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Characterization of Mineral Content in Fruits of Northeast Agrobiodiversity of Brazil

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HIGHLIGHTS

- Characterization of fruits of the Brazilian biodiversity.
- Potential alternative fruits that provide health benefits.
- Spreading information that stimulates valorization of the Brazilian biodiversity.

Abstract: Mineral profiles of eleven fruits from the northeastern Brazilian agrobiodiversity have been determined. Samples of cajui, murici, pequi, jenipapo, mangaba, bacuri, caja, umbu-caja, umbu, pitanga and araçá fruits were digested and element content determined by inductively coupled plasma optical emission spectrometry (ICP-OES). The accuracy of method was performed using SRM 2338 and all elements were statistically similar with 95% of confidence. Potassium is present in higher amounts in the edible part of the fruits, ranging from 107 to 402 mg 100 g⁻¹, followed by P in the range 16 - 150 mg 100 g⁻¹. Iron, presents the lowest content, ranges from 0.07 to 1.1 mg 100 g⁻¹. Caja and umbu-caja fruits are noteworthy sources of P. Analysis of variance (ANOVA) and Principal Component Analysis were performed in order to check similarities between the fruit groups according to the trace element content. The data provide a source of information characterizing the Brazilian biodiversity and it may help the nutritional intake of these fruits in the region.

Keywords: trace element analysis; dietary reference intakes; nutritional function; Pattern recognition analysis; Inductively Coupled Plasma Optical Emission Spectrometry.

INTRODUCTION

Although Brazil is the largest holder of biodiversity in the world, many economic activities associated with agriculture, livestock and others are based on imported crops. The "Biodiversity for Food and Nutrition (BFN)" project aims to conserve and promote the sustainable use of biodiversity in programs that contribute to the improvement of food security and human nutrition, prioritizing the "Plants for the Future" initiative. This proposal, supported by the international scientific community, warns of the loss of world biodiversity, highlighting the need for characterization of biodiversity to ensure its preservation for future generations [1].

The current work is part of the strategy of scientific leaders of different countries (Brazil, Kenya, Sri Lanka and Turkey), who coordinate actions, to improve the knowledge and evidence base on their biodiversity, guiding government policies and the ability to generate partnerships and awareness of individuals in favor of the food and nutrition benefits of each population [2].

The Brazilian fruit biodiversity is an excellent resource still unexplored showing potential technological and economic, mainly for the food / nutritional and pharmaceutical sectors. The biodiversity of these fruits shows the particularity of constituents, when they are harvesting in different types of cultivation and environmental conditions [3].

Fruits, a good source of micronutrients recognized by food scientists, nutritionists and farmers, can be readily consumed as sources of these nutrients by the general population [4]. However, in order to exploit their nutritional and medicinal benefits and to develop value-added food products, it is useful to characterize the chemical composition of these fruits, as well as to study their component bioavailability and metabolism in humans [5].

There are few studies that detail the composition of the fruits of Brazilian biodiversity, especially in relation to micronutrients. Therefore, the analysis of the chemical composition of food is always extremely important. In addition to providing a database and assisting in future studies. This knowledge favors food and nutritional security, reaching the inclusive of local citizens [3].

Depending on their concentrations, minerals are nutrients that can be sub-divided into macro- and micro-mineral categories [6]. They are involved in several functions in the human body, including building bones and teeth, the transmission of nerve impulses, comprise the structural part of enzymes and hormones, regulation of heart rate, formation of erythrocyte cells, regulation of glucose levels and blood pressure control [7]. Metabolic reactions are achieved using specific amounts of each mineral. The Dietary Reference Intakes (DRI) are nutrient and energy recommendation values adopted by the United States and Canada and have been published and revised since 1997 by expert committees of the Institute of Medicine and Health Canada [8].

Articles reported in the literature that explore the characterization of Brazilian native fruits generally present the contents of antioxidants, total phenolic compounds and vitamin C. However, works that report the mineral composition in the native fruits from Brazil, particularly from the Northeast region, are limited [9-12]. Sample preparation for solubilization of fruit samples is commonly required for trace element analysis by flame atomic emission (FAES) [9] and absorption spectrometry (FAAS) [10], as well as mass spectrometry with inductively coupled plasma (ICP-MS) [11].

Brazilian fruits of the biome "cerrado" are sources for some minerals. As examples, the sweet passion fruit pulp contributes to the DRI of P and Fe; marolo fruit contributes to the DRI of K and Mg and the genipap pulp is rich in Ca [9]. Native fruits of the Amazon region are rich in K, Ca and Mg and can be included in the diet to improve human health [10]. Native fruits from the northeast provide a good dietary source of Fe, Mn, and Cu [11].

Recent studies have contributed to our knowledge of the composition of fruits grown in Brazil. In addition to the consumption of fruit pulp, in some situations, epicarp and seeds are valuable sources of minerals and essential fatty acids [12]. These fruits are a native resource with economic potential for application in the pharmaceutical, cosmetic, and nutritional industries. However, some actions are necessary for them to be introduced into production systems on a commercial scale. Complementary studies must be carried out to elucidate the mechanism of action of these nutrients, taking into account the synergism between them and the bioavailability in the human body [9].

The aim of this study was to quantify the mineral content (Ca, Cu, Fe, K, Mg, Mn, Na, P, Se, Zn) of cajui (*Anacardium sp.*), murici (*Byrsonima crassifolia* (L.) Kunth), pequi (*Caryocar coriaceum* Wittm), jenipapo (*Genipa Americana* L.), mangaba (*Hancornia speciosa* Gomes), bacuri (*Platonia insignis* Mart.), caja (*Spondias mombin* L.) umbu-caja (*Spondias bahiensis* P. Carvalho, Van Den Berg & M. Machado), umbu (*Spondias tuberosa* Arruda), pitanga (*Eugenia uniflora* L.) and araçá (*Psidium sbralianum* Landrum & Proença) Northeastern Brazilian fruits in order to contribute the information to an international database.

MATERIAL AND METHODS

Samples, Standards and Reagents

Fruit samples were collected from different geographic locations in the Northeast Region of Brazil. Sampling occurred during the months of January until December of 2016.

