mode, equipped with a OneNeb nebulizer, double-pass cyclonic nebulization chamber, Czerny-Turner monochromator and charge-coupled device (CCD) detection. Plasma was generated using nitrogen gas obtained from atmospheric air through an N_2 generator (4107, Agilent). The quantified elements with their respective analytical spectral lines and the instrumental parameters applied are presented in Table I.

Table I. Operating conditions used for the determination of metals by MIP OES

Parameter	Setting
Wavelength (nm)	Al 396.152 (I)*; Co 340.512 (I)*; Cr 425.433 (I)*; Cu 324.754 (I)*; Fe 371.993 (I)*; Mn 403.076 (I)*; Ni 352.454 (I)*; Pb 405.781 (I)*; V 437.923 (I)*; Zn 213.857 (I)*.
Nebulizer flow (L min^{-1})	Al 0.95; Co 0.75; Cr 0.90; Cu 0.70; Fe 0.65; Mn 0.90; Ni 0.70; Pb 0.75; V 0.50; Zn 0.45.
Applied plasma power (W)	1000
Reading time (s)	3
Number of replicas	3
Sample capture time (s)	15

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Table I. Operating conditions used for the determination of metals by MIP OES (continuation)

Parameter	Setting
Stabilization time (s)	15
Pump speed (rpm)	15
Background broker	Automatic
Sample introduction	Manual

*(I): Atomic line

Reagents, materials and solutions

The reagents used in the assays were of analytical grade and the solutions were prepared using ultrapure water (Millipore, Bedford, MA, USA; resistivity of 18.2 MΩ cm). Diluted nitric acid solutions were prepared from a 65% stock solution (Merck, Darmstadt, Germany). A 30% hydrogen peroxide solution (Synth, São Paulo, SP, Brazil) was used in the decomposition step. A multielement standard solution for calibration containing Al, Co, Cr, Cu, Fe, Mn, Ni, Pb, V and Zn was prepared from a stock solution (1000 μg mL^{-1}, Sigma-Aldrich, St. Louis, USA). Conventional glassware was decontaminated using 10% HNO_3 for at least 24 hours.

Sample acquisition and preparation

Ground coffee samples were purchased from supermarkets or directly from family farmers in nine cities in the Chapada Diamantina and Southwest regions of Bahia. The focus of the study was to evaluate two coffee producing regions and not just the cities; therefore, three samples were collected in each city. The sample collected in Salvador was included for comparison purposes only. Table II presents a description of the samples and Figure 1 shows a map of the collection sites.

To prepare the samples, approximately 0.2 g of coffee powder was subjected to decomposition in a high-pressure reactor with 1.75 mL of 7.0 mol L^{-1} nitric acid, 0.5 mL of 30% hydrogen peroxide and 2.25 mL of ultrapure water. The mixture was then subjected to an oven for 3.5 hours at 150 ± 10 ºC. After cooling the digests, they were made up with ultrapure water to a final volume of 10.0 mL and stored in the refrigerator until analysis. Analytical blank solutions were subjected to the same process as the samples.

Data processing

To obtain the geographic coordinates and altitude, a Global Positioning System (GPS, Garmin Etrex 30x) was used. The maps were created using the geographic information software QGIS 3.38. Spatial interpolation, where the geostatistical method of Ordinary Kriging (OK) was applied, used the SAGA GIS software version 7.8.2.

With the element concentration data, the basic statistical parameters were obtained using Excel®, and the multivariate parameters through PCA were obtained using Statistica® 12. For the treatment using Kohonen neural networks, a tool package developed by the Laboratory of Computer and Information Science (Helsinki University of Technology, Finland) was used, implemented using MatLab (version R2018b, MathWorks, USA). The implementation code was adapted by the research group from algorithms suggested in the literature (Haykin, 2009).[21] The Kohonen map was trained with the input data set using a batch training algorithm. The function that limited the neighborhood used in the training of the platform and for the network structure was hexagonal. Network architecture was evaluated based on qualitative indices such as quantization error (QE) and topological error (TE).

Table II. Information about the ground coffee samples and description of the locations where they were produced

Municipality of collection	Coffee (species)	Additional information
Salvador	Arabica	Supermarket purchase / Industrial processing without identification of production origin
*Barra do Choça	Arabica	Supermarket purchase / Organic coffee
*Itapetinga	No information on the label	Supermarket purchase / Industrial production
*Itiruçu	No information on the label	Supermarket purchase / Industrial production
*Maracás	Arabica	Acquisition at the planting site / Family farming production
*Poções	Arabica	Purchased at an open-air market / Family farming production
**Barra da Estiva	Arabica	Purchased directly from the producer / Family farming production
**Brumado	No information on the label	Supermarket purchase / Industrial production
**Ibicoara	Arabica	Supermarket purchase / Artisanal roasting / Agroecological coffee
**Ituaçu	Arabica	Supermarket purchase / Family farming production

Regions in Bahia: *Southwest; **Chapada Diamantina.

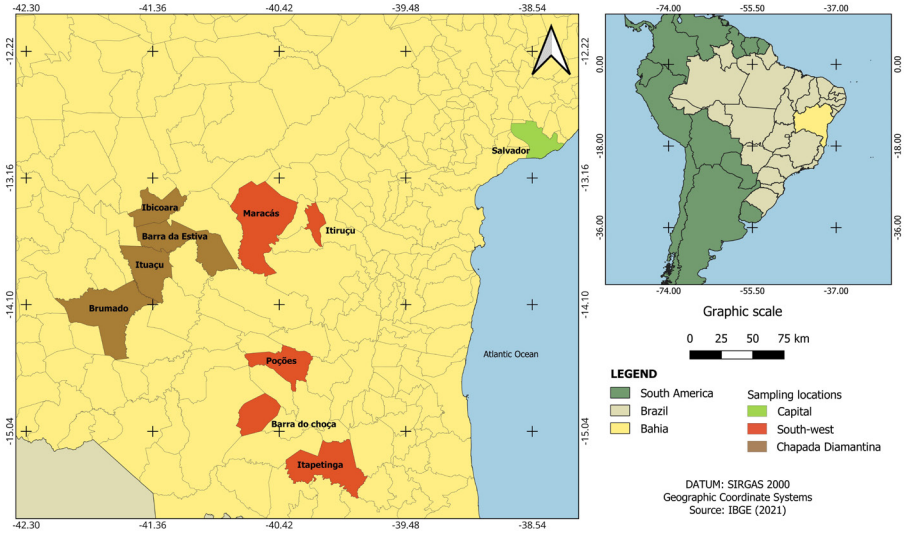

Figure 1. Map illustrating the municipalities localization where ground coffee samples were produced.