Two up to 10 units of each fruit were collected. The number of fruits acquired varied according to the weight and yield of each species. The unit weight of each fruit studied ranged from 3 grams (pitanga and murici) to 180 grams (bacuri, pequi and jenipapo). The yield ranged from 10% (bacuri and pequi) to 80% (cajuí and araçá).

All samples were immediately processed after acquisition. The epicarp of bacuri, pequi and jenipapo, as well as the seeds of all fruits were removed. The edible portion (mesocarp) was homogenized using an industrial blender Skimssen LC4, fitted with precleaned stainless steel blades, identified, packed in 100 g plastic bags and stored in a freezer at -18°C. The blender was cleaned before use by grinding a disposable subsample and discarding it before processing the sample used for analysis. Afterwards, they were frozen, lyophilized and stored in a vacuum desiccator.

Vessels and glassware were decontaminated before use by immersion in a 10% v v⁻¹ HNO₃ solution for 24 h and then rinsed with ultrapure water. Dilutions were done with ultrapure water (resistivity 18.2 MΩ cm) obtained from a Milli-Q water purification system (Millipore, Bedford, MA, USA).

Working standard solutions of the analytes (Ca, Cu, Fe, K, Mg, Mn, Na, P, Se, Zn) were prepared by appropriate dilutions of 1000 mg L⁻¹ stock solutions (Acros Organics, Belgium). The analytical curve ranged from 1 to 20 mg L⁻¹ for elemental analysis.

Sample preparation for elemental analysis was accomplished using 65% w w⁻¹ HNO₃ and 38% w w⁻¹ HF (Vetec, Rio de Janeiro, Brazil). The accuracy of the results was validated using NIST SRM 2383a Baby Food.

Instrumentation

A LIOTOP LP 510 freeze dryer (São Carlos, São Paulo, Brazil) was used to lyophilize the samples. Sample digestions were done using a TECNAL TE-007D block digester (Piracicaba, São Paulo, Brazil) equipped with 15 Teflon® tubes (50 mL) with lids.

A dual view Perkin Elmer 4300 DV inductively coupled plasma optical emission spectrometer (ICP-OES) (Massachusetts, EUA) equipped with a cross-flow nebulizer and double-pass spray chamber was used for elemental analysis. ICP operational parameters were as follows: 1.3 kW forward power; 15 L min⁻¹ Ar plasma gas flow rate; 0.5 L min⁻¹ auxiliary Ar gas flow rate; 0.8 L min⁻¹ nebulizer Ar gas flow rate and sample uptake rate of 1.4 mL min⁻¹. An alumina injector tube of 2.4 mm was used. The analytical wavelengths (nm) chosen were: Ca (II) 317.933, Cu (I) 327.393, Fe (II) 238.204, K (I) 766.940, Mg (I) 285.213, Mn (II) 257.610, Na (II) 589.592, P (I) 213.617, Se (I) 196.026, Zn (I) 213.587 nm. Calcium, K, Mg, Na and P were determined using radial view. All the other elements were measured in axial view.

Sample preparation procedure

An accurately weighed nominal 0.250 g subsample was placed into the Teflon® tubes with 5 mL of 65% w w⁻¹ HNO₃. The mixture was left overnight, after which 2 mL of 38% HF w w⁻¹ were added and the capped tubes placed into the heated digester block for 3 h at 120 °C. The resultant solutions were then diluted with ultrapure water to 25 mL and taken for analysis by ICP-OES.

SRM 2383a (baby food composite) was submitted to the same solubilization procedure described above in order to validate the accuracy of the proposed methodology.

The contribution to the RDA (Recommended Dietary Allowances) has been calculated considering the food intake of 100 g per day according to the Equation 1:

$$\%RDA = Ct/RDA \times 100 \quad (1)$$

Where Ct is the total concentration of minerals in the sample and the RDA set by the Institute of Medicine (IOM).

Figures of Method (LOD/LOQ)

Limits of detection (LOD) and quantification (LOQ) were estimated recommendation using “LOD = 3*BEC* δ /100” and “LOQ = 10*BEC* δ /100”, where δ is the relative standard deviation of 10 measurements of procedural blank, BEC is the concentration equivalent of the background signal and “s” is the slope of the analytical calibration curve. The BEC was calculated as “ I_{blank}/s ”, where I_{blank} is the emission intensity of the blank and s is the slope of the analytical calibration curve equation [13].

Statistical Analysis

Analysis of variance was performed using ANOVA. Principal Component Analysis (PCA), a chemometric pattern recognition tool, was used for treatment of the raw data obtained in the determination of the elements in 12 samples. Pirouette software (version 6.5, Infometrix, Bothell, WA, USA) was used to the multivariate data treatment.

RESULTS

Accuracy of the proposed method

The accuracy of the sample preparation and analysis methodology was evaluated using NIST SRM 2383a Baby Food Composite reference material. The SRM 2383a (baby food composite) is a mixture of fruits, vegetables, macaroni, rice flour, and milk powder. Data, summarized in Table 01, present the average and confidence interval (CI) for three replicates along with certified values and their expanded uncertainties. A comparison of the data was undertaken applying a "t-test" (Student t test) at the 95% level of confidence and 2 degrees of freedom.

Table 1. Results of the element analysis in the NIST SRM 2383a Baby Food (average \pm CI, n=3).

Element	Proposed Method - (mg kg ⁻¹)	Certified Value - (mg kg ⁻¹) ¹
Ca	370.7 \pm 20.0	342.6 \pm 5.0
Cu	0.671 \pm 0.060	0.758 \pm 0.082
Fe	4.72 \pm 0.06	4.42 \pm 0.51
Mg	215.8 \pm 6.0	212.2 \pm 4.0
Mn	1.140 \pm 0.070	0.963 \pm 0.064
P	433 \pm 14	453 \pm 11
K	2936 \pm 254	2910 \pm 220
Na	199 \pm 34	195 \pm 29
Se	< 0.04	0.028 \pm 0.001
Zn	2.69 \pm 0.60	2.22 \pm 0.18

¹ average \pm U, k=2

The LOD calculated in the present method are 1.1; 0.01; 0.01; 0.55; 0.01; 4.3; 2.4; 0.10; 0.04; 0.01 mg kg⁻¹ for Ca, Cu, Fe, Mg, Mn, P, K, Na, Se, Zn, respectively.

Trace element analysis of the fruit samples

Results for the trace element analysis using the proposed method are summarized in Table 02.

Table 2. Trace element content in mg 100g⁻¹ of the fruit samples of the Brazilian agrobiodiversity (Mean ± IC, n=3, t=4.303 (95%))

Fruit	Lot	Ca	Cu	Fe	K	Mg	Mn	Na	P	Se	Zn
Cajuí	L1	0.40±0.12	<0.03 ^b	0.15±0.07	79.8±12.2	8.60±2.21	<0.03	11.7±0.2	32.6±11.9	<0.12	<0.02
	L2	0.52±0.07	<0.03	0.16±0.05	109±17	7.17±0.50	<0.03	12.1±1.7	47.0±2.7	<0.12	<0.02
	L3	0.44±0.07	<0.03	0.34±0.03	134±44	7.14±3.77	<0.03	5.21±0.45	40.3±7.2	<0.12	<0.02
	Average	0.45		0.22	108	7.64		9.67	40.1		
Murici	L1	33.7±3.0	<0.03	0.11±0.05	255±20	10.3±0.7	<0.03	26.0±1.7	41.9±9.2	<0.12	<0.02
	L2	34.4±9.9	<0.03	0.07±0.02	319±47	11.9±2.2	<0.03	24.3±0.2	48.6±3.5	<0.12	<0.02
	L3	29.3±1.5	<0.03	0.04±0.05	198±73	7.79±0.3	<0.03	10.9±1.0	31.3±10.3	<0.12	<0.02
	Average	32.6		0.0	261	10.0		20.4	40.6		
Pequi	L1	11.2±2.7	<0.03	0.12±0.05	219±20	15.6±5.0	<0.03	2.13±0.05	93.5±15	<0.12	<0.02
	L2	10.2±3.7	<0.03	0.58±0.22	249±55	22.6±5.2	<0.03	2.59±0.89	66.8±20	<0.12	<0.02
	L3	21.6±5.0	<0.03	1.37±0.32	237±52	31.3±5.0	<0.03	3.75±0.62	124±23	<0.12	<0.02
	Average	14.		0.69	235	23.2		2.82	94.8		
Jenipapo (Mesocarp)	L1	<0.33	<0.03	<0.01	<2.4	<0.55	<0.03	<0.3	<12.9	<0.12	<0.02
	L2	8.2±1.7	<0.03	0.40±0.07	366±39	15.6±1.5	<0.03	8.3 ± 0.5	20.4±2.0	<0.12	<0.02
	L3	14.7±3.0	<0.03	0.25±0.07	270±74	17.1±5.2	<0.03	3.0 ± 0.5	70.2±2.0	<0.12	<0.02
	Average	11.4		0.32	318	16.3		5.6	45.3		
Jenipapo (mesocarp and epicarp)	L1	15.0±4.5	<0.03	0.29±0.08	332±32	18.3±1.0	<0.03	9.43±1.0	40.5±14.6	<0.12	<0.02
	L2	20.9±1.2	<0.03	0.64±0.05	348±32	30.2±4.0	<0.03	5.66±0.45	38.8±2.0	<0.12	<0.02
	L3	35.8±6.0	<0.03	0.73±0.17	527±77	28.1±3.0	<0.03	5.59±0.60	116±25	<0.12	<0.02
	Average	23.9		0.55	402	25.5		6.89	65.1		
Mangaba	L1	<0.33	<0.03	0.42±0.08	163±12	6.56±0.25	<0.03	23.7±3.7	<12.9	<0.12	<0.02
	L2	<0.33	<0.03	0.29±0.08	86.2±29.0	0.81±0.67	<0.03	12.4±0.5	24.0±11.4	<0.12	<0.02
	L3	<0.33	<0.03	0.71±0.35	211± 50	5.57±2.14	<0.03	21.1±2.7	<12.9	<0.12	<0.02
	Average			0.47	153	4.31		19.1			
Bacuri	L1	5.60±1.42	<0.03	0.35±0.10	153±35	27.8±2.5	<0.03	36.3±8.9	27.7±9.2	<0.12	<0.02
	L2	11.1±2.48	<0.03	0.56±0.12	145±8	13.2±2.5	<0.03	53.6±12.4	45.1±0.2	<0.12	<0.02
	L3	15.8±5.1	<0.03	1.14±0.27	157±14	37.5±3.2	<0.03	22.9±5.5	43.9±13.7	<0.12	<0.02
	Average	10.8		0.68	152	26.2		37.5	38.9		