RESULTS AND DISCUSSION

Figures of merit

After preparing the ground coffee samples, Al, Co, Cr, Cu, Fe, Mn, Ni, V and Zn were quantified using MIP OES. The concentrations of the elements in the samples were calculated through linear regression obtained by least squares. The correlation coefficients were greater than 0.9988, which implies good linearity of the method; R^2 values greater than 0.998 are satisfactory, according to the National Institute of Metrology, Standardization and Industrial Quality (INMETRO).[22]

The limits of detection (LOD) and quantification (LOQ) were calculated by two methods: 1) by multiplying the standard deviation of ten analytical blank measurements by three and ten, respectively, and dividing the result by the slope of the analytical curve; 2) using the residual standard deviation of the regression line. The values obtained are presented in Table III. Although the values obtained by the second method are greater than the first, these limits were satisfactory for the quantification of the elements in ground coffee samples, with the exception of Pb, where the concentration value obtained was lower than the calculated LOQ for both methods and Cr, where the concentration of some samples was higher than the LOQ using the second method.

Intermediate precision (n=15) was evaluated by applying the same analytical methodology on different days considering the influence of random effects. The RSD (%) was in the range of 0.70 – 6.8 for the dataset, which indicates that the method has an acceptable intermediate precision, as shown in Table III.

Accuracy was evaluated by calculating the percent recovery of the analyte at three different concentration levels using spike tests (Table III). Recoveries ranging from 71.3 to 110% were obtained and are considered acceptable. Therefore, the method presents adequate precision and accuracy for the analysis of the nine metals in ground coffee samples.

Table III. Figures of merit obtained for the method applied in the analysis of ground coffee samples produced in municipalities of the Southwest and Chapada Diamantina regions of Bahia

Analyte	LOD (μg g^{-1})		LOQ (μg g^{-1})		Intermediate precision RSD (%)	Accuracy (Recovery - %)		
	Method I	Method II	Method I	Method II		Spike 1	Spike 2	Spike 3
Al	0.31	0.55	1.0	1.8	0.91	71.3	105	108
Co	0.090	0.11	0.30	0.36	3.0	88.4	91.7	84.8
Cr	0.17	0.21	0.57	0.70	1.7	80.0	96.8	96.0
Cu	0.53	1.0	1.7	2.3	0.80	73.7	80.2	81.3
Fe	1.1	1.7	3.6	5.7	0.91	74.3	96.2	94.2
Mn	0.35	0.66	1.2	2.3	3.0	77.9	94.4	85.0
Ni	0.070	0.10	0.23	0.34	1.0	110	100	98.9
Pb	0.081	0.19	0.26	0.61	6.8	75.4	95.3	94.1
V	0.032	0.037	0.10	0.11	3.7	93.0	85.8	79.2
Zn	0.45	0.99	1.4	3.1	0.70	82.1	87.9	87.7

LOD: Limit of Detection; LOQ: Limit of Quantification; RSD: Relative Standard Deviation; Method I: calculated by multiplying the standard deviation of analytical blank measurements; Method II: calculated using the residual standard deviation of the regression line.
Spike 1: 12.5 μg g^{-1} for Fe; 6.25 μg g^{-1} for Al, Ni, Pb, V and Zn; 1.25 μg g^{-1} for Co, Cr, Cu and Mn.
Spike 2: 200 μg g^{-1} for Fe; 125 μg g^{-1} for Al, Ni, Pb, V and Zn; 20.0 μg g^{-1} for Co, Cr, Cu and Mn.
Spike 3: 625 μg g^{-1} for Fe; 325 μg g^{-1} for Al, Ni, Pb, V and Zn; 312 μg g^{-1} for Co, Cr, Cu and Mn.

Application of the method in real samples

After obtaining the figures of merit for the method, Al, Co, Cr, Cu, Fe, Mn, Ni, V and Zn were quantified in ground coffee samples from ten municipalities in the State of Bahia. The results of the analyses obtained by MIP OES, represented as mean and standard deviation (n=3), are presented in Table IV and the interpolation maps with the mean concentrations are presented in Figure 2. The results for Pb were not presented, as the concentration values were below the LOQ of the technique for this element. Ultra-trace concentrations of Pb for food matrices represent relevant information, since Pb is a potentially toxic element.

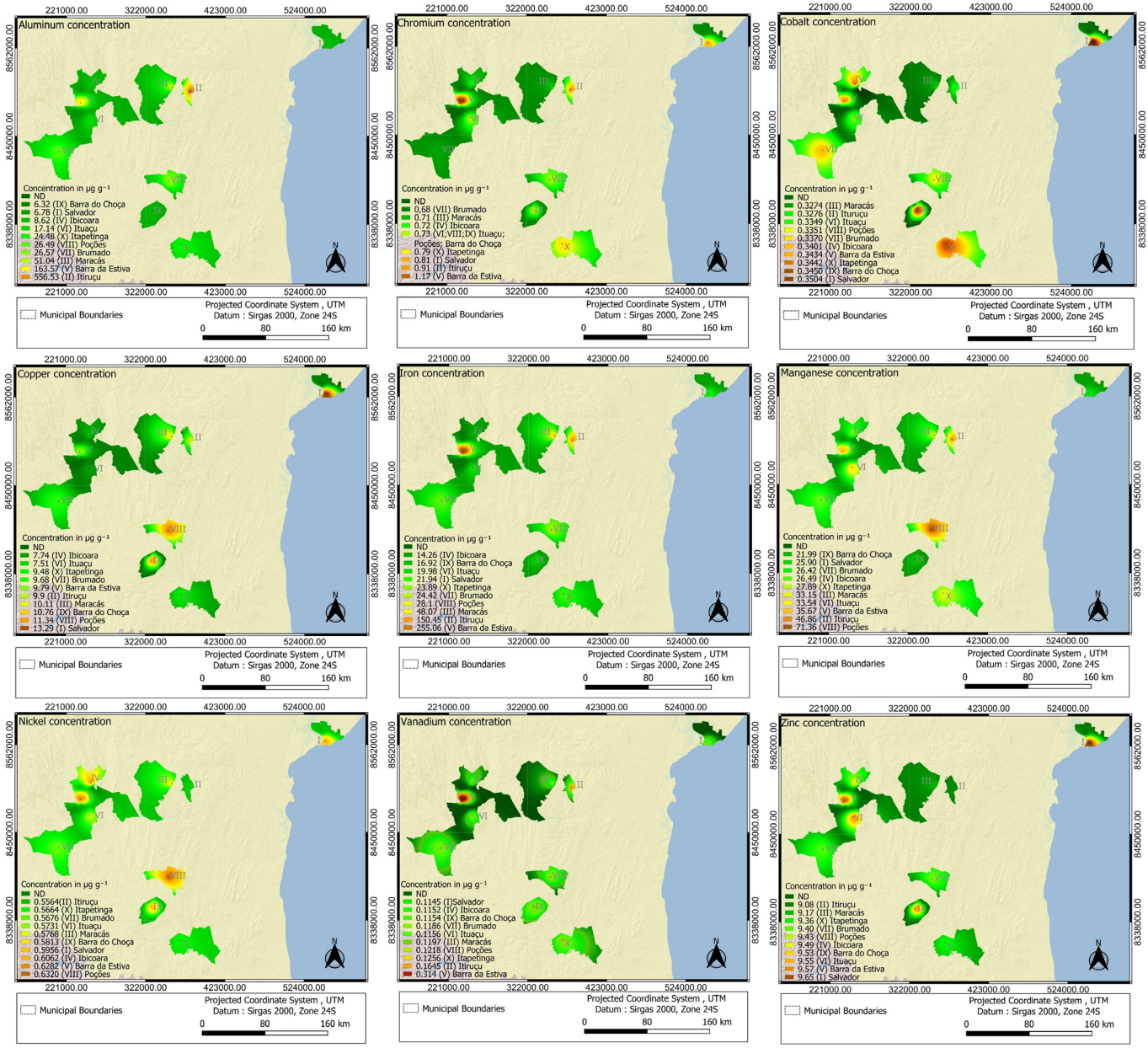

Figure 2. Interpolation maps with the mean concentrations obtained by analysis of ground coffee samples produced in municipalities of the Southwest and Chapada Diamantina regions of Bahia.

Table IV. Concentrations of elements quantified in ground coffee samples produced in municipalities of the Southwest and Chapada Diamantina regions of Bahia

Sample	Statistical parameters	Concentration (µg g^{-1})								
		Al	Co	Cr	Cu	Fe	Mn	Ni	V	Zn
Salvador	Mean	6.78	0.351	0.812	13.3	21.9	25.9	0.587	0.109	9.65
	SD	0.60	0.0030	0.051	0.38	3.7	1.6	0.0091	0.0031	0.050
	RSD (%)	8.8	0.85	6.3	2.9	17	6.2	1.6	2.8	0.52
*Barra do Choça	Mean	6.32	0.345	0.731	10.8	16.9	22.0	0.581	0.111	9.53
	SD	0.16	0.0030	0.010	0.21	0.58	0.57	0.0032	0.0012	0.10
	RSD (%)	2.5	0.87	1.4	1.9	3.4	2.6	0.55	1.1	1.1

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Table IV. Concentrations of elements quantified in ground coffee samples produced in municipalities of the Southwest and Chapada Diamantina regions of Bahia (continuation)

Sample	Statistical parameters	Concentration (μg g^{-1})								
		Al	Co	Cr	Cu	Fe	Mn	Ni	V	Zn
*Itapetinga	Mean	24.5	0.337	0.793	9.48	23.9	27.9	0.570	0.118	9.36
	SD	1.6	0.0011	0.023	0.13	1.9	0.44	0.0039	0.0012	0.038
	RSD (%)	6.5	0.23	2.9	1.4	7.9	1.6	0.68	1.1	0.41
*Itiruçu	Mean	556	0.328	0.912	9.90	150	46.9	0.558	0.161	9.08
	SD	20	0.0012	0.010	0.068	2.2	1.2	0.011	0.0032	0.041
	RSD (%)	3.6	0.37	1.1	0.69	1.5	2.6	2.0	2.0	0.45
*Maracás	Mean	51.0	0.335	0.711	10.1	48.0	33.2	0.582	0.122	9.17
	SD	2.1	0.0010	0.032	0.49	4.2	0.90	0.018	0.0010	0.078
	RSD (%)	4.1	0.30	4.5	4.9	8.8	2.7	3.1	0.82	0.85
*Poções	Mean	26.5	0.327	0.733	11.3	28.1	71.4	0.630	0.121	9.43
	SD	2.2	0.0011	0.011	0.73	1.1	0.71	0.011	0.0010	0.012
	RSD (%)	8.3	0.34	1.5	6.5	3.9	0.99	1.8	0.83	0.13
**Barra da Estiva	Mean	164	0.341	1.17	9.79	255	35.7	0.631	0.310	9.57
	SD	4.7	0.0012	0.040	0.14	18	0.54	0.051	0.021	0.038
	RSD (%)	2.9	0.35	3.4	1. 4	7.1	1.5	8.1	6.8	0.40
**Brumado	Mean	26.6	0.342	0.678	9.68	24.4	26.4	0.568	0.121	9.40
	SD	2.2	0.0042	0.031	0.051	0.47	0.62	0.0020	0.0012	0.081
	RSD (%)	8.3	1.2	4.6	0.53	1.9	2.4	0.35	1.0	0.86
**Ibicoara	Mean	8.62	0.340	0.719	7.74	14.3	26.5	0.612	0.109	9.49
	SD	0.53	0.011	0.023	0.42	0.59	0.40	0.022	0.0028	0.22
	RSD (%)	6.2	3.2	3.2	5.4	4.1	1.5	3.6	2.6	2.3
**Ituaçu	Mean	17.1	0.331	0.731	7.51	20.0	33.5	0.571	0.112	9.55
	SD	1.2	0.0010	0.060	0.12	0.47	0.60	0.0011	0.0010	0.068
	RSD (%)	7.0	0.30	8.2	1.6	2.4	1.8	0.19	1.0	0.71

Regions in Bahia: *Southwest; **Chapada Diamantina. SD: Standard Deviation; RSD: Relative Standard Deviation.