Cont. Table 2

Caja	L1	20.7±5.2	<0.03	0.45±0.10	388±40	13.0±1.7	<0.03	2.50±0.40	167±10	<0.12	<0.02
	L2	12.4±3.0	<0.03	0.25±0.12	297±47	7.42±0.50	<0.03	2.00±0.42	122±10	<0.12	<0.02
	L3	8.35±1.99	<0.03	0.43±0.05	368±57	12.6±1.5	<0.03	3.36±0.35	135±15	<0.12	<0.02
	Average	13.8		0.37	351	11.0		2.62	141		
Umbu-caja	L1	29.8±0.3	<0.03	0.45±0.05	324±60	16.2±0.5	<0.03	1.86±0.08	159±42	<0.12	<0.02
	L2	21.5±2.7	<0.03	0.37±0.05	289±55	11.9±3.5	<0.03	1.39±0.08	153±22	<0.12	<0.02
	L3	20.9±0.3	<0.03	0.27±0.10	304±82	10.2±1.0	<0.03	1.43±0.47	139±12	<0.12	<0.02
	Average	24.		0.36	306	12.7		1.56	150		
Umbu	L1	18.5±1.2	<0.03	0.16±0.05	169±17	14.6±0.3	<0.03	0.45±0.05	59.1±7.7	<0.12	<0.02
	L2	17.4±5.7	<0.03	0.32±0.05	214±53	8.20±5.64	<0.03	1.50±0.92	42.2±1.0	<0.12	<0.02
	L3	19.9±3.0	<0.03	0.11±0.05	185±20	11.5±3.0	<0.03	<0.3	75.0±28.3	<0.12	<0.02
	Average	18.6		0.20	190	11.4		0.97	58.8		
Pitanga	L1	5.12±1.71	<0.03	0.33±0.17	72.3±16.9	4.89±1.20	<0.03	4.03±0.05	38.1±3.0	<0.12	<0.02
	L2	14.7±0.50	<0.03	0.41±0.05	147±17	17.2±0.5	<0.03	4.08±0.07	124±21	<0.12	<0.02
	L3	7.55±0.35	<0.03	0.40±0.10	123±20	4.97±0.35	<0.03	1.92±0.05	36.5±13.2	<0.12	<0.02
	Average	9.12		0.38	114	8.98±		3.34	66.2		
Araça	L1	16.6±1.7	<0.03	1.26±0.47	361±62	10.7±1.2	<0.03	1.75±0.05	14.9±0.7	<0.12	<0.02
	L2	18.9±0.5	<0.03	0.83±0.05	412±99	10.6±0.2	<0.03	1.72±0.05	15.5±5.0	<0.12	<0.02
	L3	18.1±1.0	<0.03	1.05±0.47	366±12	11.5±1.2	<0.03	1.56±0.12	17.9±2.5	<0.12	<0.02
	Average	17.8		1.05	380	10.9		1.68	16.1		

Principal Component Analysis

The elements and fruits were classified using Principal Component Analysis (PCA) pattern recognition techniques applied to the entire data set. The pre-treatment applied to the samples was a normalization known as "autoscale", which was the mean data centered followed by division by the standard deviation. PCA techniques have been used with the purpose of verifying the existence of similarities between the samples from the point of view of similarities in their chemical composition.

Figure 01 (1A) presents the Loadings plot in which the first Principal Component (PC1) contains 50.68 % of the information of the data set and the second Principal component (PC2) 16.97%. PC1 and PC2 together account for 67.65 % of the data. The ellipses presented in the Loadings plot represent groups of fruits having similarity in their concentrations of the elements, with 95% confidence. According to the plot, PC1 is responsible for the separation of one group containing caja, umbu-caja, umbu, pitanga and araçá fruits, and a second group formed by pequi, murici, jenipapo (P- epicarp), cajui, mangaba and bacuri fruits. PC2 is responsible for the separation of the two main groups in PC1 into two further groups. Thus, considering both PC's we may have 4 groupings of fruits.

Figure 01 (1B) shows the scores plot arising from the PCA analysis. PC1 of the scores plot shows two groups of variables. The positive side of PC1 presents a large group containing Fe, K, Mg, Na and P while on the other side (negative) there is only the element Na

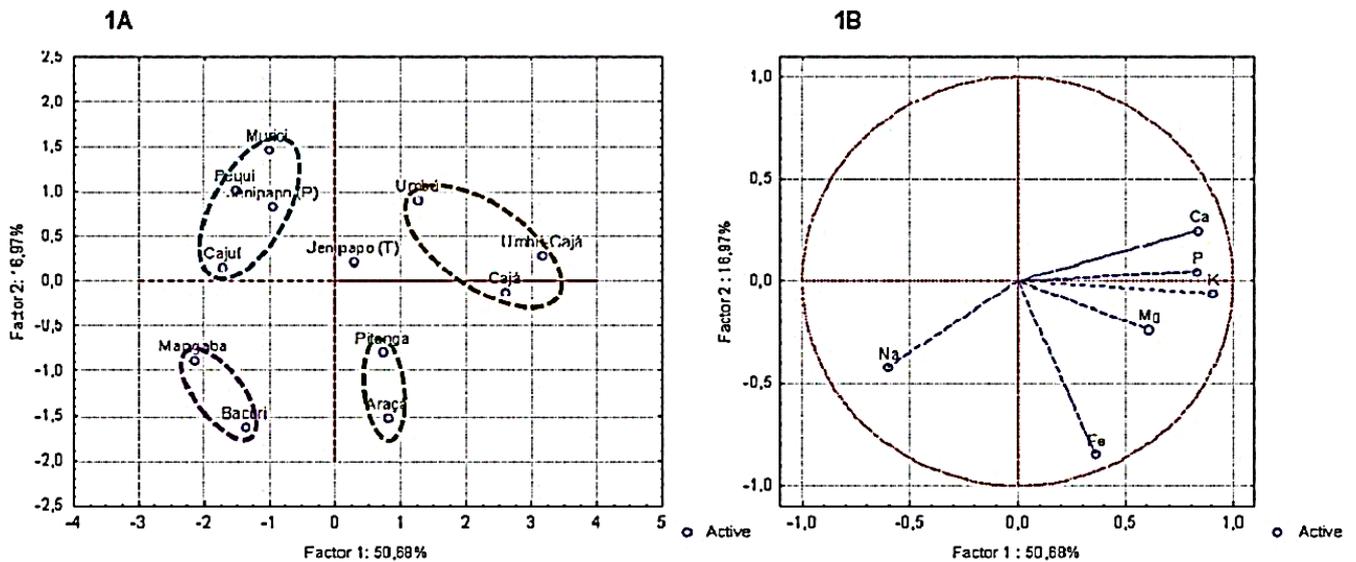


Figure 1. Principal Component Analysis plot: (1A) Loadings plot, (1B) Scores plot.

Daily Food Recommendation

The contribution of the fruits to the "Daily Food Recommendation" (RDA) of each mineral studied is listed in Table 03 and calculated by considering ingestion of 100 g of each fruit per day, according to the equation: $\% RDA = Ct / RDA * 100$; where Ct is the total concentration of each element in the fruit and the RDA is the value established by the Institute of Medicine (IOM).

Table 3. Recommended Dietary Allowances (RDA) for adults (19 to 50 years old) and average of the amount of the elements determined in the fruit samples of the agrobiodiversity of the Brazilian Northeast.