For aluminum, the highest concentration was 556 μg g^{-1} for the Itiruçu sample, followed by 164 μg g^{-1} for the Barra da Estiva sample. The lowest concentration (6.32 μg g^{-1}) was found for the Barra do Choça sample. The mean concentration obtained among the samples was 88.7 μg g^{-1}. For cobalt, the highest concentration was 0.351 μg g^{-1} for the Salvador sample, followed by 0.345 μg g^{-1} for the Barra do Choça sample. The lowest concentration (0.327 μg g^{-1}) was obtained for the Itiruçu sample. The mean concentration among the samples was 0.345 μg g^{-1}. In the case of chromium, the sample from Barra da Estiva presented the highest concentration (1.17 μg g^{-1}), followed by the sample from Itiruçu (0.912 μg g^{-1}). The sample acquired in Brumado had the lowest concentration (0.678 μg g^{-1}). The mean concentration obtained was 0.803 μg g^{-1}.

The Salvador sample had the highest concentration of copper (13.3 μg g^{-1}), followed by the Poções sample (11.3 μg g^{-1}). The lowest concentration (7.51 μg g^{-1}) was observed in the Ituaçu sample. The mean concentration obtained among the samples was 9.96 μg g^{-1}. For iron, the highest concentrations were 255 μg g^{-1} for the Barra da Estiva sample and 150 μg g^{-1} for the Itiruçu sample. The lowest concentration (14.3 μg g^{-1}) was detected in the Ibicoara sample. The mean concentration obtained among the samples was 60.3 μg g^{-1}.

For manganese, the coffee purchased in Poções had the highest concentration (71.4 μg g^{-1}) and 46.9 μg g^{-1} was found as the second highest value for the sample from Itiruçu. The lowest concentration was 22.0 μg g^{-1} for the sample from Barra do Choça and 34.9 μg g^{-1} was obtained as the mean concentration.

The highest concentration found for nickel was 0.631 μg g^{-1} for the samples from Barra da Estiva and Poções, followed by 0.612 μg g^{-1} for the sample from Ibicoara. The lowest concentration (0.558 μg g^{-1}) was found for the sample from Itiruçu and a mean concentration of 0.594 μg g^{-1} was found among the samples. For vanadium, the highest concentration was 0.310 μg g^{-1} for the samples from Barra da Estiva, followed by 0.161 μg g^{-1} for those from Itiruçu. The lowest concentration was 0.109 μg g^{-1} for the sample from Salvador. The mean concentration among the samples was 0.137 μg g^{-1}. Finally, the sample acquired in Salvador presented the highest zinc concentration (9.65 μg g^{-1}), followed by the sample from Barra da Estiva (9.57 μg g^{-1}). Itiruçu presented the lowest concentration (9.08 μg g^{-1}). The mean concentration among the samples was 9.42 μg g^{-1}.

In general, the concentrations found for each of the metals for the different samples are close to each other, with the exception of the values found for aluminum in the sample from Itiruçu (556 μg g^{-1}) and Barra da Estiva (164 μg g^{-1}) and for iron from Barra da Estiva (255 μg g^{-1}), which were much higher than in the other locations. For all samples, the elements with the highest concentrations were manganese, iron, aluminum, zinc and copper; and the lowest concentrations were observed for chromium, nickel, cobalt and vanadium. Table S1 (Supplementary material) presents the results organized in a decreasing concentration order. It is possible to verify that there is no single pattern obtained, mainly due to the differences in the origin of these samples. The similarity is present only for the elements found at lower concentrations, with the sequence Cr > Ni > Co > V being identified in all samples.

The variation in the concentration of metals in ground coffee is associated with different natural and anthropogenic factors, including atmospheric deposition; the chemical composition and pH of the soil; the form of management; contamination by fertilizers, correctives and pesticides used in cultivation; and even the proximity of plantations to large centers and highways.[23] In addition, the influence of the machinery used in the production and storage process should be taken into account which, depending on the conservation and maintenance conditions, can influence the quality of the final product.[24]

Several metals are essential for the development of plants, animals and humans. Copper, manganese, zinc and nickel are essential for the development of coffee crops, being increased via soil or leaves, which can, therefore, result in their presence in the beans. Furthermore, copper and zinc are indispensable in human metabolism and participate in enzymatic activities, while iron significantly contributes to the cellular reactions of the organism.[25,26] However, the metals studied in this research are considered potential contaminants. Factors such as concentration, route of exposure, as well as age, genetics and nutritional status of the exposed individuals are taken into consideration.[27] This further reinforces the need for studies on the concentrations present in food matrices, both for monitoring and nutritional reasons. It is also worth noting that recent information on the elemental composition of ground coffee samples in the regions studied is rare.

Data processing using multivariate analysis

A multivariate evaluation of the results obtained after the determination of the analytes by MIP OES (Table IV) was performed using principal component analysis and Kohonen neural networks. These mathematical treatments become an interesting alternative to improve the understanding and interpretation of the generated data, since it increases the understanding of the information by exploring the presence or absence of clusters among the samples.

Principal component analysis

A data matrix was initially created (10 samples × 9 variables) containing information regarding the ground coffee samples arranged in rows and information regarding the variables (individual element concentration values) arranged in columns. The Supplementary material (Table S2) presents the loading values that represent the importance of each variable to establish the principal components. Value above 0.60, highlighted in bold in the table, was considered a significant contribution.

The variables that most contribute to total variance (Al, Cr, Fe and V) presented significant values in PC1, highlighting that the first component represents 37.5% of data variance. The second principal component (PC2) accounts for 27.9% of data variance, with Co, Ni and Zn being the variables that present the highest values in PC. The third component (PC3) is responsible for 15.1% of the variance and is related to Mn. The fourth principal component (PC4) is responsible for only 10.6% of data variance and is related to Cu. The sum of the first four PCs accounts for 91.2% of data variance.

Data using PCA is interpreted through the axes of the principal components, where the score plot presents the coordinates of the samples on the new axes and the loading plot presents the eigenvectors, allowing data identification and expression, highlighting their similarities and differences. Figure 3a presents the score plot and Figure 3b presents the loading plot with the most significant PCs (PC1 × PC2). To include manganese in the evaluation, score plots (Figure 3c) and loading plots (Figure 3d) were generated using PC1 × PC3. These graphs allow the evaluation of the contribution of each variable in group separation.

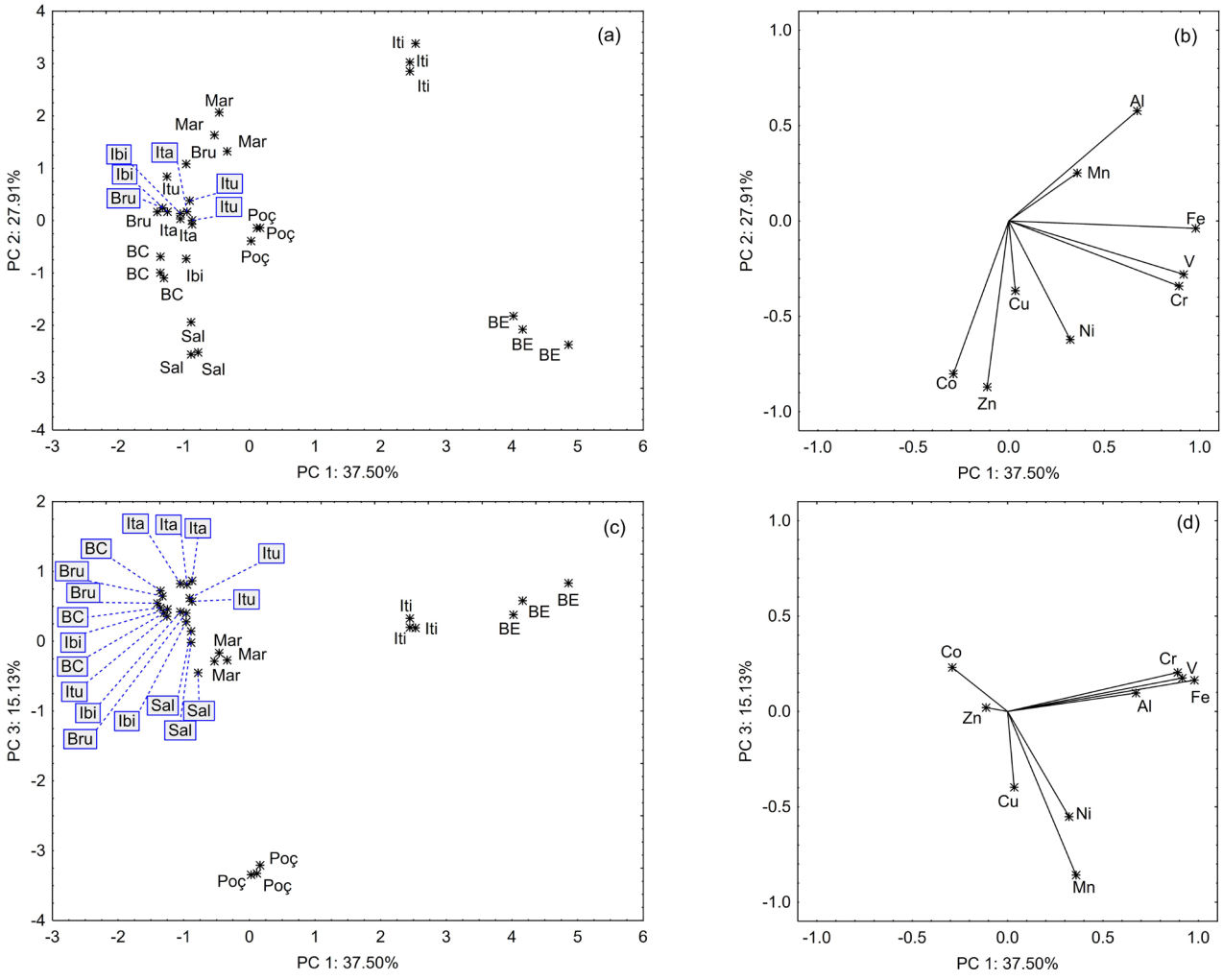

Figure 3. Plots generated from principal component analysis of the data obtained by analysis of ground coffee samples produced in municipalities of the Southwest and Chapada Diamantina regions of Bahia: (a) Score plot for PC1 × PC2; (b) Loading plot for PC1 × PC2; (c) Score plot for PC1 × PC3; and (d) Loading plot for PC1 × PC3.

Analyzing Figures 3a and 3b, it is possible to verify that the samples are separated into three parts, one consisting of the majority of the samples and the other two with isolated samples. There is a high similarity

between the samples from Barra do Choça, Brumado, Ibicoara, Itapetinga, Ituaçu, Maracás, Poções and Salvador. The grouping of these samples is due to the low concentrations of Al, Co, Cr, Fe, Ni, V and Zn. The sample from Itiruçu (present in the positive part of components 1 and 2) was isolated in the plot due to the higher concentration of Al in relation to the others. Likewise, the sample from Barra da Estiva (present in the positive part of component 1 and negative part of component 2) was isolated due to the higher concentration of Cr, Fe and V.

Analyzing Figures 3c and 3d, it is also possible to verify the formation of three clusters. The Poções sample was isolated in the plot due to the higher concentration of Mn present in relation to the other samples. Sample clustering of Barra da Estiva and Itiruçu is due both to the higher concentrations found for Al, Cr, Fe and V, and to the intermediate concentrations found for Mn. The main group observed in PC1 × PC2 is maintained when evaluating PC1 × PC3.

Neural Networks

Kohonen self-organizing maps (KSOM) are an exploratory analysis tool that identifies sample groups and variables that constitute the generated maps, in addition to interpreting linear and nonlinear variables, unlike PCA, which is only applicable to linear variables. Due to its data modeling capacity, KSOM can be used to corroborate or disconfirm PCA data. In this context, KSOM was used to evaluate whether the pattern recognition capacity could be improved.

The 5 × 3-dimension map can be seen in Figure 4a, showing the best sample distribution according to their similarities. Each hexagon represents a neuron in the map, and each sample is represented by a neuron. Figure 4b presents the unified distance matrix where warm colors (red) indicate high distance values, while cold colors (blue) indicate low distance values and the highlighted neurons (hexagons) make up the position on the map (circle) of the samples.