	RDA (mg d ⁻¹)	Cajui	Murici	Pequi	Jenipapo (Mesocarp)	Jenipapo (Mesocarp and epicarp)	Mangaba	Bacuri	Cajá	Umbu- cajá	Umbu	Pitanga	Araçá
% RDA Ca	1000	0.05	3.25	1.43	1.14	2.39	<LQ	1.06	1.38	2.41	1.86	0.91	1.79
% RDA Fe	18	1.22	0.39	3.83	1.78	3.06	2.67	3.78	2.11	2.00	1.11	2.11	5.83
% RDA K	4700 ¹	2.28	4.72	5.00	6.76	8.56	3.26	3.23	7.47	6.50	4.03	2.43	8.08
% RDA Mg	420	1.82	2.38	5.51	3.88	6.08	1.03	6.23	2.62	3.04	2.72	2.15	2.60
% RDA Na	1500 ¹	0.64	1.36	0.19	0.38	0.46	1.27	2.51	0.17	0.10	0.07	0.22	0.11
% RDA P	700	5.71	5.80	13.5	6.47	9.28	3.43	4.13	20.2	21.5	8.39	9.44	2.30

¹Values expressed as AI (Adequate Intake).

Source: Institute of Medicine (IOM) of the National Academies. Phosphorous, Magnesium (1997); Selenium (2000); Copper, Iron, Manganese, Zinc (2001); Potassium and Sodium (2005); Calcium (2011).

DISCUSSION

The reference material, SRM 2383a (baby food composite), is a fruit-based mixture, therefore, it is as similar as possible to the matrix used in the present work and it has gone through all stages of sample preparation and treatment for the trace element analysis. Results obtained for analysis of SRM 2383a certified reference material using the proposed method are accurate for all elements. The precision of the proposed method (<15%) is fit-for-purpose.

The sample preparation method was effective for the total solubilization of the samples in this study. The use of HF is necessary for the decomposition of some silicates found in seeds, peels, and edible part of the fruit. Despite the fact of the alumina injector of the plasma torch being resistant to HF, the digests were diluted for minimizing possible interferences.

The contents of trace elements in the studied fruits show low concentrations, these results were expected in these samples. Literature data suggests that high ash contents (5 to 10%) in plants correlate with an abundance of mineral elements [14]. Accordingly, the ash content of Brazilian agrobiodiversity presents low values; for example, it has been found in percent by weight of the jenipapo fruit (0.74 ± 0.01) [15] mangaba fruit (0.43 ± 0.01) [16], bacuri fruit (2.0 ± 0.7) [17], caja fruit (0.58 ± 0.02) [18], araçá fruit (0.44 ± 0.02) [19], pequi fruit *in natura* (0.70 ± 0.03) [20] follow this trend.

Similarly, protein content and concentrations of some elements may also be directly correlated in fruit samples [21]. Protein content in the edible part of the fruits of the Brazilian agrobiodiversity are relatively low, as evidenced by the results of the percentage in weight of some presented as follow, jenipapo fruit (1.59 ± 0.12) [15], mangaba fruit (0.86 ± 0.03) [16], bacuri fruit (6.4 ± 0.1) [17], cajá fruit (0.82 ± 0.01) [18], araçá fruit (1.87 ± 0.65) [19], pequi fruit *in natura* (2.4 ± 0.1) [20]. The use of more sensitive techniques as ICP-MS or vapor generation coupled to spectrometric techniques (for Se) could be capable to quantify the elements found below LOQ.

Recent literature has also highlighted the relationship that may exist between some amino acids (of the proteins) and minerals, particularly transition metals such as Cu, Fe, Mn, and Zn [22]. The authors of this work verified the presence of these minerals in flaxseed samples, mainly in the protein phase. Correspondingly, since fruits are normally low in protein, they are expected to have low concentrations of these minerals.

Literature studies suggest a similar pattern with the concentrations of minerals determined in this study, despite the different geographic location of the samples, which may be significant for the composition of the fruit. Hence, such a comparison is worthwhile. Fruits such as cajui, murici, umbu, umbu-caja, caja and pitanga have scarce data of protein and ash content available in the literature, and no data about their trace element content.

Analysis of variance of the data concerning the determined element contents showed that there is no significant difference in the sample lots (t-test, 95% confidence) for most elements. The element Na presented 30-35% difference in the L3 values for cajui, murici and jenipapo fruits. The mangaba fruit also showed discrepant values in the L2 for Mg and Na elements. According to the Resolution of the Collegiate Board of Directors – RDC Nº 54: Technical Regulation on Complementary Nutrition Information, a food should be considered as a source of minerals when it contributes to at least 15% of the RDA, per 100 g or 100 mL of the food. Moreover, to be considered a rich source, the food must provide at least 30 % of the RDA per 100 g or 100 mL of the food [23].

As an example, phosphorus is an essential mineral, primarily used for growth and repair of body cells and tissues. Together with calcium, phosphorus provides structure and strength. Phosphorus is also required for a variety of biochemical processes including energy production and pH regulation [24]. The umbu-caja and caja fruits present a P average content of 150 mg and 141 mg in 100 g of sample (wet), respectively, which represent 21.4 % and 20.1 % of the RDA, being considered a rich food source for P, according to the IOM. The pequi fruit has a P average content of 94.8 mg in 100 g of sample (wet), representing 13.5 % of the RDA.

The pulp of the jenipapo and bacuri fruits present, 25.5 mg and 26.1 mg of Mg in 100 g of sample, respectively, which represents 11.6 % and 11.9 %, and can be considered close to a rich source of food for these elements.

Fruits are traditionally an important component of the human diet as they contain a lot of biologically active substances (antioxidants, antibacterial compounds etc) that present beneficial effects on health. Few fruits can be considered as a source of minerals for the daily diet, unlike other foods such as milks and its derivatives, fish and seafood, liver and meat, vegetables, dried fruits, nuts, green leaves, dehydrated fruits, orange, avocado and bananas [7].

Almonds may contribute to the minerals needed by the human body as they are considered a good source of Mg, Ca, Cu, Mn, Zn and Fe [25]. Green leaves and nuts are also rich sources of minerals, particularly Ca and Fe [26].