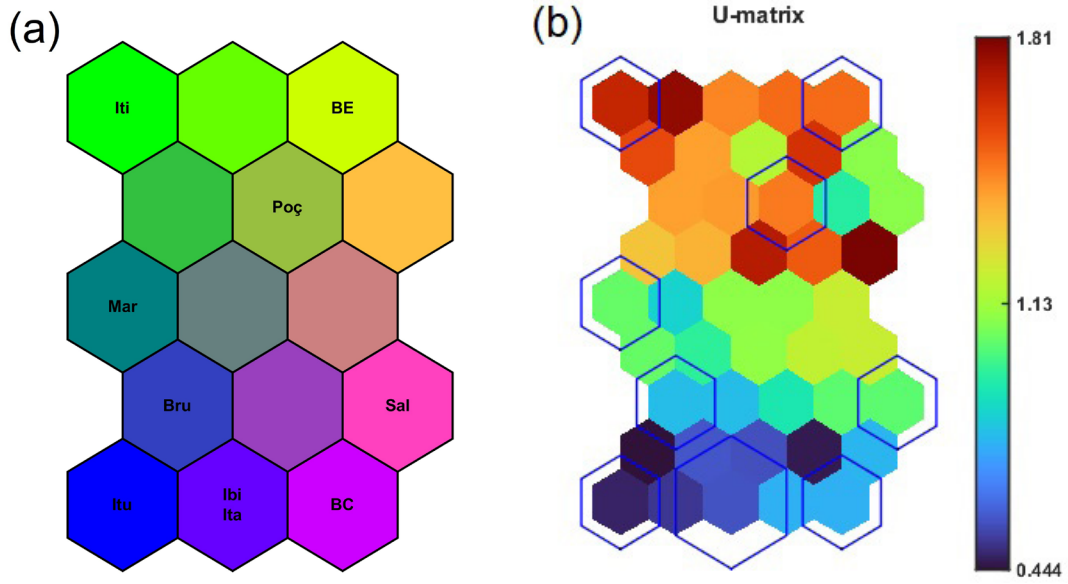

Figure 4. Graphs produced after Kohonen Self Organizing Maps application on the metal concentrations in ground coffee samples produced in municipalities of the Southwest and Chapada Diamantina regions of Bahia: (a) Best sampling distribution according to similarities and (b) Unified distance matrix.

Analyzing Figure 4, it is possible to observe a cluster formed by the cities of Poções and Barra da Estiva at first and then by Itiruçu, since both are located in the upper part on the right and left, respectively. It is also possible to see a large cluster in the lower part formed by the other cities: Barra do Choça, Brumado, Ibicoara, Itapetinga, Ituaçu, Maracás and Salvador.

The influence of variables on the formation of city clusters can be seen in the component maps (Figure 5). The position occupied by a sample on the dimensional map corresponds to the same position on the variable map. Warm colors (red) indicate high concentration values for the variable under study, while cold colors (blue) indicate low values.

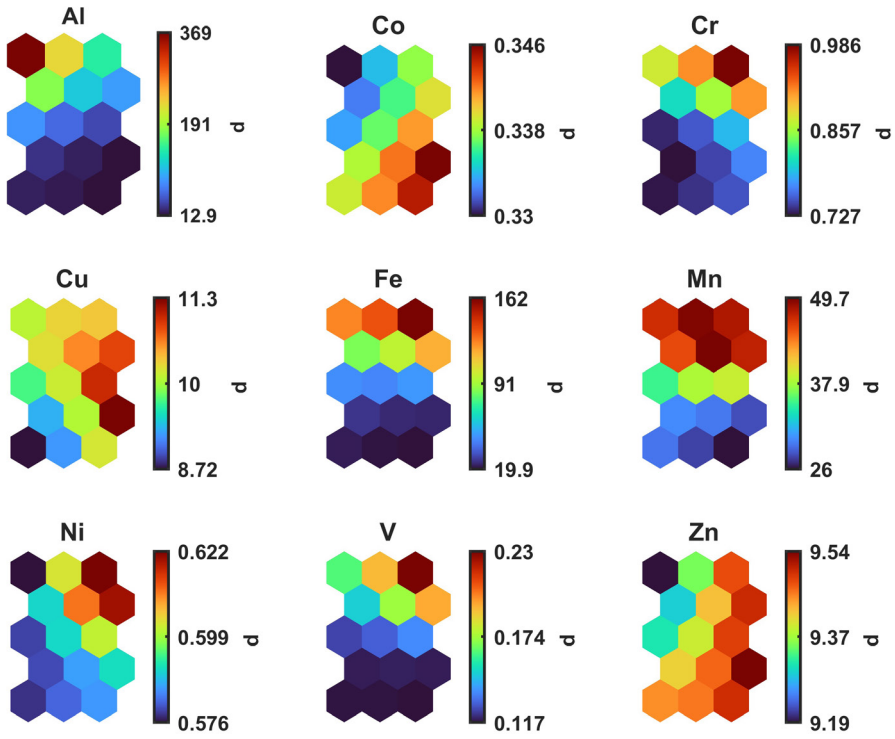

Figure 5. Neural maps showing as metals concentrations contribute in the neural modeling after Kohonen Self Organizing Maps application in data from ground coffee samples produced in municipalities of the Southwest and Chapada Diamantina regions of Bahia.

It can be seen that the cluster formed by Poções and Barra do Estiva refers to high concentrations of Fe, V and Cr and, secondly, the cluster formed with Itiruçu, is due to high concentrations of Al.

A comparative evaluation of the multivariate analyses performed using PCA (Figures 3a and 3b) and KSOM (Figures 4 and 5) reveals coherent and complementary information regarding the similarity patterns of the ground coffee samples assessed. Both PCA and KSOM indicated the formation of three distinct groups among the evaluated samples. In the PCA score plot (Figure 3a), most samples were clustered together, whereas two samples – Itiruçu and Barra da Estiva – were clearly separated due to their high concentrations of specific elements. A similar clustering pattern was observed in the KSOM map (Figure 4a), in which a cluster was formed by the samples from Poções and Barra da Estiva, followed by the isolated positioning of the Itiruçu sample. The remaining samples, collected from Barra do Choça, Brumado, Ibicoara, Itapetinga, Ituaçu, Maracás, and Salvador, were grouped together, suggesting a high degree of similarity in their mineral composition.

The variables responsible for sample separation were also consistent across both multivariate approaches. In the PCA loading plot (Figure 3b), aluminum, chromium, iron, and vanadium were identified as the main contributors to the isolation of the Itiruçu and Barra da Estiva samples. This behavior was corroborated by the KSOM component maps (Figure 4), in which high concentrations of these elements were highlighted in the corresponding clusters. Moreover, both methods consistently distinguished the sample from Poções due to its higher manganese content, as evidenced in the PCA score plot using PC1 × PC3 (Figure 3c) and in the neural network component maps (Figure 4).