Literature reports this trend by showing the quantification of 10 elements in native fruits of Brazilian cerrado and is significant as a result of its high content of potassium and boron [27]. Another article reports the determination of 12 elements in tropical Brazilian fruits serving as a good source of Se, Fe and P [4], and low amounts of other minerals.

Consideration should also be given to the bioavailability of the nutrient. It is important to consider the extent of nutrient utilization depending on its bioavailability in each food [28]. Since the bioavailability and absorption of minerals are dependent on dietary enhancers, inhibitors and different processing techniques, there is a wide range of efficiency in the absorption of minerals [29]. Some studies have shown that the bioavailability of minerals can be compromised due to the presence of absorption inhibitors such as phytates, tannins and oxalates present in some foods of plant origin [30]. However, a low total content of a mineral does not mean low bioavailability, it may have substances that aid in absorption, so even at low concentration a high bioavailable content exists.

In order to overcome such interferences and to promote a balanced and adequate mineral consumption, different fortification strategies can be used, either in addition to processed foods or in agricultural activities, ultimately reflecting in the composition of the fruit *in natura* [7, 29, 31]. Thus, in addition to this study of the simple mineral composition of different fruits from the Northeastern biodiversity, bioavailability studies will be necessary to fully understand the nutritional function of these fruits.

For analyze possible correlations between the fruits a Principal Component Analyze was performed, in this approach the original, commonly correlated variables are linearly transformed into a smaller number of uncorrelated variables, the so-called principal components (PC's). Some of these relationships can be valuable for data interpretation. An understanding of the properties of PCA is mandatory to provide appropriate use of the captured relations [32].

The experimental results for the PCA are presented in the form of plots to facilitate interpretation of the data, since the identification of groups of samples with similar characteristics is almost immediate, besides being able to verify which of the variables analyzed are the main ones responsible for the formation of the groups of samples [33]. Two plots are useful to analyze and extract information from the data, one is related to the variables (Loadings) and the other is related to the samples (Scores).

The analysis of both plots together shows the relationship of the groupings between the samples and the variables. Fruits such as caja, umbu-caja, umbu, pitanga and araçá are grouped together with the elements Ca, Fe, K, Mg and P, meaning they present higher amounts of those elements. On the other quadrant it is evident that the mangaba and bacuri group of fruits are associated with the higher content of Na.

The high levels of Na may be due to the coastal geographic location in which the mangaba and bacuri fruits were collected. The phenomenon called sea spray, in which waves of sea salts move to the terrestrial area, thus influencing the accumulation of nutrients in nearby cultivated fruits, has been earlier reported for the case of the fruits studied in this work [34]. Pitanga and araçá are separated by their Fe content. It should be noted that these fruits are the only ones harvested in a domestic environment, so this higher iron content may possibly be a consequence of the water supply that may have been used to wet the plants, or even the mineral content of the soil.

Studies on the nutritional composition of tropical fruits are scarce in the literature, and further research is needed to determine their trace element contents, as well as the bioavailability of these nutrients and the use of fruits in the processing of foods to yield high added value [35].

A compilation carried out from 2014 to 2016, in which a SiBBR (Brazilian Biodiversity Information System) was generated and Specific searches in CAPES Periodicals databases were also conducted from 2017 to 2021, serves to verify the statement cited above, showing the scarcity of registered publications which consider the analysis of these products. It was noted that only three reliable scientific studies present trace element analysis, which are shown in Table 04.

Table 4. Literature summary of the content of trace elements (mg 100g⁻¹ wet sample) in fruits of the agrobiodiversity.

Fruit	Ca	Cu	Fe	K	Mg	Mn	Na	P	Se	Zn
Murici (without epicarp) [36]	88.8±0.6	0.09±0.01	0.71±0.01	347±1	43.7±13.2	0.08±0.01	45.4±5.9	7.69±0.45	2.36±0.24	0.09±0.01
Mangaba [36]	8.52±1.09	0.08±0.04	0.95±0.07	240±10	70.3±13.4	Nd	33.8±2.2	6.05±0.48	0.80±0.04	0.12±0.01
Bacuri [17]	17.1±0.8	0.38±0,04	0.45±0.07	150±3	22.2±0.4	-	26.4±1.5	10.8±0.63	-	1.04±0.11
Umbu [36]	30.1±4.2	0.07±0.01	0.41±0.01	205±49	10.8±1.43	Nd	2.07±0.08	29.4±5.37	0.11±0.00	0.14±0.17
Araça [33]	21.0 ± 0.0	-	0.21±0.02	-	-	-	-	-	-	0.50 ± 0.12
Araça [19]	48.5 ± 0.1	0.32 ± 0.03	0.55 ± 0.01	-	29.2 ± 0.02	-	-	9.75 ± 0.02	-	0.27 ± 0.02
Cajá [37]	23.66 ± 3.12	0.24 ± 0.01	1.22 ± 0.44	0.42± 0.01	45.50 ± 2.12	-	4.16 ± 0.68	-	-	0.06 ± 0.06
Umbu [38]	64 ± 0	-	2 ± 0	1.24 ± 12	57 ± 1	-	6.0 ± 0	150 ± 1	-	0.7 ± 0.0

Nd (Not determined)

Table 4 shows the content of some elements presented in the literature. The data presented in Table 4 show results in wet sample (results obtained from literature) and our data (Tabel 2) is in dry sample. Most of fruits present 70 to 90% water; therefore, in order to make comparison it is important to consider converting results. Anyway, the trace element content may be different due to the location of sampling as they present differences in the soil characteristics.

These results show the importance of carrying out more studies to characterize the content of inorganic trace elements in exotic fruits.

Importantly, the chemical composition of other cerrado fruits (cagaita, araticum, buriti, and coconut) are under studies [37], as well as other fruits like jatoba, baru and macauba [39].

Therefore, it is relevant to highlight that studies presenting centesimal analysis [39,40] and vitamins [40,41] of fruits from Brazilian biodiversity have been published, although the chemical composition analysis of these fruits is scarce.

The characterization of nutritional properties of native fruits is important for the knowledge of biodiversity in the northeast region and open the possibility of generation of added-value products. Moreover, this could allow to incorporate the consumption habits of the tropical fruits to the diet of the northeastern population, thus contributing to the nutritional recommendation of some minerals singly [36].