Despite the convergence of results, the two multivariate techniques differ in their analytical approach and graphical representation. PCA is restricted to identifying linear relationships among variables and relies on the interpretation of score and loading plots. In contrast, KSOM enables the analysis of both linear and non-linear relationships, providing a more intuitive visualization of sample proximity and the influence of individual variables through the unified distance matrix and component maps.

Furthermore, KSOM allows for a clearer and more direct interpretation of variable contributions to sample grouping, as indicated by the color gradients in the distance matrix (Figure 4b) and in the component maps (Figure 5). In comparison, PCA does not visually express the distance magnitude between samples and is limited to the variance explained by the principal components.

Some additional insights can be realized by KSOM compared to PCA. Although PCA is limited to the identification of linear relationships, KSOM effectively captured both linear and non-linear patterns within the dataset, thereby enhancing the interpretation of complex data structures. Specifically, KSOM offered a topological representation of sample similarity through the unified distance matrix (U-Matrix), which visually quantified the degree of dissimilarity among samples. This characteristic provided an intuitive understanding of sample distribution, a level of detail not accessible in PCA score plots. Additionally, the component maps generated by KSOM facilitated a localized assessment of the influence of each variable on sample clustering, complementing the global overview offered by PCA loading plots.

The topology-preserving characteristic of KSOM ensured that samples with similar mineral profiles were positioned adjacently on the map, allowing the identification of subtle patterns that may not have been discernible through PCA alone. In summary, KSOM proved to be a valuable complementary tool to PCA, providing a more detailed and comprehensive visualization of sample similarity and variable contribution, as well as capturing complex, non-linear relationships within the ground coffee dataset.

The error check was made using (i) quantization error, representing the average of the distances between each data vector and the corresponding weight vector of the winning neuron. The quantization error does not have a standard value; however, the smaller the error, the better the winning neuron will define the input vectors and (ii) topographic error, which quantifies the ability of the map to describe the topology of the input data. It is calculated by checking all inputs, as well as which neuron is the best and which is the second best.[28] Likewise, the topographic error does not have a standard value, but it is better when the values tend to zero. In this study, the values of the quantization and topographic errors were equal to 1.360 and 0.000, respectively, evidencing good accuracy of the sample data to represent the topology of the obtained network.

The results obtained did not reveal any significant differences in the concentrations of the elements between the samples from artisanal processing (family farming) and those from industrial processing. High concentrations of Al and Fe were found in samples from cities (Barra da Estiva and Itiruçu) that process coffee differently. On the other hand, the sample from industrial processing located in Salvador presented the highest concentrations for Co, Cu and Zn, and the lowest for V. Further studies are necessary to assess whether there is a change in the elemental composition depending on the sample processing method.

In the current Brazilian legislation, there are no maximum consumption limits required for any the metals analyzed in this study. However, considering the maximum permitted limits (μg g^{-1}) in Decree No. 55,871 of March 26, 1965, revoked in 2019 (Cu: 30.0; Cr: 0.10; Ni: 5.0 and Zn: 50.0),[29] the average values found for chromium are above the limit. The other elements mentioned are below the maximum values established. The concentration values found in this study were compared to values described in the literature for the same analytes in different types of coffee, as shown in Table V.

Table V. Comparison of the values obtained for the ground coffee samples with other studies reported in the literature

Reference	Sample characteristics	Applied technique	Analyte	Observed concentration range in the literature (μg g^{-1})	Observed concentration range in this study using MIP OES (μg g^{-1})
Oleszczuk et al., 2007.[30]	Green coffee beans (Brazil)	ICP OES	Co	0.100 – 0.300	0.327 – 0.351
			Cu	10.0 – 16.0	7.51 – 13.3
			Mn	15.0 – 32.0	22.0 – 71.4
Habte et al., 2016.[31]	Green coffee beans (Ethiopia)	ICP OES ICP-MS	Al	4.23 – 173	6.32 – 556
			Co	0.0190 – 0.0610	0.327 – 0.351
			Cr	0.0710 – 0.255	0.678 – 1.17
			Cu	13.2 – 16.9	7.51 – 13.3
			Fe	21.1 – 127	14.3 – 255
			Mn	12.6 – 24.0	22.0 – 71.4
			Ni	0.139 – 0.509	0.558 – 0.631
			V	0.00500 – 0.102	0.109 – 0.310
			Zn	3.00 – 8.27	9.08 – 9.65
Semen et al., 2017.[32]	Green coffee beans (Turkey)	ICP-MS	Al	4.56 – 45.3	6.32 – 556
			Co	0.0900 – 0.250	0.327 – 0.351
			Cu	9.85 – 14.7	7.51 – 13.3
			Ni	0.270 – 0.810	0.558 – 0.631
			Zn	3.79 – 42.4	9.08 – 9.65
Pohl et al., 2022.[33]	Ready-to-drink coffee after infusion (Europe)	ICP OES	Cu	0.0261 – 0.0450	7.51 – 13.3
			Fe	0.0331 – 0.175	14.3 – 255
			Mn	0.257 – 0.451	22 – 71.4
			Zn	0.0233 – 0.0948	9.08 – 9.65
Barbosa et al., 2014.[34]	Organic coffee (Brazil)	ICP-MS	Al	3.80 – 16.4	6.32 – 556
			Co	0.0505 – 0.373	0.327 – 0.351
			Cr	1.10 – 1.80	0.678 – 1.170
			Mn	15.3 – 37.7	22.0 – 71.4
			Ni	0.220 – 0.990	0.558 – 0.631
			Zn	2.90 – 6.30	9.08 – 9.65
	Conventional coffee (Brazil)	ICP-MS	Al	8.30 – 118	6.32 – 556
			Co	0.00940 – 0.368	0.327 – 0.351
			Cr	1.00 – 1.70	0.678 – 1.170
			Mn	17.3 – 30.3	22.0 – 71.4
			Ni	0.0600 – 0.960	0.558 – 0.631
			Zn	3.80 – 28.4	9.08 – 9.65

(continues on next page)

Table V. Comparison of the values obtained for the ground coffee samples with other studies reported in the literature (continuation)