Although wild fruits are generally not widely marketed in the northeastern region of Brazil, knowledge of their nutritional potential may result in expansion of cultivated areas and their increased commercialization, bringing economic benefits to local farmers [42].

CONCLUSION

The study provides accurate data related to the content of Ca, Fe, K, Mg, Na and P in 11 tropical fruits from agrobiodiversity of Brazil. Although the content of other trace element as Cu, Mn, Se and Zn were found in concentrations below the limits of quantification of the proposed methodology the data can be useful for future studies for characterization of these tropical fruits.

Results obtained for caja and umbu-caja are relevant as they can be considered a rich source of phosphorus according to the RDA (Recommended Dietary Allowances). The other fruits studied did not present enough content for diet recommendation for trace element ingestion. New studies focusing on the bioavailability of nutrients should be performed to fully understand the mineral function of the fruits in the diet.

Principal Component Analysis permitted differentiation of the fruits into four distinct groups according to their mineral element profiles. The formation of two groups can be explained by the geographic location of harvest, inferring the importance of this factor in the mineral content of the fruits.

It is noteworthy that these fruits are naturally found throughout the region and are available to the entire population, including low-income people. The study of mineral characterization in these regional fruits is relevant to serve as a scientific basis for encouraging their popular consumption.

Data generated in the present work will augment the international bank of food composition, which will aid in the development of dietary plans and studies of consumption or food standards.

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REFERENCES

1. Brasil M do MA. Biodiversidade para Alimentação e Nutrição [Internet]. 2017. Available from: <http://www.mma.gov.br/biodiversidade/conservacao-e-promocao-do-uso-da-diversidade-genetica/biodiversidade-para-alimentacao-e-nutricao>.
2. Hunter D, Özkan I, Beltrame DMO, Samarasinghe WLG, Wasike VW, Charrondièrè UR. Enabled or Disabled: Is the Environment Right for Using Biodiversity to Improve Nutrition? *Front Nutr.* 2016; 3: 1–6.
3. Biazotto KR, Mesquita LMS, Neves BV, Braga ARC, Tangerina MMP, Vilegas W. Brazilian Biodiversity Fruits: Discovering Bioactive Compounds from Underexplored Sources. *J Agric Food Chem.* 2019;67(7):1860–76.
4. Roupheal Y, Colla G, Graziani G, Ritieni A, Cardarelli M, Pascale S. Phenolic composition, antioxidant activity and mineral profile in two seed-propagated artichoke cultivars as affected by microbial inoculants and planting time. *Food Chem.* 2017; 234:10–9.

5. Tang ZX, Shi LE, Aleid SM. Date fruit: Chemical composition, nutritional and medicinal values, products. *J Sci Food Agric*. 2013; 93(10):2351–61.
6. Lukaski HC. Vitamin and mineral status: Effects on physical performance. *Nutrition*. 2004; 20:632–44.
7. Gharibzahedi SMT, Jafari SM. The importance of minerals in human nutrition: Bioavailability, food fortification, processing effects and nanoencapsulation. *Trends Food Sci Technol*. 2017; 62:119–32.
8. Institute of Medicine I. Dietary Reference Intakes for Vitamin C, Vitamin E, Selenium, and Carotenoids [Internet]. 2000. Available from: <http://www.nap.edu/catalog/9810>
9. Souza VR, Pereira PAP, Queiroz F, Borges SV, Carneiro JDS. Determination of bioactive compounds, antioxidant activity and chemical composition of Cerrado Brazilian fruits. *Food Chem*. 2012; 134:381–6.
10. Berto A, Silva AF, Visentainer JV, Matsushita M, Souza NE. Proximate compositions, mineral contents and fatty acid compositions of native Amazonian fruits. *Food Res Int*. 2015; 77:441–9.
11. Policarpi PDB, Turcatto L, Demoliner F, Ferrari RA, Bascuñan VLA, Frescura A. Nutritional potential, chemical profile and antioxidant activity of Chichá (*Sterculia striata*) nuts and its by-products. *Food Res Int*. 2018; 106:736–44.
12. Morais DR, Rotta EM, Sargi SC, Bonafe EG, Suzuki RM, Souza NE, et al. Proximate composition, mineral contents and fatty acid composition of the different parts and dried peels of tropical fruits cultivated in Brazil. *J Braz Chem Soc*. 2017; 28(2):308–18.
13. Barbosa JTP, Santos CMM., Peralva VN., Flores EMM., Korn M., Nóbrega JA., Korn MGA. Microwave-assisted diluted acid digestion for trace elements analysis of edible soybean products. *Food Chemistry*. 2015,175,212–217.
14. Pedro FGG, Arruda GL, Oliveira JC, Santos AD, Sigarini KS, Hernandez T, et al. Composição centesimal e mineral de plantas medicinais comercializadas no mercado do Porto de Cuiabá, Mato Grosso, Brasil. *Rev Bras Pl Med*. 2016;18(1):297–306.
15. Hamacek FR, Moreira AVB, Martino HSD, Pinheiro-Sant’Ana HM. Valor nutricional, caracterização física e físico-química de jenipapo (*Genipa americana* L.) *Alim Nut Braz J Food Nutr*. 2013; 24(1): 73–7.
16. Assumpção C, Bachiega P, Morzelle MC, Nelson DL, Ndiaye EA, Rios AO, Souza EC. Characterization, antioxidant potential and cytotoxic study of mangaba fruits. *Ciência Rural*. 2014; 44(7): 1297–303.
17. Rogez H, Buxant R, Mignolet E, Souza JNS, Silva EM, Larondelle Y. Chemical composition of the pulp of three typical Amazonian fruits: araçá-boi (*Eugenia stipitata*), bacuri (*Platonia insignis*) and cupuaçu (*Theobroma grandiflorum*). *Eur Food Res Technol*. 2004; 218: 380–4.
18. Mattietto RA, Lopes AS, Menezes HC. Physical and physicochemical characterization of caja fruit. *Braz J Food Technol*. 2010;13(3):156–64.
19. Damiani C, Vilas Boas EVB, Asquieri ER, Lage ME, Oliveira RA, Silva EP, Pinto DM, Rodrigues LJ. Characterization of fruits from the savanna: Araça (*Psidium guinnensis* Sw.) and. *Ciência e Tecnol Aliment*. 2011; 31(3): 723–9.
20. Paz JG, Pacheco P, Silva CO, Pascoal GB. Análise da composição nutricional e de parâmetros físico-químicos do pequi. *Rev Científica*. 2014; 1: 73–86.
21. Kinup VF, Barros IBI. Protein and mineral contents of native species, potential vegetables and fruits. *Cienc. Tecnol Aliment*. 2008; 28(4): 846–57.
22. Oliveira JPS, Silva FLF, Monte RJG, Matos WO, Lopes GS. A new approach to mineralization of flaxseed (*Linum usitatissimum* L.) for trace element analysis by flame atomic absorption spectrometry. *Food Chem [Internet]*. 2017; 224:335–41. Available from: <http://linkinghub.elsevier.com/retrieve/pii/S0308814616321173>.
23. Brasil. RDC no 54, de 12 de novembro de 2012. Diário Oficial da União [Internet]. 2012; Available from: http://portal.anvisa.gov.br/documents/33880/2568070/rdc0054_12_11_2012.pdf/c5ac23fd-974e-4f2c-9fbc48f7e0a31864.
24. Uribarri J, Calvo MS. Dietary phosphorus intake and health. *Am J Clin Nutr*. 2014; 99(2): 247–8.
25. Millena CG, Sagum RS. Philippine Pili (*Canarium ovatum*, Engl.) varieties as source of essential minerals and trace elements in human nutrition. *J Food Comp Anal*. 2018; 69: 53–61.
26. Leterme P, Buldgen A, Estrada F, Londono AM. Mineral content of tropical fruits and unconventional foods of the Andes and the rain forest of Colombia. *Food Chem*. 2006; 95(4): 644–52.
27. Guedes MNS, Rufini JCM, Marques TR, Melo JOF, Ramos MCP, Viol RE. Minerals and phenolic compounds of cagaita fruits at different maturation stages. *Rev Bras Frutic*. 2017; 39(1): 1–9.
28. Silva FLF, Lima JPS, Melo LS, da Silva YSM, Gouveia ST, Lopes GS. Comparison between boiling and vacuum cooking (sous-vide) in the bioaccessibility of minerals in bovine liver samples. *Food Res Int [Internet]*. 2017;100(July):566–71. Available from: <http://linkinghub.elsevier.com/retrieve/pii/S0963996917303915>.