Reference	Sample characteristics	Applied technique	Analyte	Observed concentration range in the literature (μg g^{-1})	Observed concentration range in this study using MIP OES (μg g^{-1})
Jarošová et al., 2014.[35]	Ground coffee (India, Kenya, Honduras, Colombia and Ethiopia)	ICP-MS	Cr	0.0200 – 0.850	0.678 – 1.17
			Cu	16.6 – 19.3	7.51 – 13.3
			Fe	23.9 – 47.7	14.3 – 255
			Mn	27.3 – 123	22.0 – 71.4
			Ni	0.0700 – 3.69	0.558 – 0.631
			Zn	1.71 – 7.12	9.08 – 9.65
Voica et al., 2016.[36]	No identification (various countries)	ICP-MS	Al	0.540 – 308	6.32 – 556
			Co	0.0400 – 1.05	0.327 – 0.351
			Cr	0.900 – 57.0	0.678 – 1.170
			Cu	0.460 – 151	7.51 – 13.3
			Fe	5.90 – 521	14.3 – 255
			Mn	7.57 – 70.1	22.0 – 71.4
			Ni	0.220 – 12.2	0.558 – 0.631
			Zn	1.68 – 22.4	9.08 – 9.65
Albals et al., 2021.[37]	Green and roasted coffee beans (Jordan)	ICP-MS	Al	70.90 – 182	6.32 – 556
			Co	0.27 – 0.970	0.327 – 0.351
			Cr	2.03 – 4.06	0.678 – 1.170
			Cu	24.85 – 30.8	7.51 – 13.3
			Fe	132.20 – 196	14.3 – 255
			Mn	45.10 – 86.2	22.0 – 71.4
			Ni	0.75 – 2.67	0.558 – 0.631
			V	0.72 – 1.62	0.109 – 0.310
			Zn	5.99 – 10.6	9.08 – 9.65

ICP OES: Inductively Coupled Plasma Optical Emission Spectrometry; ICP-MS: Inductively Coupled Plasma Mass Spectrometry; MIP OES: Microwave Induced Plasma Optical Emission Spectrometry.

In the comparisons presented in Table V, it can be observed that the variations in the concentrations found for aluminum and iron were also greater for Habte et al.,[31] Barbosa et al.,[34] Voica et al.[36] and Albals et al.,[37] indicating agreement with this study. Both the high concentrations of iron and aluminum can be directly associated with soil pH, since these elements have greater availability for plants in acidic soils.

Pohl et al.[33] determined the concentrations of copper, iron, manganese and zinc for ready-to-drink coffee after infusion, and the values found were much lower than those of the roasted and ground coffee samples in our study. This is justifiable, considering that not only is the concentration of the elements extracted in the aqueous infusion process of the beverage influenced by the initial concentrations of the elements present in the ground coffee used, but also by the preparation conditions of the beverage, the coffee matrix and the physical and chemical characteristics of the elements. The degree of leachability is different for each element and for each type of coffee, as a function of factors such as the nature and strength of the ion complexes of the elements formed with coffee constituents.

Barbosa et al.[34] conducted a comparative study between samples of conventionally grown and organically grown coffee. Aluminum and zinc levels in conventionally grown coffee samples were higher, while cobalt, chromium, manganese and nickel levels were similar between the two types of crops. These values are consistent with those observed in our study, with the exception of aluminum.

CONCLUSIONS

In this study, it was possible to efficiently apply a method for decomposing ground coffee samples using diluted acid and hydrogen peroxide. Samples from different regions of Bahia were analyzed and the results could be evaluated in relation to the content of Al, Co, Cr, Cu, Fe, Mn, Ni, V and Zn, quantified by MIP OES. Regarding Pb, MIP OES did not show quantification capacity for direct analysis.

The analyses performed through PCA and KSOM indicated the formation of three distinct groups among the evaluated samples. KSOM revealed specific zones with high concentrations of Co, Zn, and Cu, which contributed to the differentiation of certain sample clusters – information that was less evident in the PCA analysis. The use of multivariate techniques efficiently contributed to data analysis and interpretation, demonstrating that they are coherent and complementary.

In comparison with the literature, greater differences were observed in relation to aluminum and iron. The results presented in this study are important not only for nutritional and toxicological evaluation, but also to add value to coffee produced by small properties. Likewise, it provides relevant nutritional information about the coffee produced in Bahia. Such information are important for several areas of science, such as chemistry, agronomy, nutrition, health and food.

Conflicts of interest

The authors declare no conflict of interest.

Acknowledgements

The authors thank: "Fundação de Amparo à Pesquisa do Estado da Bahia" (FAPESB - INCITE grant number PIE0006/2022), "Conselho Nacional de Desenvolvimento Científico e Tecnológico" (CNPq - grant number 307904/2022-9) and "Coordenação de Aperfeiçoamento de Pessoal de Nível Superior" (CAPES - Finance Code 001).

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SUPPLEMENTARY MATERIAL

Table S1. Elements quantified in ground coffee samples produced in municipalities of the Southwest and Chapada Diamantina regions of Bahia in decreasing concentration order

Sample	Elements in decreasing concentration order (μg g^{-1})
Salvador	Mn > Fe > Cu > Zn > Al > Cr > Ni > Co > V
*Barra do Choça	Mn > Fe > Cu > Zn > Al > Cr > Ni > Co > V
*Itapetinga	Mn > Al > Fe > Cu > Zn > Cr > Ni > Co > V
*Itiruçu	Al > Fe > Mn > Cu > Zn > Cr > Ni > Co > V
*Maracás	Al > Fe > Mn > Cu > Zn > Cr > Ni > Co > V
*Poções	Mn > Fe > Al > Cu > Zn > Cr > Ni > Co > V
**Barra da Estiva	Fe > Al > Mn > Cu > Zn > Cr > Ni > Co > V
**Brumado	Al > Mn > Fe > Cu > Zn > Cr > Ni > Co > V
**Ibicoara	Mn > Fe > Zn > Al > Cu > Cr > Ni > Co > V
**Ituaçu	Mn > Fe > Al > Zn > Cu > Cr > Ni > Co > V

Regions in Bahia: *Southwest; **Chapada Diamantina.

Table S2. Loading values that represent the importance of each variable related to metals concentration in ground coffee samples to establish the principal components

Parameter	PC1	PC2	PC3	PC4
Al	**0.673**	0.577	0.0970	-0.308
Co	-0.290	**-0.802**	0.231	-0.149
Cr	**0.891**	-0.341	0.205	-0.105
Cu	0.0350	-0.365	-0.397	**-0.821**
Fe	**0.979**	-0.0380	0.164	0.0121
Mn	0.359	0.252	**-0.858**	0.0881
Ni	0.322	**-0.622**	-0.552	0.350
V	**0.916**	-0.279	0.176	0.148
Zn	-0.113	**-0.869**	0.0202	0.0472

PC: principal component