29. Nosratpour M, Jafari SM. Bioavailability of Minerals (Ca, Mg, Zn, K, Mn, Se) in Food Products. In: Encyclopedia of Food Chemistry [Internet]. Elsevier; 2019. p. 148–54. Available from: <https://linkinghub.elsevier.com/retrieve/pii/B9780081005965216181>.
30. Lazarte CE, Carlsson NG, Almgren A, Sandberg AS, Granfeldt Y. Phytate, zinc, iron and calcium content of common Bolivian food, and implications for mineral bioavailability. *J Food Compos Anal*. 2015; 39:111–9.
31. Cruz AF, Almeida GM, Wadt PGS, Pires MC, Ramos MLG. Seasonal variation of plant mineral nutrition in fruit trees. *Braz Arch Biol Technol*. 2019; 62: 1-8.
32. Camacho J, Picó J, Ferrer A. Chemometrics and Intelligent Laboratory Systems Data understanding with PCA: Structural and Variance Information plots. *Chemom Intell Lab Syst*. 2010; 100(1): 48–56.
33. Correia, PRM; Ferreira MMC. Educação. *Quim Nov*. 2007; 30(2): 481–7.
34. Zheng WW, Chun IJ, Hong SB, Zang YX. Vegetative growth, mineral change, and fruit quality of 'Fuji' tree as affected by foliar seawater application. *Agric Water Manag*. 2013; 126: 97–103.
35. Silva MR, Santos GG, Mendes D, Martins DO. Caracterização química de frutos nativos do cerrado. *Cienc Rural*. 2008;38(6):1790–3.
36. Almeida MMB, Sousa PHM, Fonseca ML, Magalhães CEC, Lopes MFG, Lemos TLG. Evaluation of macro and micro-mineral content in tropical fruits cultivated in the northeast of Brazil. *Food Sci Technol*. 2009; 29(3): 581–6.
37. Nascimento ALAA., Brandi IV, Durães CAF, Lima JP, Soares SB, Mesquita BMAC. Chemical characterization and antioxidant potential of native fruits of the Cerrado of northern Minas Gerais. *Braz J Food Technol*. 2020; 23(e2019296):1-9.
38. Ribeiro LO, Viana ES, Godoy RLO, Freitas SC, Freitas SP, Matta VM. Nutrients and bioactive compounds of pulp, peel and seed from umbu fruit. *Cienc Rural*, 2019; 49(4): 1-8.
39. Berto A, Da Silva AF, Visentainer JV, Matsushita M, De Souza NE. Proximate compositions, mineral contents and fatty acid compositions of native Amazonian fruits. *Food Res Int*. 2015; 77:441-9.
40. Silva NRRN, Mendes NSR, Silva FA. Nutritional composition and total phenolic compounds content of pequi pulp (*Caryocar brasiliense* Cambess.). *J. Bioen. Food Sci*. 2020; 07:1-10.
41. De Assis RC, De Lima RGS, Siqueira ACP, De Rosso VV, De Sousa PHM, Mendes AEP, Costa EA, Carneiro APG, Maia CSC. Determination of water-soluble vitamins and carotenoids in Brazilian tropical fruits by High Performance Liquid Chromatography. *Heliyon*. 2020; 6(10):1-10.
42. Sereno BA, Bampi M, Santos IE, Ferreira SMR, Bertin RL, Kruger CCH. Mineral profile, carotenoids and composition of cocona (*Solanum sessiliflorum* Dunal), a wild Brazilian fruit. *J Food Compos Anal*. 2018; 72: 32–8.



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